STUDIES ON CORROSION MITIGATION OF MILD STEEL USED IN OIL AND NATURAL GAS INDUSTRIES WITH SUITABLE CORROSION INHIBITORS

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SUBMITTED BY
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UNDER THE GUIDANCE OF
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STATEMENT BY THE CANDIDATE

As required by the University Ordinance 770, I wish to state that the work embodied in this thesis titled, "**Studies on corrosion mitigation of mild steel used in oil and natural gas industries with suitable corrosion inhibitors**" forms my own contribution to the research work carried out under the guidance of **Dr. R. S. Dubey** at the **Ramniranjan Jhunjhunwala College, Ghatkopar (W), Mumbai-400086.** This work has not been submitted for any other degree of this or any other University. Whenever reference have been made to previous works of others, it has been clearly indicated as such and included in the Bibliography.

Signature of candidate

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Certified by

Signature of Guide

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CERTIFICATE

I certify that the thesis submitted by **Kamble Pratap Pandurang Savitri** represents his original wok, which was carried out by him in Chemistry Research Laboratory, Department of Chemistry, Ramniranjan Jhunjhunwala College, Ghatkopar (W), Mumbai-400086, from **June 2014** to **November 2018.**

I further certify that I am the opinion there is prima facie case for consideration of the thesis.

Dr. R. S. Dubey
Research Guide

DEDICATED TO MY
BELOVED FAMILY

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Kamble Pratap Pandurang Savitri

CONTENTS

LIST OF ABBREVITIONS

AC: Alternate Current

AFM: Atomic Force Microscopy

API: American Petroleum Institute

ARXPS: Angle Resolved X-ray Photoelectron spectroscopy

ASM: American Society for Microbiology

ASTM: American Society for Testing and Materials

β_a: Anodic Beta (Tafel) coefficient

β_c: Cathodic Beta (Tafel) coefficient

C_{dl}: Double layer Capacitance

CII: Confederation of Indian industry

CMC: Critical Micelle Concentration

CR: Corrosion Rate

CI: Corrosion Inhibitor

CRA: Corrosion Resistance alloy

CSIR: Council of Scientific and Industrial Research

DC: Direct Current

DFT: Density Functional Theory

DST: Department of Science and Technology

E_{PZC}: Potential of Zero Charge

E_{op}: Open circuit potential

E_{corr}: Corrosion potential

E_{HOMO}: Energy of Highest Occupied Molecular Orbital

E_{LOMO}: Energy of Lowest Occupied Molecular Orbital

EDAX: Energy Dispersive Analysis by X-Ray

EDS: Electron Dispersive X-ray spectroscopy

EDX: Electron Dispersive X-ray spectroscopy

EFM: Electrochemical Frequency Modulation

EIS: Electrochemical Impedance Spectroscopy

FTIR: Fourier Transform Infrared Spectroscopy

GDP: Gross Domestic Product

GNP: Gross National Product

HIC: Hydrogen Induced Cracking

HOMO: Highest Occupied Molecular Orbital

I_{corr}: Corrosion Current

IE: Inhibition Efficiency

IGA: Inter Granular Attack

IR: Infra Red Spectroscopy

IIT: Indian Institute of technology

LEED: Low Energy Electron Diffraction

LOMO: Lowest occupied Molecular Orbital

MC: Monte Carlo Simulation

MD: Molecular Dynamic Simulation

MIC: Microbiologically Influenced Corrosion

MS: Mild Steel

MFL: Magnetic Flux Leakage tools

NACE: National Association of Corrosion Engineers

NLLS: Non-linear Least Squares Fitting

NML: National Metallurgical Laboratory

NRB: Nitrate Reducing Bacteria

OCP: Open Circuit Potential

PD: Potentiodynamic Polarization

QC: Quantum Chemical calculation

R_p: Polarization Resistance

R_s: Solution Resistance

R_{ct}: Charge Transfer Resistance

RED: Reflection Electron Diffraction

SCC: Stress Corrosion Cracking

SCE: Standard Calomel electrode

SEM: Scanning Electron Microscopy

SHE: Standard hydrogen Electrode

SRB: Sulphate Reducing Bacteria

TGA: Thermo Gravimetric Analysis

TLC: Thin Layer Chromatography

UGC: University Grand Commission

VCI: Volatile Corrosion Inhibitors

WDS: Wavelength Dispersive X-ray Spectroscopy

XRD: X-Ray Diffraction

XPS: X-Ray Photoelectron Spectroscopy

Chapter 1

INTRODUCTION

Chapter 1

INTRODUCTION

The choice of materials to be used in oil and gas industry is often a compromise. There are many factors that have to be considered such as the corrosion resistance, strength, weldability and cost in selecting and evaluating the appropriate material of construction. The corrosivity of the environment will play a significant role in material selection because the choice for surface environment will be different from the downhole/pipeline environment. Over the years, mild steel (MS) is one of the most frequently used construction material for pipelines and some other equipment in oil and gas production because it is of a lower cost compared to other materials offering similar physico-chemical properties. However, if not properly protected, mild steel is susceptible to corrosion. Given sufficient time, in the presence of CO_2, H_2S, oxygen and water, mild Steel material will eventually change entirely to rust and disintegrate [1].

Corrosion can be viewed as a universal phenomenon, omnipresent and omnipotent. It is there everywhere, air, water, soil and in every environment, we encounter. Undoubtedly, corrosion has an enormous economic and environmental effect on virtually all facets of the world's infrastructure, like bridges and buildings, oil and gas structures, chemical processing and highways structures, wastewater treatment systems etc. There is no single figure for loss to the nation due to corrosion. It can be a minimum of 3.5% of the nation's GDP. Losses due to corrosion could be around Rs. 2.0 lakh crores per annum in India. Corrosion costs manifest in the form of premature deterioration or failure necessitating maintenance, repairs and replacement of damaged parts. In the US, total direct cost of corrosion is estimated at about 300 billion dollars per year; which is about 3.2% of gross domestic product.[2] Fig 1.1 shows various industries contributing towards corrosion cost in United States of America

Awareness to corrosion and adaptation of timely and appropriate control measures hold the key in the abatement of corrosion failures.. In addition to the economic significance, corrosion also poses large ecological and safety problems as a result of corrosion-caused damage to industrial and civil structures.[4]

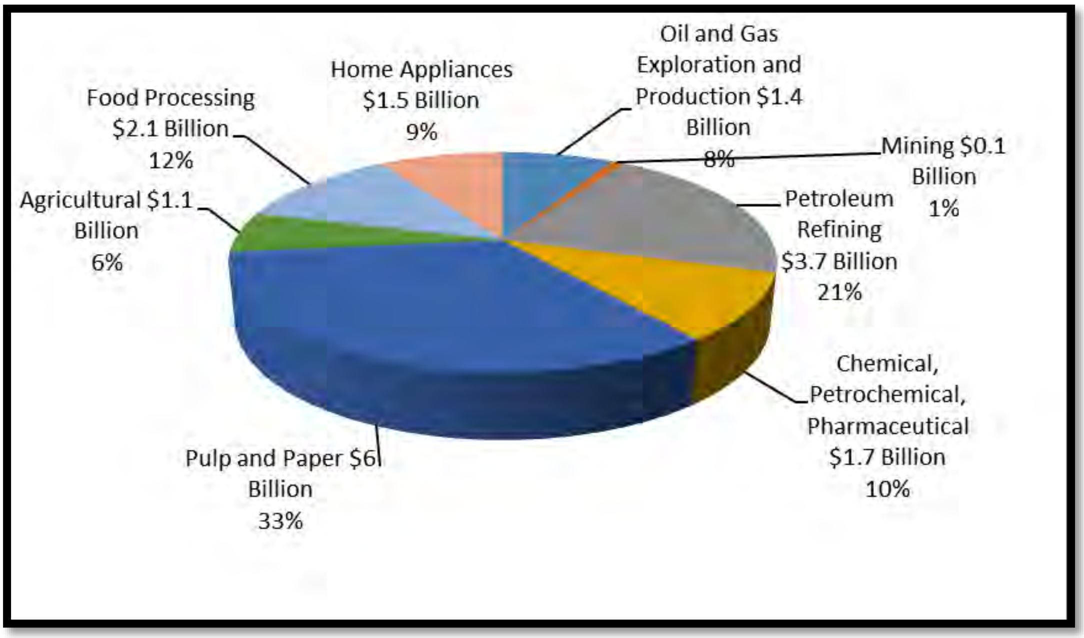

Fig.1.1: Annual cost of corrosion in various industries [3]

In the Oil & Gas upstream production systems, corrosion is possibly the most significant and costly cause of severe operational problems. Corrosion can occur anywhere in the production line, from production wells to transporting vessels of produced gas or oil heading to the refineries. Because corrosion is a natural occurring process, it is impossible to completely avert it. However, it can be controlled so that materials and equipment likewise can perform for a predicted optimum length of time. Hence, corrosion detection, monitoring and control become dominant considerations when seeking maximum equipment lifetime, minimum cost and maximum safety, in many industries[5][6].

1.1 Corrosion of mild steel in Oil and Gas Industry

Corrosion is the deterioration of materials as a result of reaction with its environment and a natural potential hazard associate with oil and gas production and transportation facilities [7]. Oilfield pipelines play significant roles in transportation of oil and gas products at all stages of the production. Risers are used mainly to transport crude oil, natural gas, and formation water from downholes to wellhead platforms. Likewise, flowlines are used to transport the well fluids from the well platform to the treatments platform which acts as a reservoir for oil and gas from different wells[8]. Pipelines are used to transport oil and gas to treatment plants, storage facilities and refinery plants.

The integrity of the pipelines is very important in ensuring safe operation, avoidance of environmental pollution, and fitness for purpose of major producing assets. The integrity of oilfield pipelines is under serious threat by both internal and external corrosion.Figure 1.2 shows different conditions leading to corrosion issues in the oil and gas industry industries.

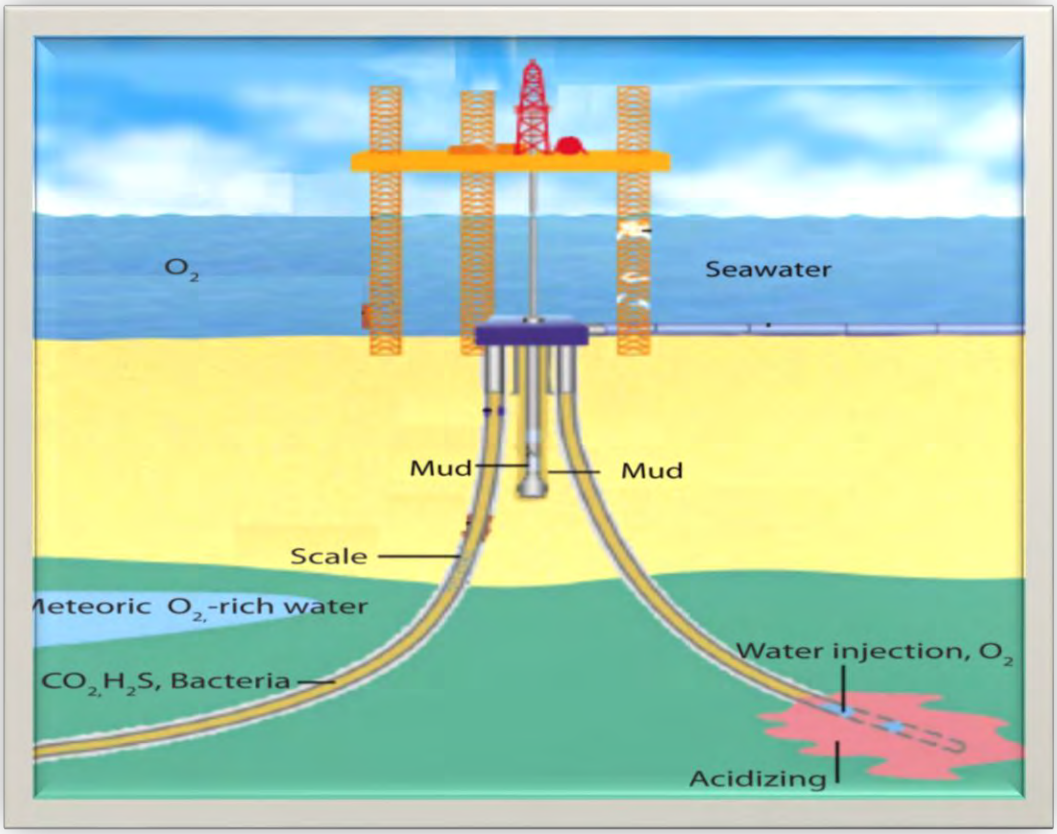

Figure 1.2: Schematic diagram of offshore rigs, illustrating likely sources of Corrosion [9].

Oxygen and chloride (from external environment) and H_2S/CO_2, and organic acid from the production fluid (internal environment) result in corrosion of different forms of oilfield pipelines which could result in leaks and catastrophic failure if not properly monitored and controlled. Few major disasters occurred till date due to gas/oil leakage and fire hazards in India and other part of world is presented in (Table 1.1)

Year	Place	Incidence	Toxological effects
1965	Louisiana, Tennessee, USA	Gas transmission pipeline exploded from stress corrosion cracking	17 killed.
1982	Amoco field, Canada	A high profile blowout releasing sour gas for 67 days to environment.	2 human and hundreds of cattle death.
1984	Bhopal, Madhya Pradesh	Gas leakage	Death of thousands of people due to choking, reflexogenic circulatory collapse and pulmonary oedema, and Peri- and neonatal death rates increased.
1989	Eastern Pakistan	Gas Pipeline ruptured and exploded.	12 killed; hundreds injured.
1989	Russia	Liquefied natural gas Pipeline explosion	575 deaths.
1989	Ufa, Russia	Sparks from two passing trains detonated gas leaking from an LPG pipeline	645 deaths
1990	Nagothane, Maharashtra	Natrual Gas leakage	Vapour cloud formation occurs due to leakage in pipeline carrying ethane and propane gas leads to 31 people set to fire and death.
1996	Lively, Texas, USA	An 8-inch diameter LPG pipeline transporting liquid butane burst due to inadequate corrosi- on protection.	2 men killed, 25 families evacuated, damages cost over $217,000.

1997	Visakhapatnam , Andhra Pradesh	Refinery fire	70 people killed as gas leak and mixed with clouds which pour down in form of rain.
1998	Jesse Village Delta, Nigeria	Oil pipeline explosion while villagers were scooping fuel from a ruptured pipe line	Over 2000 deaths.
1999	Bellingham, Washington	A gasoline pipeline ruptured. 250,000 gallons of gasoline escaped into a creek land resulted into fire.	3 deaths, 8 injured, over $45 million property damages.
2000	Colombia	Pipeline explosion	43 deaths.
2003	Chongqing, China	A gas well blew out releasing toxic sour gas cloud to the environment	243 deaths.
2004	Ghislenghin, Belgium	Explosion of a major natural gas pipeline.	23 killed, 122 injured.
2006	Lagos, Nigeria.	A vandalized oil pipe line exploded	Over 500 deaths.
2007	Carmichael, USA	Propane pipeline explosion.	2 deaths, 5 injured.
2008	Ijegun, Lagos, Nigeria.	A bulldozer accidentally struck an oil pipeline which eventually exploded	100 deaths. 15 homes and 20 vehicles burnt.
2009	Shah Oilfield, AlGharbia, UAE	A pipeline from the 50,000 barrel per day oilfield got leaking due	3 killed by inhaling high concentration of H_2S gas, 1 injured.

		to corrosion and released H_2S gas to the environment before explosion	
2013	Visakhapatnm Andhra Pradesh	Refinery explosion	01 killed and 39 injured when gas leakage catches fire. The under construction cooling tower on site collapse leading to major damage. The pungent smell spread due to leakage causes eye irritation and respiratory problem causing suffocation .
2014	Nagaram village, Andhra Pradesh	Blasting of pipeline	14 people killed and 15 injured due to blast in pipeline belong to GAIL. This cause heavy noise pollution and fire engulf a entire village. Birds and domestic animals are also the victim of this disaster.
2014	Raipur, Chattisgarh	Gas leakage	Methane gas leakage from the pipeline of water pump house in Bhilai Steel Plant leading to death of 06 worker and 40 injured.
2015	Vadodara Gujrat	Gas leakage	20 people were hospitalized. The victims complained of irritation in their eyes and throat.
2017	Tughlakabad New delhi	Gas leakage	More than 475 students of the Rani Jhansi Sarvodya Kanya Vidyalaya girls' school and a government girls’ senior secondary school, along with nine teachers, were hospitalized. The

			gas caused eye and throat irritation and acute dizziness.
2017	Kanpur Uttar pradesh	Gas leakage and explosion	Five laborers died immediately. Eight more suffered serious injuries, and four of them passed away in hospital.
2018	Mumbai, Maharashtra	Boiler blast	45 people seriously injured.

Table 1.1 Some Global Major Pipeline Accidents [10-12].

The wide-ranging environmental conditions present in the oil and gas industry provide a plethora of different degradation phenomena causing failures, with CO_2 corrosion and erosion-corrosion being two of the most pertinent types of attack.

Other important categories of corrosion include H_2S corrosion [13-18], preferential weld corrosion [19-27] and pitting corrosion [28-29].Corrosion-related failures constitute over 25% of failures experienced in the oil and gas industry. Almost half these failures are associated with sweet (CO_2) and sour(H_2S) producing fluids [30]. Table 1.2 and 1.3 gives a comprehensive analysis of oil field failure due to corrosion.

Types of failure	Frequency (%)
Corrsion (all types)	33
Fatigue	18
Mechanical damage/overload	14
Brittle fracture	9
Fabrication defects	9
Welding defects	7
Others	7

Table 1.2: Equipment failure in the oil and gas industry [30].

Types of failure	Total failure
CO_2 related	28
H_2S related	18
Preferential weld	18
Pitting	12
Erosion-Corrosion	9
Galvanic corrosion	6
Crevice corrosion	3
Impingement	3
Stress Corrsion	3

Table 1.3: Causes of corrosion-related failures in oil and gas industry industries [30].

1.2 Importance of Corrosion

The three main reasons for the importance of corrosion are: economics, safety, and conservation. To reduce the economic impacts of corrosion, corrosion engineers, with the supports of corrosion scientist, aim to reduce material losses, that results from corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures and so on.

Corrosion can compromise the safety of operating instruments by causing failure (with catastrophic consequences) of, pressure vessels, boilers, metallic containers for toxic chemicals, turbine blades and rotors, bridges and airplane components, and automotive steering mechanism. Safety is critical consideration in the design of equipments for oil and gas industries and for disposal of wastes generated during various operations.

Loss of metal by corrosion is a waste not only of the metal, but also for the energy, the water and the human efforts that was used to produce and fabricates the metal structures in the first place. In addition rebuilding of corroded equipments requires further investments of all these resources-metal, energy, water and human. [31]

1.3 Cost of Corrosion

The cost of corrosion can either be directly or indirectly. Direct losses relate to replacement cost, including parts and labour. Protection costs such as the cost of alloying, corrosion inhibitors, coatings, cathodic protection and research & development are also included in this category, whereas indirect costs caused by failure tend to be significantly larger than direct costs. Where the direct costs can be extremely high, indirect losses include lost revenue, lost product (from spills, fires, replacements etc.), lost efficiency, contamination of product, delays and lawsuits [32].

The costs attributed to corrosion damages of all kinds have been estimated to be of the order of 3% to 5% of industrialized countries' gross national product (GNP). The total annual cost of corrosion in the oil and gas production industry is estimated to be \$1.372 billion, broken down into \$589 million in surface pipeline and facility costs, \$463 million annually in down hole tubing expenses, and other \$320 million in capital expenditures related to corrosion [33]. Corrosion costs the oil and gas industry tens of billions of dollars in the form of lost income and treatment costs every year [34]. Corrosion costs US industries alone and estimated \$170 billion a year in which the oil and gas industry takes more than half of these costs [35]. Internal corrosion in wells and pipelines is influenced by temperature, CO_2 and H_2S content, water chemistry, flow velocity, surface condition of the steel etc[36]. Having a greatly reduced corrosion rate (mm/year) can dramatically increase component life, which leads to much greater benefits such as reduced maintenance costs. The problem of corrosion is challenge to the whole world and must be greatly tackled [37].

1.4 Environmental impact of Corrosion in Oil and Gas Industry

The oil and gas industry holds a major potential of hazards for the environment, and may impact it at different levels: air, water, soil, and consequently all living beings on our planet. Within this context, the most widespread and dangerous consequence of oil and gas industry activities is pollution. Pollution is associated with virtually all activities throughout all stages of oil and gas production, from exploratory activities to refining. Waste waters, gas emissions, solid waste and aerosols generated during drilling, production, refining (responsible for the most pollution) and transportation amount to over 800 different chemicals, among which, of course, prevail oil and petroleum products.

Other environmental impacts include intensification of the greenhouse effect, acid rain, poorer water quality, ground water contamination, among others. The oil and gas industry may also contribute to biodiversity loss as well as to the destruction of ecosystems that, in some cases, may be unique. Most potential environmental impacts related to oil and gas industry activities are already well documented. It is still necessary to find ways to conciliate industry development with environmental protection, that is, with sustainable development. After recovered and transported, crude oil has to go through refining processes in order to be converted into products that hold commercial value. Oil refineries are major polluters, consuming large amounts of energy and water, producing large quantities of wastewaters, releasing hazardous gases into the atmosphere and generating solid waste that are difficult both to treat and to dispose[38].

1.5 Overview of Corrosion

The most common form of corrosion in oil and gas industry occurs when steel comes in contact with an aqueous environment and rusts [39]. The metallic surface exposed to an aqueous electrolyte usually possesses site for oxidation [anodic reaction] and reduction [cathodic reaction]. The anodic reaction involves the dissociation of metal to form either soluble ionic product or insoluble compound of metal usually an oxide and cathodic reaction involves formation of oxygen which could be reduced or H_2O is reduced to produce H_2 gas. These anodic and cathodic reactions set up electrochemical cells.

Anodic reaction

The anodic reaction for iron and steel is

$$\mathbf{Fe \rightarrow Fe^{2+} + 2e^-} \qquad \mathbf{(1)}$$

Cathodic reactions

Once the metal atom at the anode site looses the electrons, there is a possibility of four cathode reactions [40].

$$\mathbf{O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O} \qquad \mathbf{(2)}$$

(Oxygen reduced in acidic solution)

$$\frac{1}{2}O_{2(g)} + H_2O + 2e^- \rightarrow 2OH^- \qquad (3)$$

(oxygen reduced in neutral or base)

$$2H^+ + 2e^- \rightarrow H_{2(g)} \qquad (4)$$

(Hydrogen evolution from acidic solution)

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \qquad (5)$$

(Hydrogen evolution from neutral water)

There are many types and causes of corrosion. The mechanism present in a given piping system varies according to the fluid composition, service location, geometry, temperature, and so forth. In all cases of corrosion, the electrolyte must be present for the reaction to occur [41].

1.6 Mechanism of Corrosion in Oil and Gas Pipelines

Internal corrosion in oil and gas industry is generally caused by water, carbon dioxide (CO_2) and hydrogen sulfide (H_2S) organic acid and bacteria. CO_2 present in oil and gas gets dissolved in water to produce carbonic acid (H_2CO_3). The carbonic acid further reacts with steel to form iron carbonate films and hydrogen gas.

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_{2(g)} \qquad (6)$$

These iron carbonate films can be protective or non-protective at the anode. The presence of CO_2 acts as a catalyst increasing the hydrogen evolution thereby increasing the corrosion rate of steel in aqueous solution [42].

The carbonic acid (H_2CO_3) either serves as an extra source of H^+ or undergoes reduction as shown in equation:

$$2H^+ + 2e^- \rightarrow H_{2(g)} \qquad (7)$$

$$2H_2CO_3 + 2e^- \rightarrow H_{2(g)} + 2HCO^-_3 \qquad (8)$$

The dissolved iron concentration will increase until Fe^{2+} is the same as the precipitation rate of $FeCO_3$ [43].

When Fe^{2+} is released in corrosion process, the double amount of bicarbonate forms according to the equation:

$$\mathbf{Fe + 2H_2CO_3 \rightarrow Fe^{2+} + H_{2(g)} + 2HCO_3} \qquad \textbf{(9)}$$

The pH increases until bicarbonate and carbonate becomes so high that solid $FeCO_3$ precipitates [43] as shown in equation.

$$\mathbf{Fe^{2+} + 2HCO_3^{-} \rightarrow FeCO_{3(s)} + H_2CO_3} \qquad \textbf{(10)}$$

When all the ferrous ions produced by corrosion precipitates as iron carbonate ($FeCO_3$). The pH remains constant and overall reaction becomes,

$$\mathbf{Fe + H_2CO_3 \rightarrow FeCO_{3(s)} + H_{2(g)}} \qquad \textbf{(11)}$$

Passitivity is one of the factors responsible for control of corrosion in pipeline. It forms a protective film on metal surface and thereby controls corrosion. This protective film is removed from the surface of the pipeline through erosion, dissolution and turbulence resulting in more corrosion[44].

1.7 Types of Corrosion in Oil and Gas Pipeline

The primary chemical components that cause corrosion reaction to occur in pipeline are oxygen, acidic sulfur and acidic chloride that dissolve in the water in pipeline. The mechanism present in a given pipeline system varies according to the fluid composition, service location, geometry, temperature and so forth. In all the cases of corrosion, the electrolyte must be present for the reaction to occur.

1.7.1 Internal Corrosion

It has become an increasing problem in most oil and gas pipelines as water cuts have increased and previously oil wet pipe surfaces have become water wet and as bacterial activities increases in the production system. Internal corrosion is the largest cause of pipeline failure in oil and gas industry through different forms of corrosion like microbiologically influenced corrosion (MIC), erosion-corrosion, under deposit corrosion and so forth [45].

Fig.1.3: Internal Corrosion of oil and gas pipeline [46].

1.7.2 Erosion Corrosion

The erosion-corrosion mechanism increases corrosion reaction rate by continuously removing the passive layer of corrosion products from the wall of the pipe. The passive layer in thin film of corrosion product that actually serves to stabilize the corrosion reaction and slow it down. As a result the corrosion rate of the turbulence and high shear stress in the passive layer can be removed causing the corrosion rate to increase [47]. The erosion-corrosion is always experienced where there is high turbulence flow regime with significantly higher rate of corrosion than just corrosion or erosion in pipeline [48]. In a multiphase flow regime with a fully developed turbulent flow, bubbles development and collapse have been attributed to changes in mass transfer coefficient and an eventual increase in CO_2 corrosion in pipeline [49].

Fig.1.4: Erosion Corrosion of oil and gas pipeline [50].

1.7.3 Under Deposit Corrosion

The under deposit corrosion mechanism can increase the corrosion reaction rate by causing a localized chemical concentration which results in pitting of the metal surface under solid deposits. These deposits appear to be composed of corrosion product matrix entrapment of formation solids, sand and iron sulfate. The rate of corrosion under this mechanism is significantly lower than erosion-corrosion mechanism.

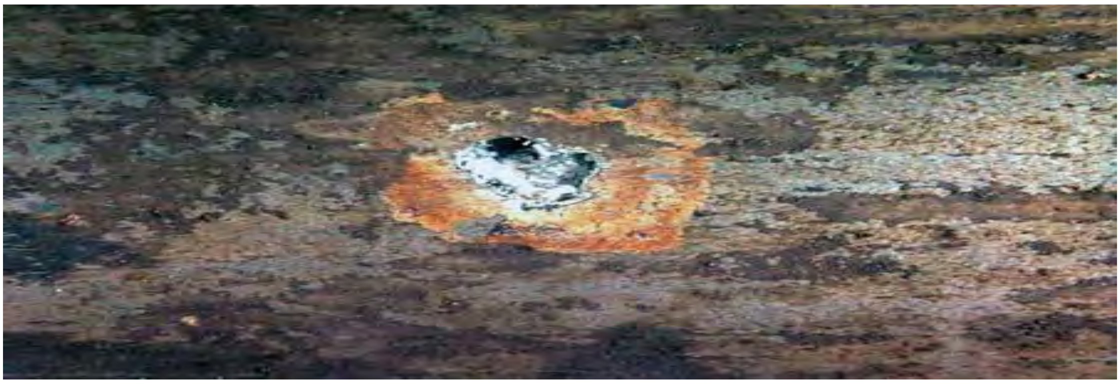

Fig.1.5: Under Deposit Corrosion of oil and gas pipeline [51].

1.7.4 Microbiologically Induced Corrosion (MIC)

This type of corrosion is caused by bacterial activities. The bacteria produce waste products like CO_2, H_2S and organic acids that corrode the pipes by increasing the toxicity of flowing fluid in pipeline. Some bacteria like sulfate reducing bacteria (SRB) consume hydrogen that is product of standard corrosion reaction process. This activity causes the existing corrosion rate to change reaction equilibrium by replacing the hydrogen consumed by bacteria. Bacteria also accumulate on pipe walls, creating deposits and under deposit corrosion. MIC is recognized by the appearance of black slimy waste material on the pipe surface as well as pitting of pipe wall underneath these deposits.

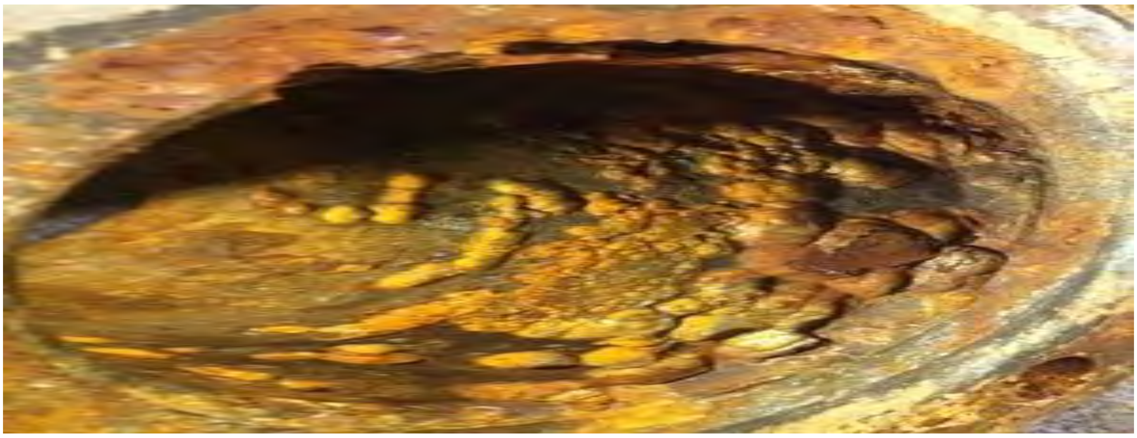

Fig.1.6: Microbiologically Induced Corrosion of oil and gas pipeline [52].

1.7.5 Pitting Corrosion

Pitting is classified as localized attack that results in rapid penetration and removal of metal at small discrete area. The initiation of a pit occurs when electrochemical or chemical breakdown expose a small local site on a metal surface to damaging species such as chloride ion. The site where pitting occurs is where there is an environmental variation in comparison to the entire metal surface. The combination of chlorine with H_2S results in localized pitting in steel [53]. This area of steel which is usually the anode normally gets highly degraded due to enormous electron transfer between the entire large area of the metal surface which is the cathode and small anode (the pitting site).

Fig.1.7: Pitting Corrosion of oil and gas pipeline [54].

1.7.6 Galvanic Corrosion

Galvanic corrosion occurs when two metallic material with different electrode potential are in contact and are exposed to an electrolytic environment. In this situation the metal with less or more negative potential becomes anode and begins to corrode. The presence of H_2S and low temperatures encourages galvanic corrosion [55].

Fig.1.8: Galvanic Corrosion [56].

1.7.7 Crevice Corrosion

Crevice corrosion is normally a localized corrosion that takes place in the narrow clearances or crevices in the metal with fluid becoming stagnant in the gap. This is normally in the form of pitting formed on the surface of the metal and gradually extending into the metal itself [57].

Fig.1.9: Crevice Corrosion [58]

1.7.8 Stress Corrosion Cracking

The cracking of metal (or) alloy by the conjoint action of a tensile stress and a corrosive environment is known as stress corrosion cracking (SCC). The susceptibility to stress corrosion cracking is due to certain metallurgical factors such as chemical composition, preferential orientation of grains, composition and distribution of precipitates, dislocation, structure and environmental factors such as temperature, stress level and structure of metal [59].

Fig.1.10: Oil and gas pipeline after being attacked by stress corrosion cracking [60].

1.7.9 Carbon Dioxide (CO_2) Corrosion (Sweet Corrosion)

In production pipelines **CO_2** corrosion is the most common type corrosion issue. It is also called as sweet corrosion. The main reason behind this because of the presence **CO_2** content in the crude oil and gas obtained from the reservoir. The hydration of dissolved carbon dioxide gives carbonic acid, carbonic acid then dissociates into bicarbonate and carbonate, and those chemical reactions are given below. The pH level reduces due to the carbonic acid which leads to corrosive pipelines.

$$CO_2\,(g) \longrightarrow CO_2\,(aq)$$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \text{ (Carbonic acid)}$$

$$H_2CO_3 \longrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \longrightarrow H^+ + CO_3^{2-}$$

The electrochemical reaction of carbon dioxide corrosion is

$$Fe + CO_2 + H_2O \longrightarrow FeCO3 + H_2$$

The formations of surface films, consists to iron carbonate **($FeCO_3$)** and their effects on the corrosion rate has significant role in **CO_2 (aq).** Iron carbonate **($FeCO_3$)** mainly depends upon temperature and it plays an important role in formation of protective layer on the surface of the metal at higher temperature. Carbon dioxide corrosion is greatly influenced by following factors, they are temperature, **CO_2** partial pressure, flow rate, pH, acetic acid concentration, water wetting, welds (metal microstructure) etc. These factors are closely linked with each other. Their influence is not yet completely understood. [61].

Fig.1.11: Oil and gas pipeline under sweet corrosion[62].

1.7.10 Hydrogen Sulfide (H_2S) Corrosion (sour corrosion)

The natural gas can be corrosive due to the significant content of hydrogen sulfide. Natural gas is said to be "sour gas" if it contains **more than 5.7 milligrams of hydrogen sulfide per cubic meter** of natural gas. Natural gas with less amount of hydrogen sulfide is called as "sweet gas". Sour gas at high temperature, pressure and in mixtures of formic acids which typically found in downhole oil well simulations will be more corrosive. Only special surface alloys can withstand to that sour gas environments. Amine solutions are generally used to remove hydrogen sulfide gas**.** **H_2S** Corrosion is electrochemical in nature. The chemical reaction happens between H_2S and iron form iron sulfide films. H_2S is non-corrosive in the absence of water**.**

$$Fe + H_2S + H_2O \longrightarrow FeS + H_2 + H_2O$$

Depending upon the environment, hydrogen sulfide can form various types of iron sulfide form like amorphous ferrous sulfide, cubic ferrous sulfide, pyrrhotite, troilite etc. Finding the kinetics of iron sulfide scale formation is difficult because of its close influences and poor understanding of mechanisms [61].

Fig.1.12: Oil and gas pipeline under sour corrosion [63].

1.7.11 Oxygen Induced Corrosion

Naturally, oxygen is not one of the constituents of oil and gas reservoir. However, the ingress of oxygen (either knowingly or accidentally) via leaking pump seals, casing, and process vents and open hatches result in an increase of the cathodic reaction of the electrochemical process[64]. Oxygen is an electron acceptor in a cathodic reaction thereby accelerating the anodic destruction (dissolution) of metal [65]. It is important to note that the presence of oxygen also increase the corrosive effects of both CO_2 and H_2S gases resulting in higher corrosion rates. Presence of oxygen in sour wells can be detrimental because it can react with and remove the protective FeS, forming elemental sulphur. Previous studies had shown that oxygen concentration as low as 5ppb could be very destructive to pipelines transporting oil and gas, and need to be removed using an oxygen scavengers[66]. Figure 2.6 showed a typical oxygen corrosion of pipeline.

Fig.1.13: Oxygen Induced Corrosion [67].

2.1 Acidization of Oil Well

Acidizing is one of the most widely used and effective means available to oil and gas operators for improving productivity (stimulation) of wells. Acidizing is commonly performed on new wells to maximize their initial productivity and on aging wells to restore productivity and to maximize the recovery of the energy resources. Figure 1.14 shows pictorial presentation of oil well acidization.

Acidizing involves pumping acid into a wellbore or geologic formation that is capable of producing oil and/or gas. The purpose of any acidizing is to improve a well’s productivity or injectivity.

There are three general categories of acid treatments:

- **acid washing,**
- **matrix acidizing,**
- **fracture acidizing.**

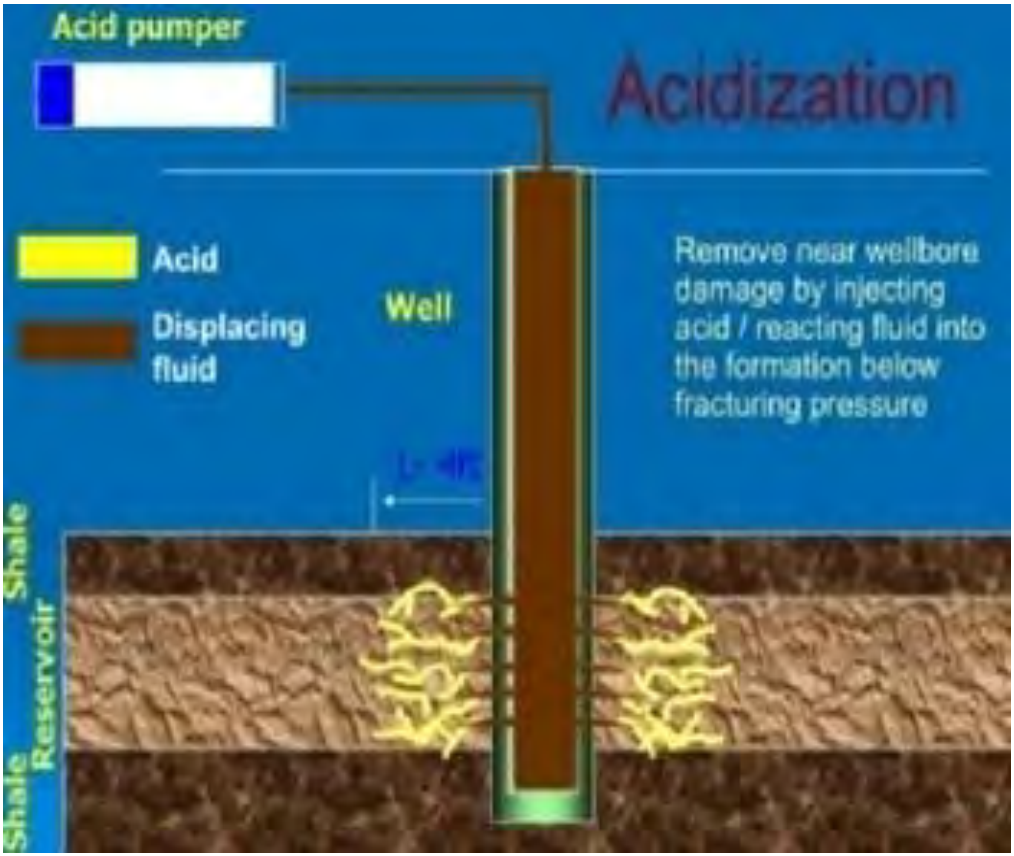

Fig.1.14: Acidization of oil wells [68].

In acid washing, the objective is simply tubular and wellbore cleaning. Treatment of the formation is not intended. Acid washing is most commonly performed with hydrochloric acid (HCl) mixtures to clean out scale (such as calcium carbonate), rust, and other debris restricting flow in the well. Matrix and fracture acidizing are both formation treatments.

In matrix acidizing, the acid treatment solution is injected below the formation fracturing pressure. In fracture acidizing, acid is pumped above the formation fracturing pressure.

The purpose of matrix or fracture acidizing is to restore or improve an oil or gas well's productivity by dissolving material in the productive formation that is restricting flow or to dissolve formation rock itself to enhance existing, or to create new flow paths to the wellbore. Two key factors dominate the treatment selection and design process when planning an acid job, formation type – carbonate, sandstone, or shale, and formation permeability – the ability of liquid to flow through the formation in its natural state[69].

A common type of acid employed to stimulate production is hydrochloric acid, which is useful in removing carbonate reservoirs, or limestones and dolomites from rock. Also HCl can be combined with mud acid or hydrofluoric acid (HF) and used to dissolve quartz, sand and clay from the reservoir rocks [70].

The acid reaction may be represented by the following equation:

$$\mathbf{2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2}$$

$$\mathbf{CaMg\,(CO_3)_2 + 4HCl \rightarrow CaCl_2 + MgCl_2 + 2H_2O + 2CO_2}$$

Different acids used in conventional acidizing treatments, are as follows:

- HCl, (Hydrochloric acid)
- HF, (Hydrofluoric acid)
- CH_3COOH,(Acetic acid)
- HCOOH, (Formic acid)
- H_2NSO_3H,(Sulfamic acid)
- $ClCH_2COOH$ (chloroacetic acid)

Various combinations of these acids are employed in specific application. HCl used in the field is 15% by weight; however acid concentration may vary between **5% to about 35%.** Acetic acid is weakly ionized, slow reacting acid, can usually be left in contact with tubing or casing for days without the danger of serious corrosion. Formic acid is a weakly ionized, slow reacting and can’t be used at higher temperature to inhibit against corrosion. Hydrofluoric acid used in oil and gas wells is normally 3% HF plus 12% HCl and employed exclusively in sandstone matrix acidizing to dissolve clays, but fast reaction time and precipitants make HF undesirable in carbonate formation.Sulfamic acid is as reactive as HCl, but before using, it should be modified to dissolve iron oxides or other iron scales. Sulfamic acid is not recommended for temperature above 180^0F. [71].

Other additives that are commonly used in an acid job include a corrosion inhibitor to protect the well tubular and related equipment’s that is exposed to the acid, an emulsion blocker (surfactant) to prevent formation of oil – well emulsions and an “iron – control agent” to retain any dissolved iron in solution. Other more specialized additives and different types of acid may also be used based on the case specific condition or needs.

3.1 Corrosion Mitigation Methods in the Oil and Gas Industry

The corrosion challenges in the oil fields are dynamic phenomena and those that are of highest concern. Hence, in order to improve the life span of structures in oil fields, corrosion needs to be fought to, at least the barest minimum. Although many methods have been highlighted in the past to combat corrosion on these offshore and onshore facilities, the mitigation methods can be classed broadly into the categories outlined below.

3.1.1 Material used for oil and gas well construction:

Corrosion attack can be handled by proper material selection, proper design of the equipment, control over operating conditions within the design range and using suitable corrosion control measures. Proper selection of materials can possibly minimize corrosion due to use of a less expensive material along with passivation methods and other corrosion control surface treatments. Proper evaluation while selecting materials of construction and deciding ways to mitigate corrosion have direct impact on the economics of a oil and gas industries. Materials having good corrosion resistance should always be considered and a proper background checks about the physico-chemical and mechanical properties of the material as well as knowledge about cost, fabrication technique and heat treatments techniques are also important factors [72].

The material used for pipeline construction play an important role in the petroleum industry as they carry liquids and gases over long distances from their source to the ultimate consumer .In oil and gas application different grades of stainless steel are used such as mild steel API N-80 (API – American Petroleum Institute), L80, J55. Applicable corrosion resistant alloys in the oil and gas industry include 13cr, 22cr duplex, 25cr duplex, 28cr stainless steel, 825 nickel alloy, 625 nickel alloy, 2550 nickel alloy and 276 nickel alloy. The speciality stainless steel includes LDX2101, 254 SMO and 654 SMO[73-74].The table-1.4 summarizes some of the commonly used materials in the hydrocarbon and oil and gas industries as presented by Nalli [75].

Material Specification	**Oil and Gas Applications**
Carbon Steels	Bulk fluids, crude pipelines, flow lines, water and steam injection lines, production and test separators, KO drums, storage tanks.
Low- and medium-alloy steels	Well head items, chokes, malifolds and well components with sour and high-temperature applications.
Straight chromium steels (chromium 12% to 18%)	Christmas trees, well heads, downhole rods, valves and casing pipes.
Chromium-nickel steels (chromium >18%, nickel >8%)	Valve trims, instruments and materials of separators and tanks, low-chloride levels.
Nickel steels (2.3%, 3.5%, 9% nickel)	Rarely used in oil and gas sectors, LNG storage tanks, piping and pumps.
Duplex stainless steels (22% chromium duplex, 25% chromium super, duplex)	Piping, vessel and tank internals where a very high level of chlorides is present.
Nickel-chrome (inconels) **Ni-Cr-Fe alloys**	Well head and flow lines, manifolds with high sour and temperature applications.
Nickel-iron (incolys) **Ni-Fe-Cr alloys**	Well head and flow lines, manifolds with high sour and temperature applications.

Table 1.4: Recommonded materials in oil and gas industries

Craig [76] presented some alloys (shown in Table 1.5) whose applications in the oiland gas industry are majorly in the absence of oxygen.

Alloys	**Nominal composition**							**Oil and gas application**
	Cr	Ni	Mo	Fe	Mn	C	N	
13Cr	13	-	-	Balanced	0.8	0.2	-	Corrosion resistance in CO_2/NaCl environments in the absence of O_2 and H_2S
316	17	12	2.5	Balanced	1.0	0.04	-	Frequently used for oil field applications in the complete absence of oxygen
22Cr	22	5	3	Balanced	1.0	0.1	0.1	Susceptible to localized corrosion in the presence of small amounts of O_2 and H_2S
25Cr	25	7	4	Balanced	1.0	0.1	0.3	Corrosion resistance in H_2S/CO_2 environments in the absence of elemental sulfur

Table 1.5: Chemical composition of recommended materials in the oil and gas industry

3.1.2 Cathodic Protection

There are two primary types of cathodic protection (CP) systems: sacrificial anode (galvanic anode) cathodic protection and impressed-current cathodic protection. Sacrificial anode CP utilizes an anode material that is electronegative to the metal under protection. When connected to the pipe, the pipe becomes the cathode in the circuit and corrosion is mitigated. Typical sacrificial anode materials for underground pipelines are zinc, magnesium and Aluminium etc. Impressed-current CP utilizes an outside power supply (battery) to control the voltage between the pipe and an anode (cast iron, graphite, platinum clad, mixed metal oxide, etc.) in such a manner that the pipe becomes the cathode in the circuit and corrosion is mitigated.[77].

Pros & Cons of Cathodic Protection:

- Cathodic protection is the only method which will reduce corrosion rate near to zero.
- Corrosion rate reduction can be attained even if total protection is not possible or practicable.
- Chances of damaging the protective coatings (cathodic disbondment) are likely when improperly applied.
- Cracking as a result of hydrogen embrittlement
- Interference of stray current (Normally onshore)

Cathodic protection is most often used in conjunction with a coating. There are always flaws in the coating due to application inconsistencies, construction damage, or the combination of natural aging and soil stresses. If left unprotected, the pipeline will undergo corrosion or SCC at these coating flaws (holidays). Often the rate of attack through the wall is much higher at the holiday than the general attack of a bare steel surface. The use of a coating greatly reduces the total amount of current required to achieve protection of the pipeline system; therefore, CP and external coatings are utilized together wherever possible [78].

3.1.3 Protective Coatings

Coatings are thin materials applied as a liquid or powder which on solidification should be firmly and continuously attached to the material they protect from corroding. These materials may be organic or inorganic. It is important that coatings are flexible, resistant to chemical attack from surrounding fluids, strongly adhesive, have little or no pores, and show thermal stability. Coatings can act as anti-corrosives, adhesives, anti-reflectives, catalysts, etc.

According to NACE Standard RP0169-2013 [79-80], a desirable coating should possess the following properties:

- **Effective electrical insulation.** As corrosion is an electrochemical process, a good coating must break the current circuit by isolating the metal from its environment (electrolyte). To assure a high electrical resistance, the coating should have a high dielectric strength.
- **High moisture (water) resistance.** Water transfer through the coating film may cause blistering, and contribute to corrosion of the metal.
- **Easy applicability.** Application of the coating to structures must be possible by a method that will not adversely affect the properties of the structure and with a minimum of defects.
- **Ability to resist development of holidays with time.** The coating's resistance to chemicals, hydrocarbons, and acidic or alkaline conditions should be sufficient to ensure their performance in contaminated environments.
- **Good adhesion to metal surface**. The coating requires a sufficient adhesion to prevent water ingress or migration between the coating and the metal structure.
- **Ease of repair.** As coatings would degrade gradually in service, repairs and recoating in the field are expected.

Protective coatings are applied for dividing the surfaces that are susceptible to corrosion from the components in environment which cause corrosion to happen. Although, that protective coatings cannot provide 100 percent protection. Protective coatings are generally applied for carbon steel pipelines in order to mitigate the corrosion. Coatings can be applied on both internal and external surface. The internal coatings should be compatible with the fluids flow inside the pipelines and the external coatings with respect to the environmental conditions. If localized corrosion at a outer layer defect is expected to origin failure, extra corrosion control measures should be applied. Poor surface preparation causes majority of coating failures. Coatings are especially useful when used in combination with other methods of corrosion command such as cathodic defense or Galvanic corrosion [78].

3.1.4 Design

The application of rational design principles can eliminate many corrosion problems and greatly reduce the time and cost associated with corrosion maintenance and repair. Corrosion often occurs in dead spaces or crevices where the corrosive medium becomes more corrosive. These areas can be eliminated or minimized in the design process. Where stress-corrosion cracking is possible, the components can be de-signed to operate at stress levels below the threshold stress for cracking. Where corrosion damage is anticipated, design can provide for maxi-mum interchangeability of critical components and standardization of components

Some important rules relating to geometrical design to minimize corrosion are:

- Provide corrosion allowance,
- Avoid Galvanic contact,
- Avoid crevices
- Avoid sharp bends and prostrations in piping systems,
- Avoid hot spots by providing uniform temperature gradients and
- Provide for easy drainage: as the design engineer tries to reduce the time that the environment will contact the metal [81-82].

4.1 Chemical Inhibitors

Inhibitors are substances or mixture that in low concentration and in aggressive environment inhibit, prevent or minimize the corrosion. [83].

Mechanism of inhibition:

- ➢ The inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect.
- ➢ The inhibitor leads to the formation of a film by oxide protection of the base metal.
- ➢ The inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex [84].

The corrosion inhibitors can be chemicals either synthetic or natural and could be classified by:

- ➢ The chemical nature as organic or inorganic;

- The mechanism of action as anodic, cathodic or a anodic-cathodic mix and by adsorption action, or
- as oxidants or non-oxidants. In general, the inorganic inhibitors have cathodic actions or anodic. The organics inhibitors have both actions, cathodic and anodic and the protective by a film adsorption.

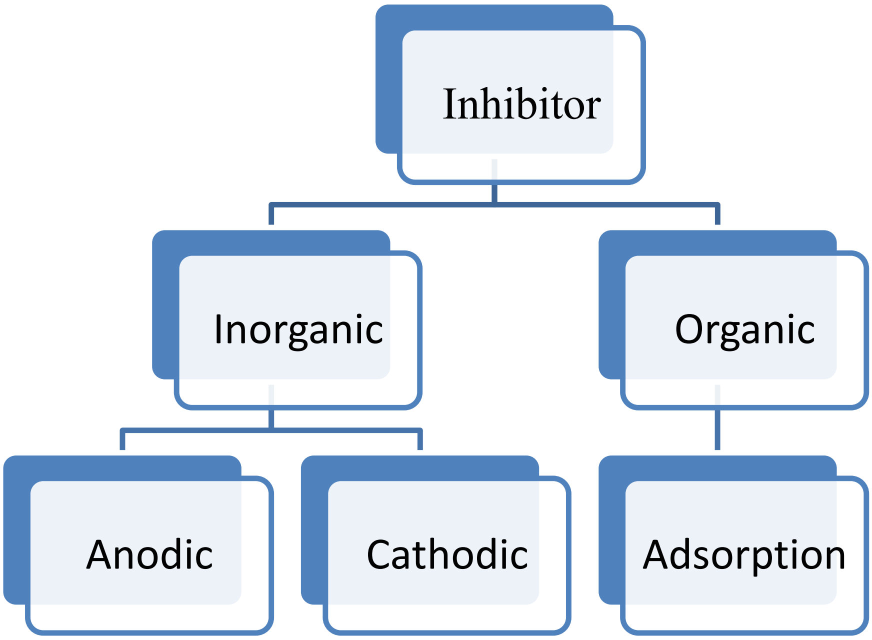

Fig 1.15: Classification of inhibitors

4.1.1 Cathodic Inhibitors

Cathodic inhibitors inhibit the hydrogen evolution in acidic solutions or the reduction of oxygen in neutral or alkaline solutions. It is also observed that the cathodic polarization curve is affected when a cathodic inhibitor is added to a system,The Figure 1.16 shows an example of a polarization curve of the metal on the solution with a cathodic inhibitor. When the cathodic reaction is affected the corrosion potential is shifted to more negative values. Substances with high over potential for hydrogen in acidic solutions and those that form insoluble products in alkaline solutions are generally effective cathodic inhibitors. Some examples of such inhibitors are inorganic phosphates, silicates or borates in alkaline solutions which inhibit the oxygen reduction at the cathodic sites. Substances such as carbonates of calcium and magnesium, due to limited solubility, block the cathodic sites [85-86].

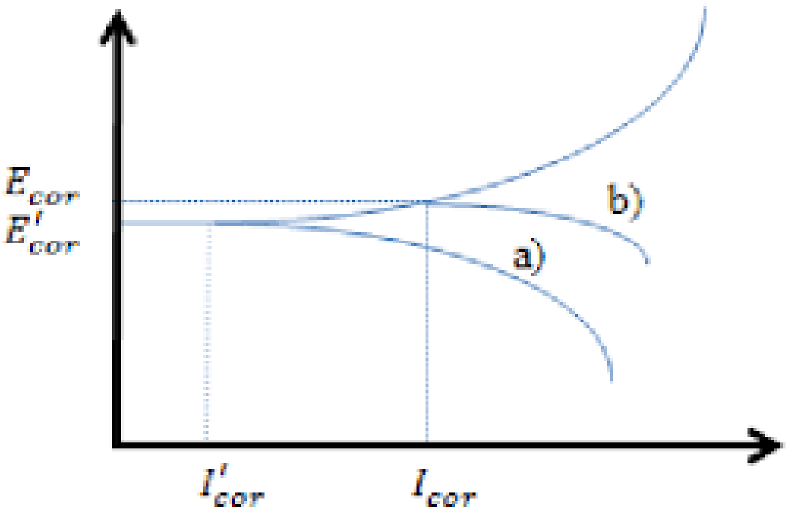

Fig 1.16: Potentiostatic polarization diagram: electrochemical behavior of the metal in a cathodic inhibitors solution (a), as compared to the same solution, without inhibitor (b)[87]

4.1.2 Anodic Inhibitors

Anodic inhibitors (also called passivation inhibitors) act by a reducing anodic reaction, that is, blocks the anode reaction and supports the natural reaction of passivation metal surface, also,due to the forming a film adsorbed on the metal. In general, the inhibitors react with the corrosion product, initially formed, resulting in a cohesive and insoluble film on the metal surface. [88-89]. Figure1.17 shows a potentiostatic polarization diagram of a solution with anodic inhibitor. The anodic reaction is affected by the corrosion inhibitors and the corrosion potential; of the metal is shift to more positive value. As well, the values of the current in the curve decreases with the presence of the corrosion inhibitor.Anodic inhibitors are generally effective in the pH range of 6.5–10.5 (near neutral to basic). Basically, oxyanions such as chromates, molybdates, tungstates and also sodium nitrite are very effective anodic inhibitors. These oxyanions are thought to play a role of repairing the defects in the passive iron oxide film on the iron surface.

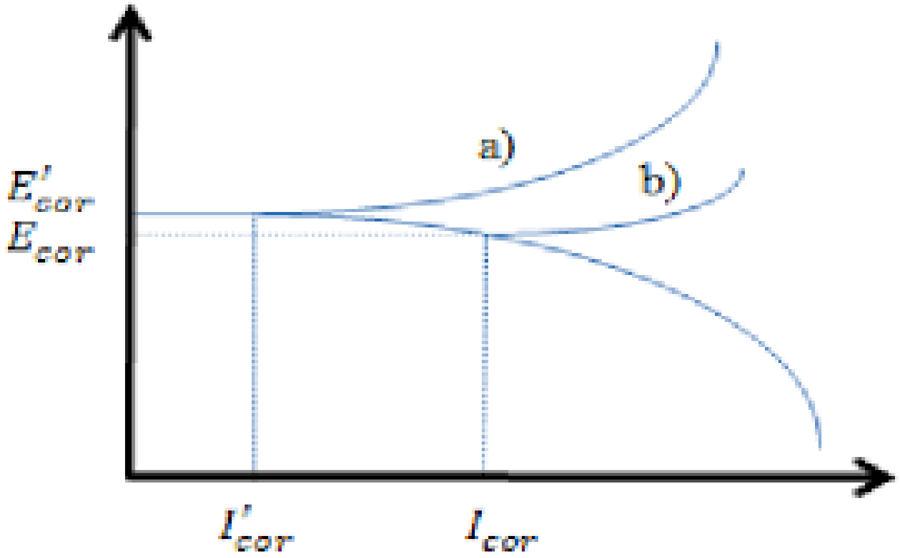

Fig.1.17: Potentiostatic polarization diagram: electrochemical behaviour of a metal in a solution with anodic inhibitor (a) *versus* without inhibitor (b)[87].

4.1.3 Mixed/Adsorption type Inhibitors

Mixed inhibitor ssuppress both the anodic and cathodic corrosion reactions, generally by adsorption on the entire surface of the steel, consequently forming a thin protecting layer. Therefore, these inhibitors are often referred to as 'adsorption inhibitors'or 'film-forming inhibitors, mixed inhibitor slow down the corrosion rate without a significant change in the corrosion potential. The corrosion potential may shift some what to either the anodic or the cathodic side, depending on which half-cell reaction is most affected, but the total effect on the corrosion potential is generally negligible (see Figure 1.18). Effective mixed inhibitors are found among organic substances with polar groups containing nitrogen (N), sulphur (S) and hydroxyl (-OH) groups [90]. Organic compounds such as amines and alkanolamines are commonly used as 'mixed inhibitors'.

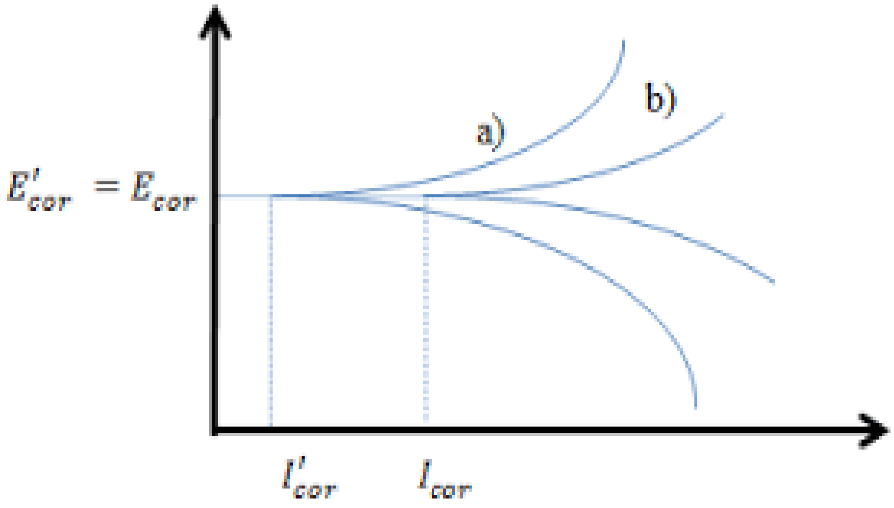

Fig.1.18: Theoretical potentiostatic polarization diagram: electrochemical behavior a metal in a solution containing a mixed inhibitor (a) compared to the same solution without the inhibitor b)[87]

4.2 Pickling Inhibitors

Corrosion inhibitors those are used in the pickling baths and known as pickling inhibitors. They are used in order to avoid the metal dissolution due to the corrosiveness and aggressiveness of the acid solutions in pickling baths limiting the acid consumption (and so they prolong the effectiveness of the pickling bath) and also to reduce fumes and spray production due to hydrogen formation.

Pickling inhibitors must fulfil several requirements in order to be effective under severe conditions.The properties required can be summarized as follows:

- effective inhibition of metal dissolution,
- no overpickling in the presence of higher iron salt contents,
- no delay of the pickling process,
- effective at low concentrations,
- effective at higher temperatures,
- thermally and chemically stable,
- effective inhibition of hydrogen up-take by the metal,
- good surfactant and foaming characteristics.

Inhibitors may operate in three different ways. Film forming inhibitors form a thin layer over the base metal and stop the reaction. Cathodic inhibitors slow the reaction kinetics of the cathodic reaction and anodic inhibitors slow anodic reaction. Mixed inhibitors slow both reactions. Often inhibitors work in multiple ways depending on the conditions. Commercial pickling inhibitors are usually mixtures of wetting agents and organic synthetic compounds. Even a small addition of pickling inhibitor to a solution (0.1– 2.0 %) can reduce corrosion by 99%. Efficiency depends on the material, acid and temperature. Higher concentrations do not increase efficiency after a certain level and can affect the pickling process. For strong acids (HCl and H_2SO_4), inhibition is required, and for other acids, it must be considered on a case-by-case basis. Active ingredients are usually organic compounds containing nitrogen, phosphorus, arsenic, oxygen, sulphur and selenium. Inhibitor compounds that contain multiple bonds tend to be more effective. Originally natural products such as tar were used, but aldehydes, amines such as methanamine, N,N-diethylamine,decan-1-amine and acetylene alcohols have replaced them. Studies have shown that environmentally friendly alternatives like plant extracts could be used for acid inhibition [91-92].

4.3 Slushing Compounds

Slushing compounds are used to protect steel surfaces temporarily from rusting during shipment or storage. They consist of oils, greases, or waxes containing small amounts of organic additives. The latter are polar compounds that adsorb on the metal surface in the form of a closely packed oriented layer. In this respect, the mechanism of inhibition by organic Additives is similar to that of inhibition by pickling inhibitors, except that for use as slushing compounds, additives must suitably adsorb in the near - neutral range of pH, whereas pickling inhibitors adsorb best in the low pH range, calling for somewhat different properties. Whether an oil or a wax is chosen as the vehicle depends on (1) the relative length of time protection is desired, the wax usually providing longer life and (2) the ease of removal before the protected machine part is put into service, withan oil being easier to wipe off or dissolve in solvents. The thickness of an applied coat varies from 0.1 mm to more than 2.5 mm (5 to more than 100 mils). Suitable organic additives for use in slushing compounds include organic amines, zinc naphthenate, various oxidation products of petroleum, alkali and alkaline - earth metal salts of sulfonated oils, and various other compounds

[93]. A substance that has been used successfully is lanolin, obtained from wool scouring; its active constituents are various high - molecular - weight fatty alcohols and acids. Sometimes, lead soaps are added to slushing compounds, with these soaps reacting to form relatively insoluble $PbCl_2$ with any NaCl from perspiration transferred to steel surfaces through handling.

4.4 Vapour phase inhibitors

Substances of low but significant vapor pressure, the vapor of which has corrosion - inhibiting properties, are called vapor - phase inhibitors. They are used to protect critical machine parts (e.g., ball bearings or other manufactured steel articles) temporarily against rusting by moisture during shipping or storage. They have the advantage over slushing compounds of easy application, with the possibility of immediate use of the protected article without first removing a residual oil or grease film. They have the disadvantage of accelerating the corrosion of some nonferrous metals, discoloring some plastics, and requiring relatively effective sealing of a package against loss of the inhibiting vapor. The latter requirement is relatively easily achieved, however, by using wrapping paper impregnated on the inside surface with the inhibitor and incorporating a vapor - barrier coating on the outside. The mechanism of inhibition has not been studied in detail, but it appears to be one of adsorbed film formation on the metal surface that provides protection against water or oxygen, or both. In the case of volatile nitrites, the inhibitor may also supply a certain amount of NO_2 that passivates the surface. Detailed data have been presented for dicyclohexylammonium nitrite [94], which is one of the most effective of the vapor - phase inhibitors. This substance is white, crystalline, almost odorless, and relatively nontoxic. It has a vapor pressure of 0.0001 mmHg at 21°C (70°F), which is about one - tenth the vapor pressure of mercury itself. * One gram saturates about 550 m 3 (20,000 ft 3) of air, rendering the air relatively noncorrosive to steel. The compound decomposes slowly; nevertheless, in properly packaged paper containers at room temperature, it effectively inhibits corrosion of steel over a period of years. However, it should be used with caution in contact with nonferrous metals. In particular, corrosion of zinc, magnesium, and cadmium is accelerated. Cyclohexylamine carbonate has the somewhat higher vapor pressure of 0.4 mmHg at 25°C and its vapor also effectively inhibits steel [95].

4.5 Green corrosion inhibitors

Most synthetic inhibitors are effective corrosion inhibitors that typically consist of one or more active ingredients, additives and other solvents .However; they have been found to be toxic and persistent. Chromates, phosphates, silicates and heavy metals are other examples of film-forming inhibitors which have a negative environmental effect due to their persistence and toxicity. Moreover, their removal is expensive and complicated. The use of these hazardous inhibitors has to be reduced in order to meet evolving environmental restrictions which are also getting firmer. Thus there is a need for alternative inhibitors which can replace them but not have any of their undesired characteristics [96-97].

Green inhibitors do not contain toxic components such as heavy metals and are biodegradable, inexpensive to formulate, renewable and easily available. Recently, there has been an increasing trend in employing readily available, natural products such as the extracts of leaves and fruits in corrosion inhibitors in an effort to create environmentally-friendly inhibitors, generally referred to as green inhibitors [98].Natural or green inhibitors make use of the natural compounds found in fruits and vegetables to inhibit the corrosion of metals. The natural compounds such as minerals, vitamins, and phenolic compounds can be harnessed from extracts of various plants such as khillah seeds, neem leaves, passion fruits, cashews; African bush peppers and many more. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. Ebenso et al. showed the inhibition of corrosion with ethanolic extract of African bush pepper (*Piper guinensis*) on mild steel [99] *Carica papaya leaves* extract [100] *neem leaves* extract (*Azadirachtaindica*) on mild steel in H_2SO_4 [101]. Zucchi and Omar investigated plant extracts of *Papaia*, *Poinciana pulcherrima, Cassia occidentalis* and *Daturastramonium seeds* and *Papaya, Calotropisprocera B, Azadirachtaindica,* and *Auforpioturkiale sap* for their corrosion inhibition potential and found that all extracts except those of *Auforpioturkiale* and *Azadirachtaindica* reduced the corrosion of steel with an efficiency of 88%–96% in 1 N HCl and with a slightly lower efficiency in 2 N HCl. Extracts of plant materials contain a wide variety of organic compounds. Most of them contain heteroatoms such as P, N, S, O. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented.

4.6 Choice of corrosion inhibitors

In literature, many reports have correlated the substituent effect and the inhibitory efficiency of molecules based on nitriles, pyridines, anilines, imidazolines, polyesters, aliphatic amines, benzoic acid, sulfides, thiophenes etc. The use of inhibitors based on these aforementioned molecules is as result of their mechanism of action, such as their electron-donating ability. Therefore, selecting the right organic inhibitor for a specific environment and metal must be done with great care as no single inhibitor is known to protect all metals in different corrosive environments. In order to choose a good corrosion inhibitor, one must consider the following:

- It should be synthesized conveniently from relatively cheap raw materials [102-103]
- It should be soluble in water or alcohol
- It should be cost effective;
- It should give good corrosion protection at very low concentration range of inhibitor;
- Elements like oxygen, nitrogen, phosphor, sulfur and the presence of multiple bonds or aromatic rings in the inhibitor molecule is preferred as this leads to increased adsorption of the compound on the metal surface and therefore to the enhancement of inhibition efficiency[104];
- It should be thermally and chemically stable;
- The price of the inhibitor is relative measure, but it should be still economic for large-scale applications;
- It should not have any side effect [105-106];
- It should not be hazardous or harmfull to user [107];
- It should be eco friendly (green)[108].

4.7 Toxic Effect of Chemical Inhibitors In the oil and Gas industry

In oil and gas industry the use of corrosion inhibitors has become a common practice. However, some of these chemicals cause harm to the environment. Many common corrosion inhibitors that are still in use are very toxic and/or environmentally unfriendly. A number of currently-used inhibitors contains chromates, nitrates (these are forbidden in most developed countries), which are believed to be toxic in nature. Molybdate salt or rare earth metals replaced chromates, but these compounds are very expensive. Therefore, it is important to find inhibitors that are nonhazardous, but could protect metals against corrosion at high corrosion efficiency. Consequently, it is paramount to study environmentally-friendly molecules that could potentially be used as corrosion inhibitors [109-110].

4.8 Adsorption of inhibitors

Adsorption may lead to an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase as a result of the operation of surface forces. Adsorption can also occur at the interface of a condensed and a gaseous phase21. The potential energy of a surface adsorbing a molecule decreases as the molecule approaches the surface. The degree of adsorption greatly depends on the specific nature of the solid and of the molecules being adsorbed and it is a function of pressure (or concentration) and temperature. An adsorbate is a molecular species of a gas or a substance dissolved in liquid which adheres to or is adsorbed in an extremely thin surface layer on a solid substance. An adsorbent (or substrate) is a condensed phase at the surface of which adsorption May occur. Adsorption of corrosion inhibitors on metal surface can be described in two ways based on the type of interaction with the metal surface:

A) Physisorption: This is due to electrostatic forces between ionic charges or dipoles on the inhibited adsorbed species and the electrical charge that occurs at the metal/electrolyte interface [111]. The adsorption is only stable at low temperature because of its low heat of adsorption. Sebhaoui et al.[112] reported on the mechanisms of organic corrosion inhibitor in HCl solution confirmed that a negative value of ΔG^0_{ads} will indicate that adsorption process on the metal surface is spontaneous, and an increased value of ΔG^0_{ads} indicates that the compound is strongly adsorbed on the mild steel surface. It was also established that when the values ΔG^0_{ads} are ~20kJ/mol or lower indicates an electrostatic attraction between a charged metal surface and charged organic molecules in the bulk solution which is an expression of physisorption adsorption.

B) Chemisorption: This is due to the charge transfer or sharing between the inhibitor molecules and the metal surface to form a coordinate type bond. Chemisorption exhibits stronger adsorption energy compared to physisorption and mostly occurs at higher temperature. ΔG^0_{ads} values of ~40kJ/mol or higher indicates that there is charge sharing or charge transfer between the metal surface and the organic molecules to form a coordinate type of bond [113].

4.9 Adsorption Isotherm

An appropriate adsorption isotherm is used to describe the adsorption process of corrosion inhibition on metal surface the adsorption of corrosion inhibitors on metal surface depend on many factors such as the charge and nature of the metal surface, electronic characteristics of the metal surface on its adsorption of corrosion inhibitor and other ionic species, temperature of the corroding environment, and the corrosion potential at the metal/electrolyte interface[114]. Isotherms can be used to determine the thermo- dynamics of inhibitor adsorption which may provide useful insights into the mechanism of corrosion inhibition [115]. The following are the adsorption isotherms normally employ to describe the corrosion inhibition on metal surface:

Name	Isotherm	Plot
Langmuir	$\frac{C}{\theta} = \frac{1}{K} + \mathrm{c}$	$\frac{C}{\theta}$ vs c
Freundlich	$\theta = k\, c^{1/n}$	log θ vs log c
Temkin	$e^{-2a\theta} = kc$	θ vs log c
Frumkin	$\frac{\theta}{1-\theta} e^{-2a\theta} = kc$	$ln \frac{\theta}{(1-\theta)c}$ vs θ

Table 1.6: Types of adsorption isotherm

Where *'k'* is the adsorption equilibrium constant; '*c*' the concentration in bulk; n is an adsorption intensity; 'θ' is surface coverage and *'a'* is energetic inhomogeneity factor. Adsorption isotherms provide important information of the nature of the metal/inhibitor interaction [116]. If the slope and Karl Pearson's coefficient (correlation coefficient) obtained from Langmuir's adsorption isotherm is one, then it can be said that ideal Langmuir adsorption isotherm model is followed. But if $R^2 = 1$ and slope $\neq 1$, then it is El-Awady adsorption isotherm [117].

El-Awady adsorption isotherm equation is: $\frac{\theta}{1-\theta} = K'C^y$

Taking log on both the sides, $\log\frac{\theta}{1-\theta} = \log K' + y \log C$

$\log \frac{\theta}{1-\theta}$ vs. log C will give a straight line with slope $y = \frac{1}{x}$ where x is the number of inhibitor molecules occupying one active site (or the number of water molecules replaced by one molecule of the inhibitor) and intercept is log K' which is related with equilibrium constant K as K = K'(1/y) .

The Flory-Huggins adsorption isotherm is used for polymer systems and is given by the equation:

$$\frac{\theta}{C} = K\,(1-\theta)^X$$

Where x, represents the number of desorbed water molecules from the surface replaced by the adsorption of one organic molecule.

Taking log on both the sides,

$$\log \frac{\theta}{C} = \log K + x \log (1-\theta)$$

The graph between $\log \frac{\theta}{C}$ and $\log (1-\theta)$ gives a straight line with slope equal to x and intercept is equal to log K. If Karl Pearson's coefficient for this straight line is nearly one, then Flory-Huggins adsorption isotherm is followed [118].

5.1 Corrosion Monitoring

Corrosion monitoring is the use of any method or methods which can deduce or predict the amount of corrosion actively occurring on any elements of a structure or entire equipment. Recording data and analysing historical corrosion trends is also a key part of corrosion monitoring and can be effectively used to manage corrosion. Lack of monitoring, insufficient review of design and inattention to technical shortcomings and warnings lead to initiation of corrosion attack. Thus, it is important to have a well managed system to tackle technical corrosion issues and provide active human response to handle them. To ensure unabated operations of industrial processes at minimum cost, corrosion inspection should be carried out from early stages of design until the period of shutdown. Corrosion engineers or experts, along with plant managers should conduct inspections from time to time and ensure that facilities are fit for service and equipment are working at proper conditions.

5.1.1 Corrosion Monitoring Techniques

Corrosion inspection and monitoring are key activities in ensuring, pipelines integrity is maintained and corrosion mitigated. In monitoring and inspection of pipelines, data are collected to enhance corrosion control by way of predicting the remaining life and the suggestion of possible mitigation measures that will help to enhance serviceability will largely depend on the experience of the personnel. In management of pipeline corrosion in oil and gas industries, proactive technique which involves determination of the corrosion standpoint prior to failure is utilized. This involves in-line and on-line monitoring system. In this system, data which could enhance the knowledge of the rate of corrosion degradation are collected and steps are taken to prevent failure. In-line system cover the installation of devices directly into the pipeline like corrosion coupons, biostuds and so forth. These need to be extracted for analysis periodically. On-line monitoring techniques include deployment of corrosion monitoring devices either directly into the process or fixed permanently to the facility. These include electrical resistance (ER) probes, linear polarization resistance (LPR) probes, fixed ultrasonic (UT) probes, acoustic emission and so forth. Whereas some corrosion monitoring techniques can be used for continuous monitoring, others are used for periodic monitoring. Corrosion monitoring techniques can either be direct or indirect parameter measure.[119-120]. This is summarized in following table.

Direct method	Indirect method
Non destructive inspection (NDI)	Biological counts
Material tests coupons	Hydrogen probes
Electrical resistance (ER) probes	pH probes
Linear polarization resistance (LPR)	Specific ions
Electrochemical impedance spectroscopy (EIS)	Temperature
Electrochemical noice (EN)	Conductivity
Galvanic current(GC)	Electric potential monitor

Table 1.7 summary of corrosion monitoring techniques [41].

5.1.2 Benefits of Corrosion Monitoring

Some significant benefits of corrosion monitoring include:

- improved safety;
- Reduced downtime;
- Early warning of impending damage or failure;
- Reduced maintenance costs;
- Reduced environmental damage;
- Longer interval between scheduled maintenance;
- Reduction in operation costs;
- Plant life extention.

Within the oil and gas industry, any supply disruptions can easily affect market prices and consumer confidence. Corrosion management and monitoring is therefore vital in preventing any environmental and financial impacts of corrosion related leakages [121].

6.1 Failure Analysis and Its Managements

Most often, failure due to corrosion in pipelines can be attributed to failure of the corrosion control systems installed. These failures do not occur suddenly. There are usually telltale signs to their eventually occurrence.

Conservation of Clean Air and Water in Europe (CONCAWE) [122] categorizes the failure

Types that can occur in oil and gas pipelines into five groups:

1. **Mechanical*:*** this type of failure results from a material defect or construction fault. It is alocalized damage of pipelines which leads to either immediate or future pipeline failure. Immediate failure typically occurs by striking with mechanical equipment (e.g. backhoe) and produces a leak at the time of damage. This type of damage occurs in three broadcategories: dents, gouges, and combined dent/gouge defects.
2. **Operational*:*** this kind of failure is a result of operational errors, break down orinsufficiency of safeguarding systems (e.g. mechanical pressure relief system) or fromoperator inaccuracy/error.
3. **Corrosion:** unprotected pipelines, whether buried in the ground, exposed to theatmosphere, or submerged in water, are prone to corrosion.
4. **Natural hazard*:*** this type of failure results from flooding, lightning strikes, shifting land, etc.
5. **Third party:** this type of failure results from accidental or intentional actions by a third party.

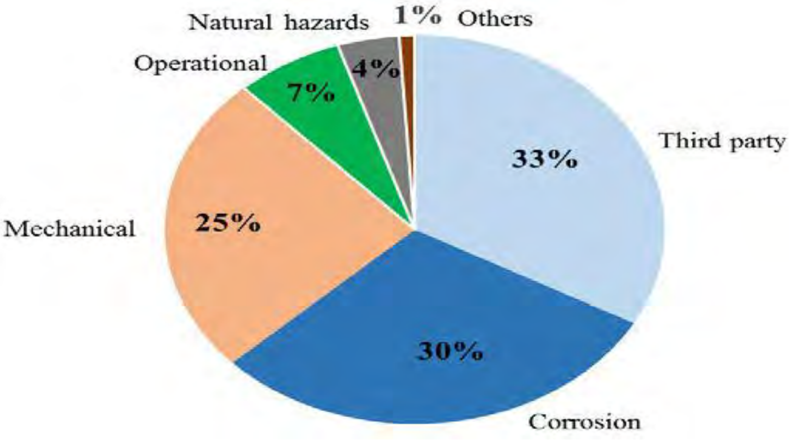

Fig.1.19: Different failure mechanisms [122].

In Figure 1.19, the distribution of failures and their occurrence rates are presented. Note that failure due to corrosion represents 30% of all failures.With diligent maintenance programs, corrosion defects can be assessed, evaluated and proper intervention made before they result in failure. This preventive maintenance approach is vital when one considers the myriad consequences that can result from a petroleum pipeline failure. Pipelines are required to be routinely inspected to ascertain their integrity. Corrosion monitoring is an integral part of this integrity management program. Various methods exist for monitoring/detection of corrosion in pipelines.

The methods aim to ensure that pipelines do not become defective and that defects are detected before they can cause damage. The methods commonly employed to detect corrosion in underground pipelines are hydrostatic testing, direct assessment and in-line inspection.

1. Hydrostatic Testing

Pipelines should be periodically hydro-tested in-service to prove their integrity. The process involves pressure testing the pipeline with water at higher pressures than the pipeline operating pressure; typically 125% of maximum operating pressure (MOP) of the pipeline [123].This is the most common method to ensure the integrity of a pipeline and establish a safe operating pressure, regardless of the flaws present in the pipeline. Any defect larger than a critical size will fail at this hydrostatic test pressure.

2. Direct Assessment

As a part of condition monitoring programs, pipeline companies commonly use field investigation (direct assessment) programs. In direct assessment field inspection programs the overall condition of the pipeline corrosion system and its coating is determined using above ground measurements. The data is then used to prioritize the system for direct examination, hydrostatic testing, in-line inspection, recoating or pipe replacement.

3. In-line Inspection

Pipelines can be monitored from the inside without disrupting the product flow by using in-line inspection tools, also called intelligent pigs. The pigs are sophisticated devices that travel with the product and via array of sensors record data about the condition of the pipe. They can measure metal loss (due to corrosion and cracking) and geometric abnormalities (e.g. dents). There are two basic types of inline tools for measuring metal loss: **magnetic flux leakage (MFL) tools and ultrasonic tools.**

Magnetic flux leakage (MFL) tools measure the change in magnetic flux lines produced by the defect and produce a signal that can be correlated to the length and depth of a defect. In recent years, the magnetics, data storage, and signal interpretation have improved, resulting in improved mapping of the flaw and a decrease in the number of unnecessary excavations. The high-resolution MFL tool is typically capable of readily detecting corrosion pits with a diameter greater than three times the wall thickness. Once detected, these tools can typically size the depth of the corrosion within +10% of the wall thickness with an 80% level of confidence. The MFL tool can be used to inspect either liquid product pipelines or natural gas pipelines.

4. Maintenance and Repair

In pipeline maintenance, two options are available to the engineer: repair or replace. Once corrosion or crack is detected, the size of the defects must be measured. Assessment of the defect size will determine the appropriate intervention. The defect size is usually ascertained by direct examination i.e.by direct measurement in the field. The length of crack is ground out to establish the maximum crack depth. Burst pressure models or fracture mechanics techniques can be used to determine the failure pressure of the affected sections. If the burst pressure is within acceptable limit the pipe is recoated. However, if it is less than the acceptable limit the pipe is replaced or repaired using steel or composite sleeves and recoated. If failure occurs in hydrostatic testing, the only option is to replace the failed sections. Replacement is also recommended when there is an extensive corrosion localized within an area in the pipeline. Improvement of the corrosion protection system to reduce corrosion or crack growth is also an option in areas where the growing crack is not an immediate threat to pipeline integrity. Generally, the maintenance or repair option is decided by the engineer after a careful assessment of the information gotten from the inspection tools. Other factors like cost, urgency and engineering considerations are also important in the choice of repair options [124]

7. Recent Review of Literature

The corrosion inhibition of mild steel in acid media has been widely studied using different organic compounds.The use of corrosion inhibitors for corrosion control has been the common practice in the oil and gas industry. The most effective corrosion inhibitors for oil field production have been found mostly organic compounds usually amines,imidazoles or quaternary ammonium salts and their derivatves containing N,S,and O atoms or multiple bonds which gets adsorbed or interact with metal surface to produce protective surface film.The planarity,pi electrons pair and quantity of O, N, P and S as heteroatoms are important features to determine the adsorptive strength of the corrosion inhibitors molecules and their ability to form physically protective barrier between metal surface and corrosive medium. The strength of active adsorption centers, determine the effectiveness and efficiency of organic inhibitors. The inhibition efficiency of heterocyclic compounds varies in the following order: O< N< S< P.

The study of scientific and technical corrosion literature reveals that a numerous number of organic compounds have been tested as corrosion inhibitors of mild steel in various medium. Use of organic compounds as a corrosion inhibitors for mild steel in hydrochloric acid investigated in recent years have been reviewed here. Details list of organic compounds reviewed as corrosion inhibitor is given table

Compounds containing functional groups with hetero atoms, which can donate lone pair of electrons, are found to be very efficient as inhibitors against metal corrosion in many environments. Many N-heterocyclic compounds with polar groups and/or π electrons are also acting as efficient corrosion inhibitors in acidic solutions. Schiff bases, an organic compound which has both these features combined in one molecule, should acts as a potential inhibitor. Schiff bases have been previously reported as effective corrosion inhibitors for steel in acid medium like hydrochloric acid, sulphuric acid, acetic acid, formic acid etc.Table 1.8 give detail information regarding organic compounds reviewed as corrosion inhibitors.

Corrosion Inhibitor	Types of Inhibitor	Corrosive medium	metal	Reference(s)
Schiff bases as corrosion inhibitors				
(E)-4-((2-(2,4-dinitrophenyl)hydrazono)methyl) pyridine(L(1)),((E)-4-(2-(pyridin-4-ylmethylene) hydrazinyl) benzonitrile (L(2)) and (E)-4-((2-(2,4-dinitrophenyl)hydrazono)methyl)phenol (L(3))	Mixed	HCl	Mild steel	125
N-(4-methoxybenzylidene)-2-[2-((*E*)-2-(4-methoxy benzylideneamino)phenyl)disulfanyl]benzenamine (Sb1))and *N*-(4nitrobenzylidene)-2-[2-((*E*)-2-(4-nitrobenzylideneamino)phenyl)disulfanyl] benzene amine (Sb2**))**	Mixed	HCl	Mild steel	126
3-(5-methoxy-2-hydroxybenzylideneamino)-2-(-5-methoxy-2-hydroxyphenyl)-2,3-dihydroquinazoline -4(1H)-one(MMDQ),and3-(5-nitro-2-hydroxybenzylideneamino)-2(5-nitro-2-hydroxyphenyl)-2,3-dihydroquinazoline-4(1H)-one (NNDQ)	Mixed	HCl	Mild steel	127
1-(2-hydroxybenzylidene)-3-(2,5-dioxoimidazo lidin-4-yl) urea (ALS)	Mixed	HCl	Carbon steel	128
(3-bromo-4-fluoro-benzylidene)-[1,2,4]triazol-4-yl-amine(BFBT),(4-trifluoromethyl-benzylidene)-[1,2,4] triazol-4-yl-amine(TMBT) and (2-fluoro-4-nitro-benzylidene)-[1,2,4]triazol-4-yl-amine (FNBT)	Mixed	HCl	Mild steel	129
(S)1-*N*-(1-hydroxy-1,1-diphenyl-3-methylbut-2-yl)-2-hydroxybenzaldimine (DPV) and (S)1-*N*-(1-hydroxy-3-methylbut-2-yl)-2-hydroxybenzaldimine (LV)	Mixed	HCl	HCS	130
N,N′-(pyridine-2,6-diyl)bis(1-(4-methoxyphenyl) methanimine) (PM)	Mixed	NaCl	J55 and N80 steel	131
N-(2-hydroxybenzylidene)thiosemicarbazide (HBTC)	Mixed	Saline water	Carbon steel	132
Polymeric schiff base	Mixed	HCl	Mild steel	133

1,13-bis-[(2-hydroxynaphtaldehyde)4,7,10-trioxatridecanediimine] (HNTTD)	Mixed	HCl	Mild steel X48	134
4-(4-hydroxy-3-methoxy benzyledene amino)-4-H-1, 2, 4-triazole-3, 5-dimethanol, HMATD	Mixed	HCl	Mild steel	135
E-*N*-(2-chlorobenzylidiene)-2-methylaniline	Mixed	HCl	Mild steel	136
(E)-4-(((4-propyl phenyl) imino) methyl) phenol (PMP) and (E)-4-((2-tolylimino) methyl) phenol (TMP)	Mixed	HCl	Mild steel	137
2-amino-6(2-hydroxybenzelideneamino)hexanoic acid (SB-1),2-amino-6-(4-methoxy benzelideneamino) hexanoicacid(SB-2)and2-amino-6-((4-dimethylamino) benzylideneamino) hexanoic acid (SB-3)	Cathodic	HCl	Mild steel	138
(4-(4-hydroxybenzylideneamino)-4H-1,2,4-triazole-3,5-diyl)dimethanol,(4-(4-methoxybenzylideneamino)-4H-1,2,4-triazole-3,5-diyl) dimethanol and (4-(3,4-dimethoxy benzylideneamino)-4H-1,2,4-triazole-3,5-diyl)dimethanol	Mixed	HCl	Mild steel	139
Quinoline derivatives as corrosion inhibitors				
2-amino-4-(2,4-dihydroxyphenyl)quinoline-3-carbonitrile (ADQC)	Cathodic	HCl	SAE 1006 steel	140
6-benzylquinoline (BQ) and 6-(quinolin-6-ylmethyl) benzene-1,2,3,4,5-pentasulfonic acid (QBPA)	Mixed	HCl	Mild steel	141
quaternary ammonium salts 1-benzylquinoline bromide (1) and 1-benzylquinoline chloride (2)	Mixed	HCl	Mild steel	142
8-quinoline sulphonyl chloride (8-QSC)	Cathodic	HCl	Mild steel	143
2-amino-7-hydroxy-4-phenyl-1,4-dihydro quinoline-3-carbonitrile(Q-1),2-amino-7-hydroxy-4-(p-tolyl)-1,4 dihydroquinoline-3-carbonitrile (Q-2),m 2-amino-7-hydroxy-4-(4-methoxyphenyl)-1,4dihydroquinoline -3carbonitrile(Q-3),2-amino-4-(4-(dimethylamino)- phenyl)-7-hydroxy-1,4-dihydroquinoline-3-carbonitrile (Q-4)	Mixed	HCl	Mild steel	144

2,6-dichloroquinoline-3-carbaldehyde (QA-1), 2-chloro-6-nitroquinoline-3-carbaldehyde (QA-2) and 2,6-dichloro-8-nitroquinoline-3-carbaldehyde (QA-3)	Mixed	HCl	Mild steel	145
Pyridine derivatives as corrosion inhibitors				
2,4-diamino-5-(phenylthio)-5H-chromeno[2,3-b] pyridine-3-carbonitrile (PPC-1) and 2,4-diamino-5-phenoxy-5H-chromeno[2,3-b]pyridine-3-carbonitrile (PPC-2)	Cathodic	HCl	N80 steel	146
(4-(4-methoxyphenyl)3,5-dimethyl-1,4,7,8-tetrahydrodipyrazolopyridine)(PP-1),3,5dimethyl-4-phenyl-1,4,7,8-tetrahydrodipyrazolopyridine(PP-2) and(3,5-dimethyl-4-(3-nitrophenyl)-1,4,7,8-tetrahydrodipyraz-olopyridine) (PP-3)	Mixed	HCl	Mild steel	147
8,9-bis(4-dimethylamino)phenyl)benzo[4,5] imi- dazo[1,2-a]pyridine-6,7-dicarbonitrile (INH)	Cathodic	HCl	Mild steel	148
2-amino-6-(2,4-dihydroxyphenyl)-4-(4-methoxyphenyl) nicotine nitrile (ADP) and 2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMP)	Mixed	HCl	N80 steel	149
2-phenylimidazo [1,2-a] pyridine (P1) and 2-(mmethoxyphenyl) imidazo [1, 2-a] pyrimidine (P5)	Mixed	HCl	C38 steel	150
2-amino-3,5-dicarbonitrile-4-(4-methoxyphenyl)-6-(phenylthio)pyridine(ADTPI),2-amino-3,5-dicarbonitrile-4 phenyl-6-(phenylthio) pyridine (ADTP II), and 2-amino-3,5-dicarbonitrile-4-(4-nitrophenyl)-6-(phenylthio) pyridine (ADTP III)	Mixed	HCl	Mild steel	151
2,6-diaminopyridine	Mixed	HCl	Mild steel	152
5-amino-9-hydroxy-2-phenylchromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile(N-1),5-amino-9-hydroxy-2-(p-tolyl)chromeno[4,3,2-de][1,6]-naphthay- ridine-4-carbonitrile (N-2), and 5-amino-9-hydroxy-2-(4-methoxyphenyl) chrome- no[4,3,2-de][1,6]naphtha-yridine-4-carbo nitrile(N-3)	Mixed	HCl	Mild steel	153

Carbonitrile derivatives as Corrosion inhibitors				
2-amino-5-nitro-4,6-diarylcyclohex-2-ene-1,3,3-tricarbonitrile (ANDT) derivatives namely, 2-amino-5-nitro-4,6-diphenylcyclohex-1-ene-1,3,3-tricarbo nitrile(ANDT-1),2-amino-4,6-bis-(4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile(ANDT-2)and2-amino-4,6-bis-(3-hydroxy-4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile (ANDT-3)	Mixed	HCl	Mild steel	154
2-amino-3-methyl-3-(4-nitrophenyl)-5-(phenylthio)-3H-pyrrole-4-carbonitrile (INH)	Mixed	HCl	Mild steel	155
2-amino-3-methyl-3-phenyl-5-(phenylthio)-3H-pyrrole-4-carbonitrile(PPCI),2-amino-3-(4-hydroxyphenyl)-3-methyl-5-(phenylthio)-3H-pyrrole-4-carbonitrile(PPCII),and2-amino-3-(2,4-dihydroxyphenyl)-3-methyl-5-(phenylthio)-3H-pyrrole-4-carbonitrile (PPC III)	Anodic	HCl	Mild steel	156
Benzenecarbonitrile and 5-bromovanillin (BNV)	Mixed	HCl	1018 carbon steel	157
4-(isopentylamino)-3-nitrobenzonitrile (PANB) and 3-amino-4-(isopentylamino) benzonitrile (APAB)	Mixed	HCl	Mild steel	158
Pyridazine derivatives as corrosion inhibitors				
6-methyl-4,5-dihydro-2H-pyridazine-3-one (MPYO), 6-phenyl-2H-pyridazine-3-one (PPYO) and 6-phenyl-2H-pyridazine-3-thione (PPYS)	Cathodic	HCl	Mild steel	159
ethyl (6-methyl-3-oxopyridazin-2-yl) acetate	Mixed	HCl	Mild steel	160
Triazole derivatives as corrosion inhibitors				
4-(4-hydroxy-3-methoxybenzyledeneamino)-4-H-1,2,4triazole-3, 5-dimethanol, HMATD	Mixed	HCl	Mild steel	161
4-((2,3-dichlorobenzylidene)amino)-3-methyl-1H-1, 2, 4-triazole-5(4H)-thione	Mixed	HCl	Mild steel	162

2-amino-1,3,4-triazole(AT),3-(2-pyridyl)-2-Amino-1,3,4-triazole (2-AT) and 3-(4-pyridyl)-2-Amino-1,3,4-triazole (4-AT)	Mixed	HCl	Carbon steel	162
3,5-diaryl-4-amino-1,2,4-triazole	Adsorption	HCl	Mild steel	164
Benzimidazole derivatives as corrosion inhibitors				
6-(dodecyloxy)-1*H*-benzo[*d*]imidazole (DBI)	Adsorption	HCl	Mild steel	165
Hydrogen bonded interaction and synergistic effect of alkyl benzimidazoles and semicarbazide pair	Mixed	HCl	Mild steel	166
2-(1-(morpholinomethyl)-1*H*-benzo[*d*]imidazol-2-yl) phenol(MBP),2-(1-((piperazine-1-yl)methyl)-1*H*-benzo[*d*]imidazol-2-yl)phenol(PzMBP)and2-(1-((pipe- ridine-1-yl)methyl)-1*H*-benzo[*d*] imida- zol-2-yl)phenol (PMBP)	Mixed	HCl	N80 steel	167
Propyl benzimidazole (PBI)	Mixed	HCl	Mild steel	168
Benzothiazole derivatives as corrosion inhibitors				
2-(*n*-hexylamino)-4-(3′-*N,N*-dimethylamino-propyl)amino-6-(benzothiazol-2-yl)thio-1,3,5-*s*-triazine (BTC$_6$T)and2-(*n*-octylamino)-4-(3′-*N,N*-dimethylamino-propyl)amino-6-(benzothiazol-2-yl)thio-1,3,5-*s*-triazine (BTC$_8$T)	Cathodic	HCl	Mild steel	169
2-(2′-hydroxylphenyl)benzothiazole,(**1**),2-(2′,5′-dihydro- xyphenyl)benzothiazole,(**2**),and(4-benzothiazole -2-yl-phenyl)-dimethyl-amine,(**3**)	Mixed	HCl	Mild steel	170
Drugs, Dyes and Plant extracts as green corrosion inhibitors				
Clozapine (CZP)	Mixed	HCl	Mild steel	171
Analgin	Mixed	HCl	Mild steel	172
Ambroxol	Mixed	HCl and H_2SO_4	Mild steel	173
Cefradine (CFD)	Mixed	HCl	Mild steel	174

Podocip (PCIP)	Mixed	HCl	Carbon steel	175
Atenolol	Mixed	HCl	Mild steel	176
Biotin	Mixed	HCl	Mild steel	177
Ginkgo leaf extract (GLE)		HCl	X70 steel	178
Xanthiumstrumarium leaves (XSL)	Mixed	HCl	Carbon steel	179
Chitosan-Thiosemicarbazide(CS-TS) and Chitosan-Thiocarbohydrazide (CS-TCH)	Mixed	HCl	Mild steel	180
Hydroxyethylcellulose (HEC)	Mixed	HCl	A1020 carbon steel	181
5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphyrin(HPTB),5,10,15,20-tetra(4-pyridyl)-21H,23 H-porphyrin(T4PP),4,4',4″,4‴-(porphyrin-5, 10,15,20-tetrayl)tetrakis(benzoic acid) (THP) and 5,10,15,20-tetraphenyl-21H,23H-porphyrin (TPP)	Mixed	NaCl	N80 steel	182
Hydroxyethylcellulose (HEC)	Mixed	NaCl	1018 carbon steel	183
Pectin	Mixed	HCl	Mild steel	184
Polysaccharide from Plantagoovata	Mixed	HCl	Carbon steel	185
Chitosan and carboxymethyl cellulose (CMC)	Mixed	NaCl	API 5L X60 steel	186
o-fumaryl-chitosan (OFC)	Mixed	HCl	Mild steel	187
Dihydropyrido-[2,3-d:6,5-d']-dipyrimidine-2,4,6,8(1H ,3H, 5H,7H)-tetraone (GPHs)	Mixed	HCl	Mild steel	188
Adenosine	Mixed	HCl	Mild steel	189

Gelatin		HCl	X60 steel	190
Acid violet 6B (AV6B)	Mixed	HCl	CRS	191
Sunset Yellow(SS), Amaranth (AM), Allura Red (AR), Tartrazine (TZ) and Fast Green (FG)	Mixed	HCl	Mild steel	192
Hydrazide derivatives as corrosion inhibitors				
N′-(4-Hydroxybezylidene)nicotinic hydrazine (HBNH)and *N′*-(4-methylybezylidene) nicotinichydra- zone (MBNH)	Mixed	HCl	Mild steel	193
N′-[(1*Z*)-phenylmethylene]-2-(quinolin-8-yloxy) acetoh- ydrazide(PQA)and *N′*-[(1*Z*)-4-chlorophenylmethylene]-2-(quinolin-8-yloxy)acetohydrazide (CPQA)	Mixed	HCl	Mild steel	194
2-(3,4,5-trimethoxybenzylidene)hydrazine carbothioamide (TMBHC)	Mixed	HCl	Mild steel	195
Azelaic acid dihydrazide	Mixed	HCl	Mild steel	196
Imidazoline derivatives as corrosion inhibitors				
2-(2-trifluoromethyl-4,5-dihydro-imidazol-1-yl)-ethylamine(1-IM)and2-(2-trichloromethyl-4,5-dihydro-imidazol-1-yl)-ethylamine (2-IM)	Mixed	HCl	Mild steel	197
2-methyl-4-phenyl-1-tosyl-4,5-dihydro-1H-imidazole (IMI)	Mixed	HCl	P110 carbon steel	198
Imidazoline-based inhibitor	Mixed	CO_2-saturated 3 wt% NaCl	X70 and Q235 steel	199
Imidazoline-based inhibitor	Mixed	CO_2-saturated 3 wt. % NaCl	Alloy steel	200

Imidazoline-based inhibitor	Mixed	CO_2-saturated 3 wt. % NaCl	Carbon steel	201
Thioureidoimidazoline and $NaNO_2$	Anodic	Acidic NaCl	X70 steel	202
Pyrazole derivatives as corrosion inhibitors				
Ethyl6-amino-3-methyl-4-(*p*-tolyl)-2,4-dihydro-pyrano [2,3,C]pyrazole-5-carboxylate(EPP-1),ethyl 6-amino-3-methyl-4(phenyl)-2,4-dihydro pyrano-[2,3,C]pyrazo- le-5-carboxylate (EPP-2), ethyl 6-amino-3-methyl-4-(3-nitrophenyl)-2,4-dihydro-pyrano[2,3,C]pyrazole-5-carboxylate (EPP-3)	Mixed	HCl	Mild steel	203
Methyl5-(4-Chlorobenzoyloxy)-1-phenyl-1*H*-pyrazole-3-carboxylate (MCPPC) and 5-(4-methoxyphenyl)-3-(4-methylphenyl)4,5-dihydro-1H-pyrazol-1-yl-(pyridi-ne-4-yl)methanone (MMDPPM)	Mixed	HCl	Mild steel	204
Surfactants as corrosion inhibitors				
1-dodecyl-2-(phenethylimino)-1-methylpyrrolidin-1-iumbromide(A),1-dodecyl-2-((2-hydroxyethyl) imino) -1-methylpyrrolidin-1-iumbromide (B) and 1-dodecyl-2-((4-hydroxyphenyl)imino)-1-methylpyrolidin-1-ium bromide (C)	Mixed	HCl	Carbon steel	205
Cationic Gemini surfactants	Mixed	HCl	AISI 304 stainless steel	206
Organic compounds as corrosion inhibitors				
Ammonium (2,4-dimethylphenyl)-dithiocarbamate)	Mixed	HCl	Mild steel	207
5-bromo-1[2-(diethylamino)ethyl]-1H-indole-2,3-dione (5-BEI), 1-[2-(diethylamino)ethyl]- 1H-indole-2,3-dione(5-HEI),and5-fluro-1[2-(diethyl-amino)ethyl]-1H-indole-2,3-dione (5-FEI)	Mixed	HCl	Carbon steel	208

(Z)-3-hydroxy-1-(pyridin-2-yl)but-2-en-1-one (KE-**1**) and (Z)-1-(1,5-dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(pyridin-2-yl)prop-2-en-1-one (KE-2)	Mixed	HCl	Carbon steel	209
Di-triethanolaminesiloxane & bis(dithiomamine-triethanolamine) siloxane	Mixed	HCl	Carbon steel	210
N,N$'$-bis(4-formylphenol)-1,2-Diaminocyclohexane (4-HCD)	Anodic	HCl	Carbon steel	211
N^1,N$^{1'}$-(1,4-phenylene)bis(N^4-(4-nitro benzylidene) benzene-1,4-diamine) SB-I, N^1,N$^{1'}$-(1,4-phenylene) bis(N^4-benzylidenebenzene-1,4-diamine)SB-II,N^1,N$^{1'}$-(1,4-phenylene)bis(N^4-(4-methylbenzylidene) benzene-1,4-diamine)SB-III, N^1,N$^{1'}$-(1,4-phenylene) bis(N^4-(4-methoxy benzylidene) benzene-1,4-diamine) SB-IV	Mixed	HCl	Mild steel	212
Acrylamide methyl ether (AAME)	Mixed	HCl	Mild steel	213
1-phenyl-1*H*-pyrrole-2,5-dione (PPD) and 1-(4-methylphenyl)-1*H*-pyrrole-2,5-dione (MPPD)	Mixed	HCl	Carbon steel	214
1-[3-(4-methylphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Me-4-PQPB), 1-(3-(4-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydro pyrazol-1-yl)butan-1-one(Mt-4-PQPB),1-[3-(3-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Mt-3-PQPB) and 1-[3-(2H-1,3-benzodioxol-5-yl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Oxo-1,3-PQPB)	Mixed	HCl	Mild steel	215
5-hydroxytryptophan (5-HTP)	Mixed	HCl	Mild steel	216
1-(4-Nitrophenylo-imino)-1-(phenylhydrazono)-propa- n-2-one (NO$_2$AM)	Mixed	HCl	Mild steel	217
4-(2,2′-bithiophene-5-yl) benzamidine (MA-0944) and 6-(2,2′-bithiophene-5-yl) nicotinamidine (MA-0949)	Mixed	HCl	Carbon steel	218

(1-benzyl-1H-1,2,3-triazole-4-yl)methanol(BTM) and(1-(pyridin-4-ylmethyl)-1H-1,2,3-triazole-4-yl)methanol (PTM)	Adsorption	HCl	Mild steel	219
Poly(vinyl alcohol-cysteine)(PVAC)	Mixed	HCl	Mild steel	220
(*E*)-2-methyl-N-(thiophen-2-ylmethylidene)aniline	Mixed	HCl	Mild steel	221
4(N,N-dimethylamino) benzaldehyde nicotinic acid hydrazone	Mixed	HCl	Mild steel	222
3-(4-Hydroxyphenylamino) propanenitrile (Para) and 3-(2-Hydroxyphenylamino) propanenitrile (ortho)	Mixed	HCl	Mild steel	223
5-arylaminomethylenepyrimidine-2,4,6-trione (AMP)	Cathodic	HCl	Mild steel	224
(*E*)-3-phenyl-2-(1H-tetrazole-5-yl)acrylonitrile, (PTA) ,(*E*)-3-(4-nitrophenyl)-2-(1H-tetrazole-5-yl)acrylonitrile(NTA), and (*E*)-3-(4-hydroxy-phenyl)-2-(1H-tetrazole-5-yl) acrylonitrile (HTA)	Cathodic	HCl	Mild steel	225
Aryl sulfonamidomethylphosphonate	Mixed	HCl	Mild steel	226
4-amino-3-hydroxy-naphthalene-1-sulfonic acid	Mixed	HCl	Mild steel	227
5,5’-thiobis (4-phenylthiazol-2amine) (DHAT-1), 4,4’-(5,5’-thiobis(2-aminothiozole-5,4-diyl))diphenol (DHAT-2) and 4,4’-(5,5’-thiobis(2-aminothiazole-5,4-diyl))bis (benzene-1,3-diol) (DHAT-3)	Mixed	HCl	Mild steel	228
4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol	Anodic	HCl	Mild steel	229
(4-(3-mercapto-5,6,7,8-tetrahydro-[1,2,4] triazolo-[4,3-b][1,2,4,5]tetrazin-6-yl)phenol)	Adsorption	HCl	Mild steel	230
2-(coumarin-4-yloxy)acetohydrazide (EFCI)	Adsorption	HCl	Mild steel	231
6-(4-hydroxyphenyl)-3-mercapto-7,8-dihydro-[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine [HT3]	Mixed	HCl	Mild steel	232

Ascorbylpalmitate (AP)	Adsorption		Carbon steel	233
Vinylimidazole (VI) and allylimidazole (AI)	Mixed	HCl	Carbon steel	234
(E)-(1-(5-(4-(3-(4-methylphenyl)-3-oxoprop-1-enyl)phenoxy)pentyl)-1H-1,2,3-triazol-4-yl)methyl acrylate (CH-5), (E)-(1-(5-(4-(3-(4-methylphenyl)-3-oxoprop-1-enyl)phenoxy)hexyl)-1H-1,2,3-triazol-4-yl)methyl acrylate (CH-6) and (E)-(1-(5-(4-(3-(4-methylphenyl)-3-oxoprop-1-enyl)phenol-xy) decyl) -1H-1,2,3-triazol-4-yl) methyl acrylate (CH-10)	Mixed	HCl	Mild steel	235
2-amino-3-((4-((*S*)-2-amino-2-carboxyethyl)-1H-imid- azol-2-yl)thio)propionic acid (AIPA)	Mixed	HCl	Mild steel	236
(1E,2E)-1,2-bis(thiophen-2-ylmethylene)hydrazine (PP2)and(1E,2E)-1,2-bis(1H-pyrrol-2-ylmethylene)hydrazine (PP3)	Mixed	HCl	Mild steel	237
N-((1H-indol-3-yl)(phenyl)methyl)-N-ethylethanamine (AAI-1), 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) and 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3)	Cathodic	HCl	Mild steel	238
Benzo 1,3-diazol 2-(4-{[4-Methyl-6-(1-methyl-1*H*-1,3-benzodiazol-2-yl)-2-propyl-1*H*-1,3-benzodiazol-1-yl] methyl} phenyl) benzoic acid (Telmisartan)	Cathodic	HCl	Mild steel	239
6-amino-4-(4-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (AMPC) and 6-amino-4-(4-chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (ACPC)	Mixed	HCl	Mild steel	240
2-Methyl-4H-benzo[*d*][1,3]oxazin-4-one (BZ1) and 3-amino-2-methylquinazolin-4(3H)-one (BZ2)	Adsorption	HCl	Mild steel	241
(Z)-2-(2-oxoindolin-3-ylideneamino)aceticacid (OYAA) and 2-(2-oxoindolin-3-ylideneamino)-3-phenylpropanoic acid (OYPA)	Mixed	HCl	Mild steel	242

3-(cyano-dimethyl-methyl)-benzoic acid thiophen-2-ylmethylene-hydrazide (CBTH) and 3-(cyano-dimethyl-methyl)-benzoic acid furan-2-ylmethylene-hydrazide (CBFH)	Mixed	HCl	Mild steel	243
4-(pyridin-2yl)-N-p-tolylpiperazine-1-carboxamide(PTC)	Mixed	HCl	Mild steel	244
Naphthalen-2-ylNaphthalene-2-Carboxammide (NNC)	Mixed	HCl	Carbon steel	245
Aminatedhydroxyethyl cellulose (AHEC)	Mixed	HCl	Mild steel	246
Thiocarbanilide	Mixed	HCl and H_2SO4	Carbon steel	247
4-hydroxy-3-methoxybenzaldehyde (HMD)	Mixed	HCl and H_2SO4	Carbon steel	248
1,5-Dimethyl-4-((2-methylbenzylidene)amino)-2-phenyl-1H-pyrazol-3(2H)-one (DMPO)	Mixed	HCl	Mild steel	249
5,5'-((1Z,1'Z)-(1,4-phenylenebis(methanylylidene) bis(azanylylidene))bis(1,3,4-thiadiazole-2-thiol) (PBB)	Mixed	HCl	Mild steel	250
4-[(2-amino-1,3,4-thiadiazol-5-yl)methoxy] coumarin (ATC)	Adsorption	HCl	Mild steel	251
2-hydrazino-4,6-dimethoxy-1,3,5-tirazine (DMeHT),2,4-dihydrazino-6-methoxy-1,3,5-triaizine (DHMeT), and 2,4,6-tridydrazino-1,3,5-triaizne (TH_3)	Mixed	HCl	Mild steel	252
2-amino-3-((4-((*S*)-2-amino-2-carboxyethyl)-1H-imid-azol-2-yl)thio)propionic acid (AIPA)	Mixed	HCl	Mild steel	253
6-phenyl-3(2H)-pyridazinone (P1) and 3-chloro-6-phenylpyrazine (P2)	Mixed	HCl	Mild steel	254
N(4)-substituted thiosemicarbazones, anisoin- and furoin N(4)-methyl(phenyl) thiosemicarbazone	Mixed	HCl	Mild steel	255
5-amino 1,3,4-thiadiazole-2-thiol (5-ATT)	Mixed	HCl	Mild steel	256
Polypropylene glycol (PPG)	Mixed	HCl	X60 pipeline steel	257

Stearamidopropyl dimethylamine (SAPDA)	Mixed	HCl	API X120 steel	258
Hexamethylenediaminetetra(methylene phosphonic acid) (HMDTMPA)	Mixed	HCl	Carbon steel	259
(E)-N-((E)-3-phenylallylidene)-2-(phenylthio) aniline (2-PTA)	Mixed	HCl	Carbon steel	260
4(N,N-dimethylamino) benzaldehyde nicotinic acid hydrazone	Mixed	HCl	Mild steel	261
1, 3, 5-tris (4-amino phenoxy) benzene (TAPOB)	Mixed	HCl	Mild steel	262
4-hydrobenzoic acid	Mixed	HCl	Mild steel	263

Table 1.8 Organic compounds reviewed as corrosion inhibitors

7.1. Schiff Bases as Corrosion Inhibitors

The inhibitive action of three Schiff-base molecules namely,(E)-4-((2-(2,4-dinitrophenyl)hydrazono)methyl)pyridine(L(1)),((E)-4-(2-(pyridin-4-lmethylene) hydrazinyl) benzo nitrile (L(2)) and (E)-4-((2-(2,4- dinitrophenyl)hydrazono) methyl) phenol(L(3)) oncorrosion of mild steel in 1M hydrochloric acid has been evaluated by using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) technique. Experimentally obtained results revealed that corrosion inhibition efficiencies followed the sequence: L(3) > L(1) > L(2). Electrochemical findings showed that inhibitors imparted high resistance towards charge transfer across the metal-electrolyte interface and behaved as mixed type inhibitors. Scanning electron microscopy (SEM) studies confirmed protective film formed on the mild steel surface. The quantum chemical calculations provided good insight about the adsorption and inhibition mechanism of Schiff-bases. Molecular dynamics (MD) simulations revealed that all the inhibitors molecules adsorbed in parallel orientation with respect to the Fe surface [125].

Two new Schiff bases namely, *N*-(4-methoxybenzylidene)-2-[2-((*E*)-2-(4-methoxy benzylideneamino) phenyl) disulfanyl] benzenamine (**Sb1**)) and *N*-(4nitroben-zylidene)-2-[2-((*E*)-2-(4-itrobenzylideneamino)phenyl)disulfanyl]benzene amine(**Sb2**)), were tested as corrosion inhibitors for mild steel in 1 M HCl solution using various techniques. The experimental results revealed that both **Sb1 and Sb2** acted as effective corrosion inhibitors and the inhibition efficiency was increased by increasing inhibitors concentration. The adsorption of these compounds obeyed the Langmuir adsorption isotherm. The **Sb1** molecule possessing an electron-donating *o*-methyl substitute showed a better inhibition performance in comparison to the **Sb2** with nitro substitute, because of the positive effect of its electron–donating substitute. The molecular dynamics simulation, in agreement with experimental outcomes and quantum chemical data, showed higher inhibition efficiency for **Sb1**. It also showed that the **Sb2** molecules oriented not beneficially on metal surface which provided a low surface coverage, and thus, a lower inhibition performance [126].

The inhibitory effect of two Schiff bases 3-(5-methoxy-2-hydroxybenzylideneamino)-2-(-5-methoxy-2-hydroxyphenyl)-2,3-dihydroquinazoline -4(1H)-one(MMDQ), and 3-(5-nitro-2-hydroxybenzylideneamino)-2(5-nitro-2-hydroxyphenyl)-2,3-dihydroquinazoline-4(1H)-one (NNDQ) on the corrosion of mild steel in 1 M hydrochloric acid was studied by using mass loss, potentiodynamic polarization and electrochemical impedance spectroscopy measurements at ambient temperature. The results indicated that the Schiff bases compounds with an average efficiency of 92% at 1.0 mM of additive concentration have fairly effective inhibiting properties for mild steel in hydrochloric acid, and acted as mixed type inhibitor. The inhibition efficiencies measured by all measurements showed that the inhibition efficiencies increased with increase in inhibitor concentration. This revealed that the inhibitive mechanism of inhibitors were primarily due to adsorption on mild steel surface, and followed Langmuir adsorption isotherm.. The differences in efficiency for two investigated inhibitors were associated with their chemical structures [127].

Ali Gürten *et al.* [128] Studied Inhibition effect of Schiff base namely 1-(2-hydroxy-benzylidene)-3-(2,5-dioxoimidazolidin-4-yl) urea (ALS) on carbon steel corrosion in 1.0 M HCl by using electrochemical and quantum chemical study. The adsorption of inhibitor on metal followed Langmuir's adsorption isotherm. The thermodynamic parameters of adsorption revealed that there is a strong interaction between inhibitor and carbon steel. The highest inhibition efficiency was observed at 5.0×10^{-4} M at 318 K. SEM and EDX observations confirmed the existence of protective inhibitor film on metal surface. Quantum chemical study supported the comparative inhibition effect of ALS.

Inhibition performance of (3-bromo-4-fluoro-benzylidene)-[1,2,4]triazol-4-yl-amine (BFBT), (4-trifluoromethyl-benzylidene)-[1,2,4]triazol-4-yl-amine (TMBT) and (2-fluoro-4-nitro-benzylidene)-[1,2,4]triazol-4-yl-amine (FNBT) were investigated for mild steel in 0.5 M HCl by chemical (weight loss) and electrochemical techniques[129]. The inhibition efficiency increased with an increase in inhibitor concentration and decreased with an increase in temperature of the medium. Adsorption of all the three inhibitors followed the Langmuir isotherm. Electrochemical impedance studies showed that charge transfer resistance increased with concentration of inhibitors. Polarisation studies proved that inhibitors were of the mixed type. SEM and FTIR studies confirmed formation of protective layer on mild steel. Quantum chemical calculations gave evidence to experimental results. Higher value of E_{HOMO}, lower value of E_{LUMO}, smaller orbital gap (ΔE) and higher dipole moment makes BFBT superior over TMBT and FNBT thus showed the maximum inhibition efficiency.

(S)1-*N*-(1-hydroxy-1,1-diphenyl-3-methylbut-2-yl)-2-hydroxybenzaldimine (DPV) and (S)1-*N*-(1-hydroxy-3-methylbut-2-yl)-2-hydroxybenzaldimine (LV) showed excellent performance for the corrosion of the high carbon steel (HCS) in 1.0 M HCl. Inhibitor DPV showed higher efficiency in comparison to that of LV. The Tafel polarization method revealed the mixed-mode inhibition of chiral Schiff bases with predominant control of the anodic reaction. The adsorption of the inhibitor molecules onto the HCS surface was found to follow the Langmuir adsorption isotherm. The values of the Gibbs free energy of adsorption strongly supported spontaneous physicochemical adsorption of inhibitor molecules on the HCS surface. The adsorption mechanism for inhibition was supported by Fourier transforms infrared (FTIR), wide-angle X-ray diffraction (WAXD), scanning electron microscopy–energy-dispersive X-ray (SEM–EDS) spectroscopic methods, and adsorption isotherm [130]. The adsorption behavior of DPV and LV is shown in Fig.1.20

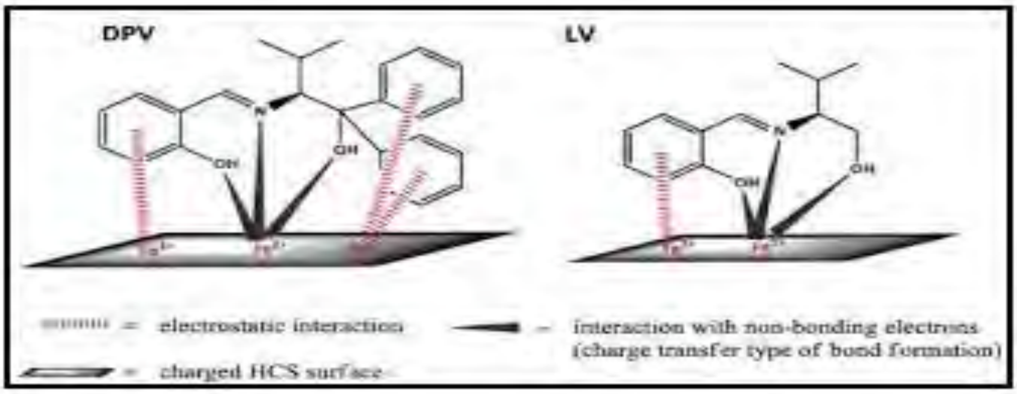

Fig 1.20:Pictorial representation of the adsorption behavior of the DPV and LV on mild steel in 1 M HCl

Singh *et al.*[131] have studied the influence of a Schiff base namely N,N′-(pyridine-2,6-diyl)bis(1-(4-methoxyphenyl) methanimine) (PM) on the corrosion of J55 and N80 steel in 3.5 wt.% NaCl solution saturated with CO_2 using chemical, electrochemical and surface analytical techniques. Potentiodynamic polarization results suggested that the inhibitor acted as a mixed type inhibitor by reducing both anodic and cathodic reactions. The adsorption of PM on the J55 and N80 steel surface obeyed the Langmuir adsorption isotherm. XRD, contact angle, SEM, AFM and SECM studies revealed that the surface of the metal was quite unaffected after the addition of inhibitor. Quantum chemical calculations and molecular dynamic simulation supported the experimental results well.

A Schiff base, namely N-(2-hydroxybenzylidene) thiosemicarbazide (HBTC), was investigated as inhibitor for carbon steel in saline water (SW) using electrochemical measurements. The results showed that HBTC acted as mixed corrosion inhibitor in SW by suppressing simultaneously the cathodic and anodic processes via adsorption on the surface which followed the Langmuir adsorption isotherm.EIS measurements also indicated that the inhibitor increased the charge transfer resistance and showed that the inhibitive performance depended on an adsorption of the molecules on the metal surface. SEM/EDS analysis showed at this stage that the main product of corrosion is a non-stoichiometric amorphous Fe(3+) oxyhydroxide, consisting of a mixture of Fe(3+) oxyhydroxides, α-FeOOH and/or γ-FeOOH, α-FeOOH/γ-FeOOH and Fe(OH)(3) [132].

Polymeric Schiff base containing aniline, formaldehyde and piperazine (AFPP) was synthesized and investigated as corrosion inhibitor for mild steel in 1 M HCl[133]. Experimental results showed that AFPP acted as effective inhibitor for mild steel in 1 M HCl and exhibited 98% inhibition efficiency. Potentiodynamic polarization studies showed that AFPP is a mixed-type inhibitor predominantly cathodic type. The adsorption of inhibitor on the mild steel surface followed Langmuir adsorption isotherm. . The positive sign of ΔH^* indicated that the adsorption process was endothermic.

The effect of a new Schiff base namely 1,13-bis-[(2-hydroxynaphtaldehyde) 4,7,10-trioxatridecane diimine] (HNTTD) as corrosion inhibitor for mild steel (MS) X48 in 1M HCl have been investigated by Benabid et al**.**[134]. All measurements showed that, inhibition efficiency increased with increasing inhibitor concentration. Polarization curves indicated that the studied compound worked as mixed type inhibitor. The adsorption of HNTTD on steel surface followed Langmuir's adsorption isotherm.DFT calculations further confirmed interaction between inhibitors and metal surface. The results of AFM studies also confirmed the inhibition action of HNTTD.

The efficiency of 4-(4-hydroxy-3-methoxy benzyledene amino)-4-H-1, 2, 4-triazole-3, 5-dimethanol, HMATD, as corrosion inhibitor for mild steel in 0.5 M HCl was studied by using weight loss measurements and electro analytical methods. Experimental studies revealed that1,2,4-triazole based schiff base HMATD with hetero atoms N, O, multiple bonds and aromatic rings, acted as an efficient inhibitor for the corrosion of mild steel in 0.5 M HCl solution. The potentiodynamic polarization studies revealed the mixed type behaviour of HMATD by inhibiting both cathodic and anodic reactions. The inhibition mechanism is attributed to adsorption process which followed Langmuir adsorption isotherm.The free energy of adsorption values obtained from isotherm suggested mixed adsorption comprehensive of physisorption and chemisorption. The major contribution of physisorption was confirmed by the higher values of E_a in presence of inhibitor compared to its absence [135].

A Schiff base, E-*N*-(2-chlorobenzylidiene)-2-methylaniline, has been synthesized and evaluated as corrosion inhibitor for mild steel 1 M HCl medium using electrochemical methods[136]. The results showed that the compound exhibited appreciable inhibition efficiency at higher concentration with potentiodynamic polarization studies revealing a mixed-type inhibitor of predominantly anodic type. Scanning electron micrographs (SEM) and EDX studies revealed the film-forming ability of the ligand on the mild steel surface. Based on the theoretical and experimental results obtained, the enhanced corrosion inhibition efficiency could be ascribed to the presence of the azomethine and the aromatic rings characteristic of the Schiff base.

Elies *et al.* [137] have synthesized two Schiff base compounds with similar backbone, but different positions and lengths of alkyl groups, (E)-4-(((4-propyl phenyl) imino) methyl) phenol (PMP) and (E)-4-((2-tolylimino) methyl) phenol (TMP) and studied their corrosion inhibition performance by electrochemical measurements. The results suggested that the two derivatives get adsorbed onto the mild steel surface and form hydrophobic films, which to an appreciable extent, protected the surface of the mild steel. Potentiodynamic polarization results strongly suggested that the investigated Schiff bases behaved as mixed-type inhibitors with a more pronounced cathodic nature, and the adsorption isotherm basically obeyed the Langmuir isotherm. Quantum chemical computations further provided explanations on the adsorption mode, and the theoretical predictions conformed to the experimental results.

Three Schiff's bases namely, 2-amino-6 (2-hydroxybenzelideneamino) hexanoic acid (SB-1), 2-amino-6-(4-methoxybenzelideneamino) hexanoic acid (SB-2) and 2-amino-6-((4-dimethylamino) benzylideneamino) hexanoic acid (SB-3) derived from lysine (amino acid) and three different aldehydes were synthesized and evaluated as corrosion inhibitors for mild steel in 1 M HCl solution. The results showed that inhibition efficiency increased with the increasing concentration of inhibitors. Among the studied SBs the SB-3 showed maximum inhibition efficiency of 95.6% at 400 mg L^{-1} concentration. Potentiodynamic polarization study revealed that the investigated SBs acted as cathodic type inhibitors. Adsorption of the SBs on mild steel surface obeyed the Langmuir adsorption isotherms. The weight loss and electrochemical results were well supported by SEM, EDX and AFM analyses [138].

The inhibition properties of three triazole Schiff's bases namely, (4-(4-hydroxybenzylideneamino)-4H-1,2,4-triazole-3,5-diyl) dimethanol,(4-(4-methoxy benzy lideneamino)-4H-1,2,4-triazole-3,5-diyl) dimethanol and (4-(3,4-dimethoxy benzy lideneamino)-4H-1,2,4-triazole-3,5-diyl)dimethanol [139] for mild steel corrosion in HCl has been tested. The results showed that synthesized compounds acted as effective inhibitors for mild steel in hydrochloric acid. Inhibition efficiency of these inhibitors increased with inhibitor concentration, but decreases with temperature and acid concentration. The inhibition efficiencies obtained from experimental studies are in good agreement with theoretically calculated values and results of spectroscopic studies.

7.2 Quinolines and their Derivatives as Corrosion Inhibitors

Verma *et al.* [140] have investigated the corrosion inhibition efficiency of 2-amino-4-(2,4-dihydroxyphenyl) quinoline-3-carbonitrile (ADQC) on SAE 1006 steel using electrochemical (EIS and Polarization), surface (SEM, EDX and AFM) and quantum chemical calculation methods. Results showed that inhibition efficiency increased with increasing ADQC concentration and maximum value of 96.12% was obtained at 25 mg/L concentration. EIS results showed the ADQC inhibits SAE 1006 steel corrosion becoming the adsorbate at metal/electrolyte interfaces. Polarization study showed that ADQC acts as cathodic type inhibitor. SEM, EDX and AFM finding supported the adsorption of ADQC on the mild steel surface. The quantum chemical calculations provide good insight about the adsorption and inhibition mechanism of ADQC. The experimental and quantum chemical calculation results were in good agreement.

The inhibition performance of two synthesized quinoline derivatives: 6-benzylquinoline (BQ) and 6-(quinolin-6-ylmethyl) benzene-1,2,3,4,5-pentasulfonic acid (QBPA),as corrosion inhibitor for mild steel in 1 M HCl solution has been examined. All experimental results indicated that BQ and QBPA extremely enhanced the corrosion resistance of mild steel and QBPA showed a better inhibitive performance than BQ. The results of potentiodynamic polarization illustrated that BQ and QBPA performed as mixed-type inhibitors. Langmuir adsorption isotherm was well fitted for the adsorption of BQ and QBPA on mild steel surface with a competitive physisorption and chemisorption mechanism. The results of quantum chemical calculations and molecular dynamics simulations showed that benzene rings of both BQ and QBPA adsorbed on the metal surface in distinct gradient direction and quinoline ring of both BQ and QBPA adsorbed nearly parallel on the steel surface [141].

Quinoline quaternary ammonium salts 1-benzylquinoline bromide (1) and 1-benzylquinoline chloride (2) have been synthesized and used as corrosion inhibitors in acidic HCl solution. Experimental results indicated that both inhibitors efficiently protected the mild steel from corrosion. The fact that (1) showed better performance than (2) under the same conditions could be attributed to the cooperative effect of counter ions on the corrosion process. The results of thermodynamic and electrochemical studies were in good agreement with the observed inhibition efficiency, indicating that counter ions may have affected the interactions between organic cations and the metal surface, and influence the stability of the protective film, which leads to the detected differences in their inhibition behavior [142].

The corrosion inhibition efficiency of 8-quinoline sulphonyl chloride (8-QSC) on mild steel was studied by using weight loss (WL), electrochemical and surface analytical techniques. Results showed that inhibition efficiency increased with increasing (8-QSC) concentration and maximum value of 82.69% was obtained at 300 ppm. EIS results showed the (8-QSC) inhibited mild steel corrosion becoming the adsorbate at metal/electrolyte interfaces. Polarization study showed that (8-QSC) acted as cathodic type inhibitor. Inhibition efficiency obtained from weight loss measurements was in good agreement with EIS, Tafel, and LPR methods. SEM and EDX studies confirmed the formation of inhibitor film on the surface of mild steel [143].

Singh *et al.*[144] have explored the corrosion mitigation effect of quinolone derivatives such as 2-amino-7-hydroxy-4-phenyl-1,4-dihydroquinoline-3-carbonitrile (Q-1),2-amino-7-hydroxy-4-(p-tolyl)-1,4 dihydroquinoline-3-carbonitrile (Q-2),m 2-amino-7-hydroxy-4-(4-methoxyphenyl)-1,4 dihydroquinoline-3 carbonitrile (Q-3), 2-amino-4-(4-(dimethyl- amino)phenyl)-7-hydroxy-1,4-dihydroquinoline-3-carbonitrile (Q-4) on mild steel in presence 1 M HCl. Among all the investigated inhibitors, Q-4 showed the maximum inhibition efficiency of 98.09% at 150 mg/l. The electrochemical impedance spectroscopy (EIS) measurements revealed that corrosion inhibition took place due to the adsorption of inhibitor molecules on the metal surface. The potentiodynamic polarization measurements showed that Q-1, Q-2, Q-3 acted as a mixed-type inhibitor while Q-4 acted as a cathodic inhibitor. The adsorption of quinolines on mild steel surface obeyed the Langmuir adsorption isotherm. The surface analysis techniques (SEM/AFM/XPS) further corroborate that the corrosion inhibition occurred due to the adsorption of the inhibitor molecules at the metal/solution interface. The adsorption behavior of quinoline derivatives is shown in Fig.1.21

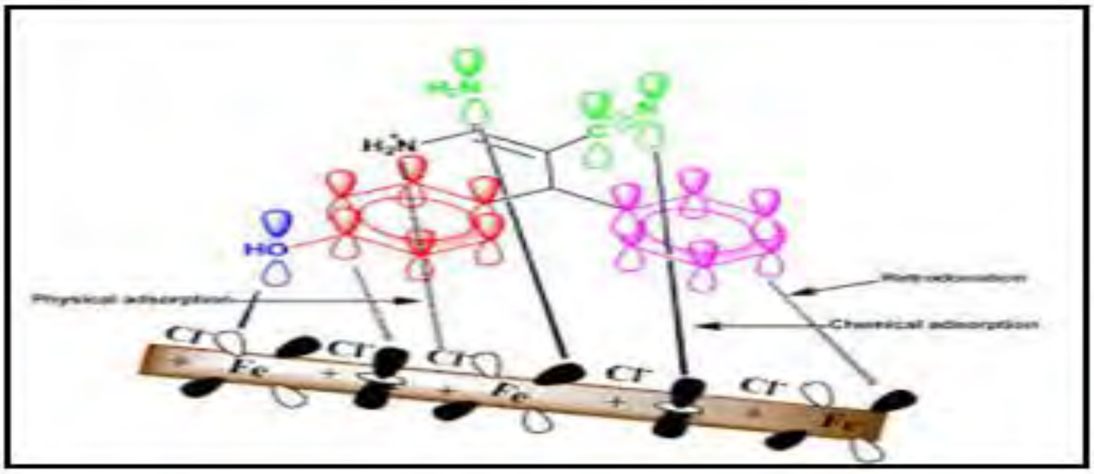

Fig 1.21:Pictorial representation of adsorption of one of quinoline derivatives on MS surface in 1 M HCl

The corrosion inhibition properties of three quinoline derivatives namely, 2,6-dichloroquinoline-3-carbaldehyde (QA-1), 2-chloro-6-nitroquinoline-3-carbaldehyde (QA-2) and 2,6-dichloro-8-nitroquinoline-3-carbaldehyde (QA-3) for mild steel (MS) in 1.0 M HCl at 303 K were studied by using electrochemical techniques, the density functional theory and molecular dynamic simulations. Experimentally obtained results showed that the quinoline derivatives acted as excellent inhibitors and that their adsorption on metal surface was found to follow the Langmuir adsorption model. Electrochemical findings revealed that quinoline derivatives behaved as mixed-type inhibitors. These inhibitors increased the polarization resistance and simultaneously lowered the double layer capacitance, thereby confirming their high potentialities to protect metal against dissolution. SEM and AFM studies confirmed the formation of protective layer non mild steel surface [145].

7.3 Pyridine derivatives as Corrosion Inhibitors

Verma *et al.*[146] studied the corrosion inhibition performance of two newly synthesized chromenopyridine derivatives namely 2,4-diamino-5-(phenylthio)-5H-chromeno[2,3-b]pyridine-3-carbonitrile (PPC-1) and 2,4-diamino-5-phenoxy-5H-chromeno[2,3-b]pyridine-3-carbonitrile (PPC-2) as potential environmentally friendly corrosion inhibitors for N80 steel in 15% (HCl) by using chemical, electrochemical and surface analytical techniques. The inhibition efficiencies given by PPC-1 and PPC-2 at 200 mg L^{-1} were 92.4% and 82.1% respectively. Tafel polarization revealed that both inhibitors are cathodic in nature. Langmuir adsorption isotherm was found to be the best fit. The impedance results indicated that the value of polarization resistance increased and double layer capacitance decreased.SEM and AFM observations indicated that both inhibitors were adsorbed on the N80 steel surface and prevented dissolution of N80. The experimental result was further supported by quantum chemical study.

The inhibition effect of three pyrazolopyridine derivatives such as (PPs) (4-(4-methoxyphenyl)3,5-dimethyl-1,4,7,8-tetrahydrodipyrazolopyridine)(PP-1),3,5di-methyl-4-phenyl-1,4,7,8-tetrahydrodipyrazolopyridine (PP-2) and (3,5-dimethyl-4-(3-nitrophenyl)-1,4,7,8-tetrahyddrodipyrazolopyridine) (PP-3) on the corrosion of mild steel in 1 M HCl solution was studied by using electrochemical and Potentiodynamic methods. The results of electrochemical studies showed that all the three pyrazolopyridines acted as excellent mixed type corrosion inhibitors. The adsorption of studied compounds obeyed the Langmuir's adsorption isotherm. Methoxy-substituted PP-1 showed maximum IE of 97% at 100mgL^{-1}. The formation of the protective film on the MS surface was confirmed by SEM and AFM techniques. [147].

The effect of 8,9-bis(4 dimethylamino)phenyl)benzo[4,5]imidazo[1,2-a]pyridine-6,7-dicarbonitrile (INH) on mild steel corrosion in 1 M HCl was studied by various experimental methods. Results showed that percentage of inhibition efficiency increased with increasing INH concentration and The maximum inhibition efficiency of 96.32% was obtained at 25 mg L^{-1} concentration. Tafel polarization measurements showed that the presence of INH in acid solution affected both cathodic and anodic reactions but acted as predominantly cathodic type inhibitor. The Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy (AFM) studies suggested the formation of adherent layer of INH on mild steel surface. The results of theoretical calculations were found to be consistent with the surface and electrochemical results [148].

Ansari *et al.*[149] have investigated the adsorption and inhibitory effects of the pyridine derivatives, namely 2-amino-6-(2,4-dihydroxyphenyl)-4-(4-methoxy phenyl) nicotine nitrile (ADP) and 2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMP) on N80 steel corrosion in 15% HCl. Among the studied compounds, ADP showed the inhibition efficiency of 90.24% at 200 mg/L. Potentiodynamic polarization curves revealed that both the inhibitors acted as mixed type but cathodically predominant. The adsorption of inhibitors obeyed the Langmuir isotherm model .SEM/EDX studies confirmed the corrosion of N80 in 15% HCl and its inhibition by pyridine derivative. The quantum chemical study further supported the experimental results. The adsorption behavior of AMP is shown in following Fig. 1.22

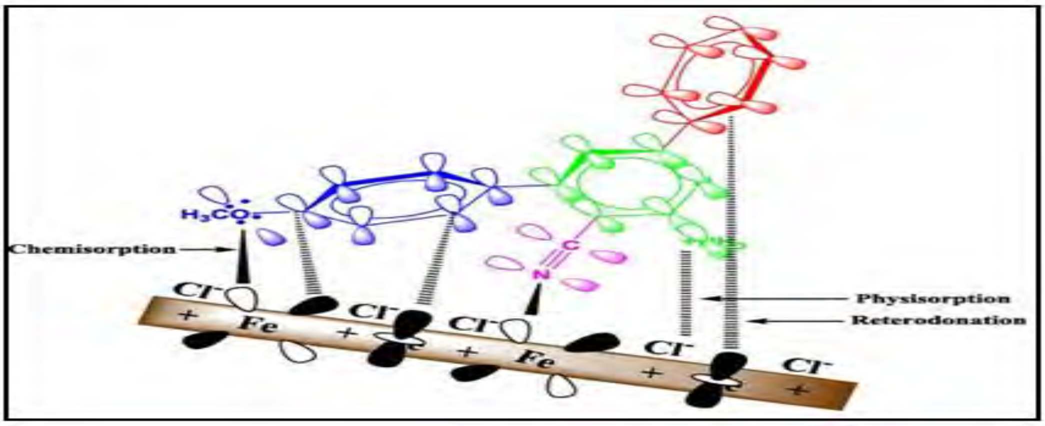

Fig. 1.22:Schematic representation of the adsorption behavior of the AMP

Corrosion inhibition of C38 steel in 1 M HCl was investigated in the absence and presence of different concentrations of two imidazo derivatives namely, 2-phenylimidazo [1, 2-a] pyridine (P1) and 2-(mmethoxyphenyl) imidazo [1, 2-a] pyrimidine (P5).Impedance measurements showed that the double-layer capacitance decreased and charge-transfer resistance increased with increase in the inhibitors concentration and hence increase in inhibition efficiency. Potentiodynamic polarization study showed that all the inhibitors acted as mixed-type inhibitors. The inhibitors were adsorbed on the steel surface according to the Langmuir adsorption isotherm model. Inhibition efficiency values obtained from various methods were in good agreement [150].

The corrosion protection efficiency of three pyridines namely 2-amino-3,5-dicarbonitrile- 4-(4-methoxyphenyl)-6-(phenylthio) pyridine (ADTP I), 2-amino-3,5-di-carbonitrile-4 phenyl-6-(phenylthio) pyridine (ADTP II), and 2-amino-3,5-dicarbonitrile-4-(4-nitrophenyl)-6-(phenylthio) pyridine (ADTP III) has been investigated[151]. The results of potentiodynamic polarization studies showed mixed-type inhibition behavior. Among them, ADTP I showed the highest inhibition efficiency of 97.6% at 1.22 mmol L^{-1}. EIS studies revealed that inhibitor functioned via adsorption at metal solution interface. The results obtained from SEM/EDX confirmed formation of protective layer on mild steel surface.

Qiang *et al.*[152] have investigated synergistic effect of tartaric acid with 2,6-diaminopyridine on the corrosion inhibition of mild steel in 0.5 M HCl using electrochemical and morphological techniques. Experimental results revealed that DAP and TTA acted as mixed-type inhibitors inhibited both anodic and cathodic processes on the corrosion of mild steel in 0.5 M HCl solution, and their inhibitive efficiencies increased with incremental concentration. Synergistic effect of TTA and DAP exhibited a better inhibitive ability than single inhibitor. Besides, morphology analysis together with the results obtained from electrochemical tests suggested that an ordered and dense layer could be formed by synergistic effect so that mild steel is protected availably. Furthermore, XPS analysis and theoretical studies indicated that the synergistic protection is mainly dominated by competitive adsorption between the DAP molecules and TTA molecules physically and chemically.

The corrosion inhibition efficiencies of three novel naphthyridines namely, 5-amino-9-hydroxy-2-phenylchromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (N-1),5-amino-9-hydroxy-2-(p-tolyl)chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (N-2), and 5-amino -9-hydroxy- 2-(4-methoxy phenyl)chromeno [4,3,2-de][1,6] naphthayridine-4-carbo nitrile (N-3) have been investigated for mild steel in 1 M HCl solution by using various experimental and theoretical techniques. These compounds showed high inhibition activities at 6.54×10^{-5} M: (N-1), 94.28%; (N-2), 96.66%; and (N-3), 98.09%. Electro- chemical impedance spectroscopy analysis revealed an increase in polarization resistance due to the adsorbed inhibitor molecules on metal surface. Potentiodynamic polarization analysis revealed that all three compounds acted as mixed-type inhibitors but of predominantly cathodic type. The adsorption of the studied compounds on mild steel surface followed the Langmuir adsorption isotherm. Surface morphology examined by using scanning electron microscopy and atomic force microscopy analysis showed a smoother surface for mild steel in the presence of naphthyridines in acidic solution. Quantum chemical parameters correlated well with the experimental results, which supported higher inhibition efficiencies of N-3 and N-2 due to the electron-donating effects of $-OCH_3$ and $-CH_3$ substituents, respectively, than of N-1, which is devoid of substituents. The magnitudes of the adsorption energies obtained from Monte Carlo simulations also agreed with the trend of the experimental inhibition efficiency [153].

Many investigators have been reported that compound containing **nitrile groups** (-CN) act as efficient corrosion inhibitors.The influence of three 2-amino-5-nitro-4,6-diarylcyclohex-2-ene-1,3,3-tricarbonitrile (ANDT) derivatives namely, 2-amino-5-nitro-4,6-diphenylcyclohex-1-ene-1,3,3-tricarbonitrile (ANDT-1), 2-amino-4,6-bis-(4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile (ANDT-2) and 2-amino-4,6-bis-(3-hydroxy-4-methoxy-phenyl)-5-nitro-cyclohex-2-ene-1,3,3-tricarbonitrile (ANDT-3) on mild steel corrosion in 1 M HCl were studied by using experimental and theoretical techniques. Among these inhibitors the ANDT-3 showed maximum inhibition efficiency of 98.96% at 25 mg L^{-1}. Adsorption of the ANDTs on mild steel surface followed the Langmuir adsorption isotherm. Polarization studies showed that ANDTs act as mixed type inhibitors. SEM, EDX and AFM techniques confirmed the existence of adherent protective film of inhibitors on the mild steel surface. The results of theoretical calculations were found to be consistent with the surface and electrochemical results [154].

2-amino-3-methyl-3-(4-nitrophenyl)-5-(phenylthio)-3H-pyrrole-4-carbonitrile (INH) was tested as corrosion inhibitor mild steel in 1M HCl solution [155].. The results showed that INH acted as efficient corrosion inhibitors, and the adsorption of INH obeyed Langmuir adsorption isotherm. Polarization curves showed that INH behaved as a mixed-type inhibitor. EIS study indicated that the INH formed a protective surface film at metal/electrolyte interface. Both SEM and AFM studies showed that surface smoothness increased due to formation of protective surface film by INH. The Monte Carlo simulation study suggested that INH has strong tendency to adsorb on mild steel surface in 1M HCl. The adsorption behavior of INH in shown in the following Fig.1.23.

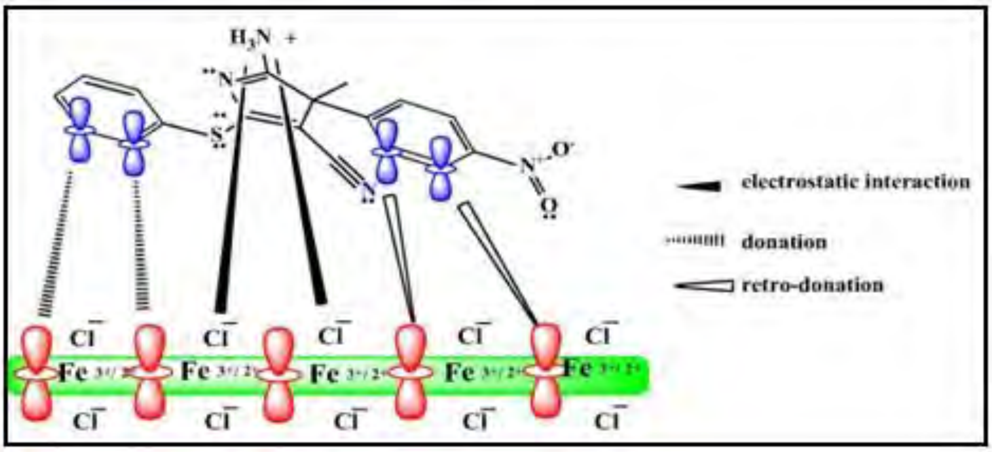

Fig.1.23: Pictorial representation of the adsorption behavior of the INH on mild steel in 1M HCl

The adsorption and inhibition effects of 5-(phenylthio)-3H-pyrrole-4-carbonitriles (PPCs) namely: 2-amino-3-methyl-3-phenyl-5-(phenylthio)-3H-pyrrole-4-carbonitrile (PPCI), 2-amino-3-(4-hydroxyphenyl)-3-methyl-5-(phenylthio)-3H-pyrrole-4-carbonitrile (PPC II), and 2-amino-3-(2,4-dihydroxyphenyl)-3-methyl-5-(phenylthio)-3H-pyrrole-4-carbonitrile (PPC III) on mild steel corrosion in 1 M HCl has been studied. Results showed that inhibition efficiency increased with concentration and maximum value was obtained at 50 mg/L concentration. From the results it is concluded that the PPCs inhibited mild steel corrosion in 1 M HCl by adsorbing on the metal surface. Polarization results showed that the PPCs acted as anodic type inhibitors. The surface morphology study was carried out by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The Monte Carlo simulation were found to be in good agreement with the experimental results.The EIS measurements suggested that PPCs form a protective covering on the mild steel surface. The results of SEM and AFM suggested that surface smoothness increases due to the formation of protective surface film. The experimental results were well supported by theoretical calculations [156].

The synergistic properties of the combined admixture of benzenecarbonitrile and 5-bromovanillin (BNV) on the corrosion resistance of 1018 carbon steel in 1 M HCl solution has been investigated [157]. Experimental results showed that the admixed organic compound was effective with optimal corrosion inhibition values of 99.33% and 90.34% at 1.25% BNV concentration from both electrochemical methods due to theeffective inhibition action and passivation characteristics of the protonated inhibitor molecules in the acid solution. Primary amines, stretch alkyl halides and C-H triple bond functional groups of the molecules were observed to actively adsorbed during the corrosion inhibition reaction from ATF-FTIR spectroscopic analysis. Calculations from thermodynamic evaluation confirmed cationic adsorption mechanism was chemisorption and obeyed the Langmuir and Frumkin adsorption isotherm. Micro-analytical observations of the inhibited carbon steel morphology significantly contrasted the unprotected steel due to visible surface deterioration and presence of micro/macro-pits. The organic derivatives showed mixed type inhibition reaction.

Two benzonitrile derivatives, namely 4-(isopentylamino)-3-nitrobenzonitrile (PANB) and 3-amino-4-(isopentylamino) benzonitrile(APAB) have been synthesized and evaluated as corrosion inhibitors for mild steel (MS) in 1 M HCl solution at 303 K. The results suggested that tested compounds were excellent corrosion inhibitors for mild steel with PANB showing superior performance. Polarization measurements revealed that PANB and APAB behaved as mixed type inhibitors. The polarization resistance, according to EIS studies, found to be dependent on the inhibitor's concentration. The adsorption of PANB and APAB on mild steel surface obeyed Langmuir's adsorption isotherm. The protection of carbon steel in 1 M HCl was confirmed by using scanning electron microscope (SEM) and Atomic Force Microscopy (AFM). Electrochemical, DFT and MD simulations results were in good agreement [158].

7.4 Pyridazine derivatives as Corrosion Inhibitors

The corrosion inhibition performance of three pyridazine derivatives, 6-methyl-4,5-dihydro-2H-pyridazine-3-one (MPYO), 6-phenyl-2H-pyridazine-3-one (PPYO) and 6-phenyl-2H-pyridazine-3-thione (PPYS) for mild steel in 1 M HCl solution has been studied by using gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The effect of molecular structure on the inhibition efficiency was theoretically studied by density functional theory (DFT).Experimental results demonstrated that the inhibition efficiency increased with inhibitor concentration and temperature and the inhibition efficiencies followed the order of PPYS > PPYO > MPYO.Polarization studies clearly revealed that the presence of pyridazines does not change the mechanism of hydrogen evolution and theyacted as cathodic inhibitors. Impedance method indicated that pyridazine compounds adsorbed on the mild steel surface with increasing charge transfer resistance and decreasing the double layer capacitance. Experimental and theoretical studies agreed well and confirmed that PPYS is the best corrosion inhibitor among the studied organic compounds which was related to the presence of a more favorable adsorption center of S atom in its molecular structure [159].

The effect of heterocyclic organic compound derived from pyridazine named ethyl (6-methyl-3-oxopyridazin-2-yl) acetate as corrosion inhibitor for mild steel in 1M HCl was studied by Ghazoui *et al.* [160].Gravimetric measurements indicated that the inhibitor had efficiency increased with the concentration and reach a maximum value of 83.1% at 10^{-3} M. In addition, potentiodynamic polarization studies revealed that the inhibitor acted as a mixed type inhibitor with predominance at cathodic domain. EIS showed that increasing the concentration of the inhibitor leads to an increase of the charge transfer resistance and reducing the double layer capacitance. The most fitting isotherms in the adsorption of inhibitor at surface of mild steel acidic media were Langmuir isotherms and the negative value of ΔG° ads was a sign of spontaneous adsorption on the metal surface.

Triazole and triazole-type compounds containing nitrogen, sulphur, and heterocycle on the corrosion inhibition of metal in acidic media have attracted more attention because of their excellent corrosion inhibition performance. Some new triazole derivatives have been still continuously synthesized and investigated as inhibitors for corrosion of metals in acidic solutions.

The efficiency of 4-(4-hydroxy-3-methoxy benzyledene amino)-4-H-1,2,4-triazole-3, 5-dimethanol, HMATD, as corrosion inhibitor for mild steel in 0.5 M HCl has been determined by weight loss and electro analytical methods. The electrochemical impedance spectroscopic measurements revealed the inhibition action of HMATD by reducing the charge transfer through metal solution interface. Polarization curves indicated the mixed type behaviour of HMATD. The inhibitor molecule functioned by blocking the active sites on metal surface by adsorption and it obeyed the Langmuir adsorption isotherm [161].

The inhibition effect and adsorption behavior of 4-((2, 3-dichlorobenzylidene) amino)-3-methyl-1H-1, 2, 4-triazole-5(4H)-thione, CBAT on mild steel (MS) in 1 M hydrochloric acid solution was studied by using weight loss and electrochemicaltechniques. The potentiodynamic polarization measurement illustrated the mixed type behavior of CBAT. It is also observed that the inhibitor adsorbed onto mild steel surface by both physical and chemical means and obeyed Langmuir adsorption isotherm. SEM micrographs revealed the presence of an adsorbed protective film on the MS surface. Density Functional Theory (DFT) calculations and Molecular dynamic (MD) simulations further explained the anti-corrosion mechanism. The theoretical results were in good agreement with the experimental data reported [162].

The effects of carbon steel immersed in 1 M HCl acid in the presence of 2-Amino-1,3,4-triazole (AT), 3-(2-pyridyl)- 2-Amino-1,3,4-triazole (2-AT) and 3-(4-pyridyl)- 2-Amino-1,3,4-triazole (4-AT) were studied by using chemical and electrochemical techniques [163].Polarization curves revealed that these compounds are mixed type inhibitors and inhibition efficiency increased with increasing concentration of inhibitors . Further, the 4-AT, displayed the best inhibiting characteristics, with a maximum *IE* of approximately 93% at a concentration of 2×10^{-3} M.

The corrosion inhibition efficiency of newly synthesized 3,5-diaryl-4-amino-1,2,4-triazole derivatives was investigated for mild steel corrosion in 1.0 M HCl medium using weight loss quantum chemical calculations and Monte Carlo simulations. It was found that the studied compounds exhibited a very good performance as inhibitors for mild steel corrosion in 1.0 M HCl. The results showed that the inhibition efficiency increased with increasing concentration of inhibitors. It was found that the adsorption for these inhibitors on the mild surface obeyed the Langmuir adsorption isotherm. The values of inhibition efficiency for all triazoles followed the order 3-APAT < 4-APAT < 4-DTAT < 4-MAT < 3,4-MAT. The 3, 4-methoxyphenyl substituted triazole (3,4-MAT) exhibited the highest inhibition efficiency of 98.5% at concentration of 1×10^{-4} M. A good correlation was observed between the quantum chemical calculation, Monte Carlo calculations and experimentally inhibition efficiency data [164].

7.5 Benzimidazole and It’s derivatives as corrosion as Inhibitors

Benzimidazole derivatives have been found to be biologically active small molecules, such as vitamin B and a variety of antimicrobial, antiparasitic, and even antitumor agents. Aside from their place in biomedical research, benzimidazoles also have a prominent place in organocatalysis, organometallic and materials chemistry Besides, a good number of benzimidazoles were found application in corrosion inhibition.

Zang *et al.* [165] have tested the corrosion inhibition properties of a new benzimidazole derivative, 6-(dodecyloxy)-1*H*-benzo[*d*]imidazole (DBI), for mild steel in 1 M HCl. Computational chemistry was performed to explore the adsorption of DBI on metal surface. Experimental results revealed that the inhibition performance of DBI is attributed to both the direct interaction of benzimidazole segment with iron surface and the barrier effect of the non-polar long chain against aggressive solution. Compared to the protonated form, the molecular form of DBI could more tightly interact with iron surface. These results showed that the long-chain alkyl-substituted benzimidazole derivative is of great potential application as corrosion inhibitor.

Hydrogen bonded interaction and synergistic effect on the corrosion protection properties of alkyl benzimidazoles and semicarbazide pair on mild steel in hydrochloric acid at 303, 308 and 313 K have been studied by polarization, electrochemical impedance spectroscopy, adsorption, surface studies and basic computational calculations. The combined form of inhibitors alkyl benzimidazole (MBI/ EBI/ PBI) and SC shown inhibitive effect on the corrosion of mild steel in 1 M HCl. Particular combination of 150 ppm alkyl benzimidazole (MBI/EBI/PBI) and 50 ppm SC exhibited good inhibition efficiency at all the studied temperatures (303 K, 308 K and 313 K).Polarization studies revealed that the alkyl benzimidazole (MBI/EBI/PBI) – SC mixture acted as a mixed type inhibitor. Quantum chemical studies and synergism parameter values supported the experimental results. The inhibitor molecules were adsorbed on mild steel surface blocking the reaction sites and obeyed the Langmuir adsorption isotherm. The surface area available for the attack of the corrosive species decreased with the addition of alkyl benzimidazole – SC mixture [166].

Yadav *et al.*[167] have studied the inhibitive action of synthesized benzimidazole derivatives, namely: 2-(1-(morpholinomethyl)-1*H*-benzo[*d*]imidazol-2-yl)phenol (MBP), 2-(1-((piperazine-1-yl)methyl)-1*H*-benzo[*d*]imidazol-2-yl) phenol (PzMBP) and 2-(1-((piperidine-1-yl)methyl)-1*H*-benzo[*d*]imidazol-2-yl)phenol (PMBP) on corrosion of N80 steel in 15% HCl solution. It was found that the inhibition efficiency of all the three inhibitors increased with increase in concentration of inhibitors and decreased with increase in temperature. The inhibitors, PzMBP,

MBP, and PMBP showed corrosion inhibition efficiency of 96.3, 94.4 and 92.9% respectively, at 200 ppm and 303 K. Polarization studies showed that the studied inhibitors were mixed type in nature. The results of the Fourier transform infrared (FTIR) and UV–visible spectroscopy provided evidence of iron/inhibitors interactions. SEM results confirmed the formation of protective layer on mild steel surface. The results of quantum chemical calculations were consistent with the experimental findings.

The inhibition efficiency of propyl benzimidazole (PBI), for mild steel in hydrochloric acid in three different concentrations at 303, 308 & 313 K has been studied.In the presence of PBI, the corrosion of mild steel exposed to HCl solution was effectively reduced. The inhibition efficiency of PBI increased with increase in its concentration at all the three temperatures studied. The inhibition efficiency of PBI was found to decreased with increase in concentration of HCl solution. PBI showed maximum efficiency in 0.5 M HCl solution at room temperature. The mode of inhibition of PBI was through adsorption on to the mild steel surface. The mode of adsorption was believed to be both physisorption and chemisorption. The adsorption obeyed Langmuir adsorption isotherm in all the cases except for that in 1.5 M HCl at 313 K, which obeyed Temkin adsorption isotherm [168].

7.6 Benzothiazole Derivatives as Corrsoin Inhibitors

Benzothiazole derivatives have been studied extensively for their diverse chemical reactivity and corrosion inhibition properties. Two benzothiazole derivatives, namely 2-(*n*-hexylamino)-4-(3′-*N,N*-dimethylamino-propyl)amino-6-(benzothiazol-2-yl)- thio-1,3,5-*s*-triazine (BTC$_6$T) and 2-(*n*-octylamino)-4-(3′-*N,N*-dimethylamino-propyl)- amino-6-(benzothiazol-2-yl)thio-1,3,5-*s*-triazine (BTC$_8$T), were synthesized and evaluated as corrosion inhibitors for steel in a 1 M HCl. solution. Polarization results showed that both tested inhibitors were predominant in cathodic nature. EIS measurements indicated adsorption of inhibitors on mild steel surface. It was also revealed that both inhibitors offered extra stability and higher inhibition efficiencies against steel corrosion than previously reported benzothiazole family inhibitors. These inhibitors can be adsorbed onto surfaces by both physical and chemical means. The theoretical parameter obtained by DFT calculation correlated the results of both the inhibitors obtained by experimental studies [169].

Salarvand *et al.*[170] have studied the inhibitive performance of 2-(2′-hydroxylphenyl)benzothiazole, (**1**), 2-(2′,5′-dihydroxyphenyl)benzothiazole, (**2**), and (4-benzothiazole-2-yl-phenyl)-dimethyl-amine, (**3**), on the corrosion of mild steel in 1 M HCl. Notably, compound **3** showed 95% inhibition efficiency at 50 ppm (by weight) concentration. The adsorption of these compounds obeyed the Langmuir adsorption isotherm with predominately chemisorption for **3** and comprehensive for **1** and **2**. Quantum chemical calculations predicted an inhibition order of **3** > **2 > 1**, is at odds with the experimental order due the structural effects. Molecular dynamic simulation revealed a nearly flat configuration for molecules on metal surface with negative binding energies in a sequence agreed by the experiments, **3** > **1 > 2**.

Nowadays, researchers are mainly focusing on the use of non-toxic and “green” corrosion inhibitors, e.g., plant extracts and drugs to obviate the harmful effect of chemicals on environment. Because of their non-toxic characteristics and negligible negative impacts on the aquatic environment, drugs (chemical medicines) seem to be the ideal candidates to replace traditional toxic corrosion inhibitors .A number of studies are available describing the application of drugs as efficient corrosion inhibitors.

7.7 Drugs as corrosion inhibitors

Mild steel coupons in 1 M HCl in the presence of an eco-friendly antipsychotic, namely clozapine (CZP) was studied by Gaz *et al.* [171]. Results showed that the CZP acted asa good inhibitor and inhibition efficiency (*IE*%) reached 96% at an optimum concentration of 10^{-3} M. Potentioynamic polarization results revealed that the CZP affected both cathodic and anodic current and may be classified as mixed type inhibitor in HCl medium. While the adsorption of tested compound on MS surface was found to followed the Langmuir isotherm, quantum chemical data also supported the experimental finding.

The corrosion inhibitive property of analgin on mild steel in 1 M HCl was determined by using experimental and theoretical studies [172]. Weight loss results showed that analgin showed 96.1% inhibition efficiency at concentration of 4000 ppm at 298 K. Polarization studies indicated that analgin acted as a mixed type inhibitor. The adsorption of analgin on metal surface obeyed Langmuir adsorption isotherm. Theoretical results obtained from molecular dynamic simulations and quantum chemical calculations using density functional theory (DFT) were in good agreement with experimental finding.

The inhibitive action of an expired Ambroxol drug on the corrosion of mild steel in 1 M HCl and 1 M H_2SO_4 acid medium has been studied. Experimental results revealed that the inhibition efficiency increased with increasing the concentration of the inhibitor. Electrochemical studies data supported that examined expired drug acted as efficient inhibitor for mild steel corrosion. The adsorption of the examined drug obeyed Langmuir's adsorption isotherm. Polarization studies indicated that this inhibitor acted as a mixed type. The protective film formed on the surface was confirmed by SEM. The data collected from the studied techniques were in good agreement to confirm the ability of expired Ambroxol drug as corrosion inhibitor for mild steel in both acid media [173].

The corrosion inhibition properties of cefradine (CFD) for mild steel corrosion in HCl solution were analyzed by using experimental method. The experimental results revealed that cefradine was found to be a good inhibitor for mild steel corrosion in acid medium. The inhibition efficiency of cefradine decreased with temperature, which leads to an increase in activation energy of the corrosion process. Potentiodynamic polarization study clearly revealed that cefradine acted as mixed type inhibitor.EIS studies showed that charge transfer resistance increased and double layer capacitance decreased in the presence of cefradine. Adsorption of inhibitor obeyed Langmuir adsorption isotherm model [174].

Dohare *et al.* [175] have investigated the use of expired Podocip (PCIP) drug as corrosion inhibitor for carbon steel in 1 M HCl medium. Polarization curves revealed that the inhibiting action of the PCIP is mixed-type. The adsorption of PCIP on carbon steel surface followed the Langmuir isotherm. Impedance analysis showed that the presence of inhibitor considerably affected the charge transfer resistance and the double layer capacitance of carbon steel surface. SEM and AFM studies evidenced the formation of a protective film over metal surface.

The inhibition performance of atenolol on mild steel in 1 M hydrochloric acid solution has been studied [176]. The results showed that the inhibition efficiency was found to increased with increasing the concentration of the inhibitor from 50 to 300 ppm. The maximum inhibition efficiency 93.8% was observed in the presence of 300 ppm inhibitor (in case of potentiodynamic polarization). Polarization curves demonstrated that the atenolol was a mixed-type inhibitor for mild steel corrosion in these solutions. EIS measurements also indicated that the inhibitor increased the chargetransfer resistance and showed that the inhibitive performance depends on an adsorption of the molecules on the metal surface. The inhibition action of atenolol was explained in terms of adsorption on the mild steel surface. The adsorption process followed Langmuir isotherm via physical adsorption. The SEM images confirmed the formation of the protective layer on the metal surface.

The corrosion mitigation efficiency of biotin drug for mild steel in 15% hydrochloric acid was thoroughly investigated by Xu *et al.* [177]. The results obtained from gravimetric and electrochemical studies revealed that the inhibition efficiency of inhibitor increased with increase in inhibitor concentration. A linear fit result was obtained for the Langmuir adsorption isotherm and was a typical chemisorption. Polarization measurements revealed that the inhibitor was of mixed type as both the anodic and cathodic processes were hindered. Surface studies confirmed the mitigation of corrosion by biotin through formation of a protective layer. Quantum chemical calculation revealed that protonated species can more easily be adsorbed on the mild steel surface than the neutral species.

7.8 Plant Extracts as Green Corrosion Inhibitor

Different plant extracts as well as organic compounds deived from plants can be used as corrosion inhibitors commonly known as green corrosion inhibitors.

The corrosion inhibition of X70 steel in 1 M HCl by *Ginkgo* leaf extract (GLE) was investigated by conducting electrochemical measurements. The inhibition efficiency exceeded 90% in the presence of 200 mg/L GLE at all of the tested temperatures. The inhibition efficiency obtained from EIS agreed well with that from polarization results. The excellent inhibition capacity, which was attributed to the formation of inhibitor–adsorption films on the surface of the X70 steel, was confirmed by field emission scanning electron microscopy and atomic force microscopy. The adsorption of GLE on steel surface followed the Langmuir adsorption model. Potential of zero charge measurement and quantum chemical calculation gave deep insight in to inhibition mechanism [178].

Anees *et al.*[179] have investigated corrosion inhibition of low carbon steel in 1 M HCl in absence and presence of *Xanthiumstrumarium leaves (XSL)* extracts as a friendly corrosion inhibitor. The result obtained showed that *Xanthiumstrumarium* *leaves* extracts acted as an inhibitor for low carbon steel in HCl and reduced the corrosion rate. The inhibition efficiency was found to increase with increase in inhibitor concentration and temperature. Higher inhibition efficiency was 94.82% at higher level of inhibitor concentration and temperature. The adsorption of *Xanthiumstrumarium leaves* extracts was found to obey Langmuir adsorption isotherm model. The values of the free energy of adsorption were more than −20 kJ/mol, which was indicative of mixed mode of physical and chemical adsorption.

Organically functionalized chitosan macromolecules namely Chitosan-thiosemicarbazide (CS-TS) and Chitosan-Thiocarbohydrazide (CS-TCH) were synthesized and evaluated as new corrosion inhibitors for mild steel corrosion in 1M HCl solution. The maximum efficiency of 92% was obtained at a concentration as low as 200mgL^{-1}. The inhibitors were found to obey Langmuir adsorption isotherm and exhibited both physical and chemical adsorption. Electrochemical impedance spectroscopy (EIS) results showed an increase in polarization resistance which supported the adsorption of inhibitors on the mild steel surface. Tafel data showed a mixed type behaviour with cathodic predominance. The data of quantum chemical calculations and molecular dynamics simulation supported the experimental findings [180].

The inhibitory effect of hydroxyethylcellulose (HEC) on A1020 carbon steel corrosion in 1M HCl solution at different concentrations and temperatures has been studied by using various experimental techniques. The Inhibition efficiency was found to increased with increase in concentration of HEC but decreased with increasing temperature. HEC adsorbed onto the mild steel surface via mixed type adsorption. Adsorption of inhibitor on the steel/solution interface followed Langmuir adsorption isotherm. EIS suggested formation of protective layer over the carbon steel surface. The SEM, EDX and AFM studies confirmed the formation of the surface protective film. The quantum chemical calculations well supported the experimental results and also showed that HEC had strong tendency to replace the water from metal surface [181].

Singh *et al.*[182] have tested the inhibition of the corrosion of N80 steel in 3.5 wt. % NaCl solution saturated with CO_2 by four porphyrins, namely 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphyrin (HPTB), 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphyrin (T4PP), 4,4',4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrakis(benzoic acid) (THP) and 5,10,15,20-tetraphenyl-21H,23H-porphyrin (TPP) using various electrochemical and morphological techniques. The results showed that the inhibition efficiency, η% increased with increasing concentration of the inhibitors. The EIS results revealed that the N80 steel surface with adsorbed porphyrins exhibited non-ideal capacitive behaviour with reduced charge transfer activity. Potentiodynamic polarization measurements indicated that the studied porphyrins acted as mixed type inhibitors. The SECM results confirmed the adsorption of the porphyrins on N80 steel thereby forming a relatively insulated surface. The SEM also confirmed the formation of protective films of the porphyrins on N80 steel surface thereby protecting the surface from direct acid attack. Quantum chemical calculations and quantitative structure activity relationship (QSAR) studied showed that the corrosion inhibition performances of the porphyrins could be related to their EHOMO, ELUMO, ω, and μ values. Monte Carlo simulation studies showed that THP had the highest adsorption energy, while T4PP had the least adsorption energy in agreement with the values of σ from quantum chemical calculations.

The inhibition effect of hydroxyethylcellulose (HEC) on 1018 C-steel corrosion in 3.5% NaCl solution has been investigated. The potentiodynamic polarization studies suggested that HEC acted as a mixed-type inhibitor. Data obtained from EIS were analyzed to model the corrosion inhibition process through equivalent circuit. Results obtained from EFM technique were shown to be in agreement with potentiodynamic and EIS techniques. The adsorption behaviour of HEC on steel surface followed the Langmuir adsorption isotherm. SEM and EDX analysis of the steel surface showed that a film of inhibitor is formed on the steel surface and this film inhibited metal dissolution in 3.5% NaCl solution. Quantum chemical calculations further supported the adsorption mechanism with the structure of HEC molecule [183].

Maria *et al.*[184] have described the successful performance of pectin as an eco-friendly corrosion inhibitor for mild steel in HCl solution. Experimental results revealed that inhibition efficiency increased with temperature while the activation energy for the corrosion rate decreased with the addition of pectin. Pectin is a mixed-type inhibitor and the mode of inhibition results from the geometric blocking effect of chemisorbed inhibitive species at the metal surface. Spectroscopic analysis pointed to the formation of a complex between pectin and Fe^{2+} ions released during the corrosion reaction.

Polysaccharide from *Plantago ovata* was investigated for its inhibition characteristics for carbon steel corrosion in 1M HCl by using chemical, electrochemical and surface analytical techniques. The mucilage of the Plantago is comprised of a highly branched polysaccharide, arabinosyl (galaturonic acid) rhamnosylxylan (AX), which is mainly responsible for the corrosion inhibition of the carbon steel. Thermodynamic and activation parameters revealed that the spontaneous adsorption of AX on carbon steel was mixed type and predominantly chemical in nature. Quantum chemical analysis supported the proposed mechanism of inhibition. AX from Plantago could serve as a green corrosion inhibitor for the carbon steel in hydrochloric acid medium with good inhibition efficiency but low risk of environmental pollution [185].

Umoren *et al.*[186] have investigated the performance of two natural polymers; chitosan and carboxymethyl cellulose (CMC) as single component corrosion inhibitors in comparison with a commercial inhibitor formulations, on API 5L X60 pipeline steel in CO_2 saturated 3.5% NaCl solution. The results indicated that there is a remarkable difference in inhibition efficiency of each inhibitor on the API 5L X60 steel and the commercial inhibitor formulations. Inhibition efficiency increased with the increase of inhibitors' concentrations. Immersion time was found to have a profound effect on the corrosion inhibition performance of all the inhibitors. Also the inhibition efficiency was found to decrease with the increase in temperature. Potentiodynamic polarization results revealed a mixed-type inhibition for all inhibitors. The adsorption of each inhibitor on the steel surface obeyed Langmuir's isotherm.

The performance of synthesised O-fumaryl-chitosan (OFC) as corrosion inhibitor for mild steel in 1M HCl has been evaluated through various studies. The initial screening by weight loss method revealed the good inhibition efficiency by the inhibitor. Thermodynamic and kinetic parameters studies revealed that the mode of adsorption was physical in nature and it followed Langmuir adsorption isotherm. Electrochemical measurements supported the inhibition of mild steel by the fumaryl derivative of chitosan. Polarisation studies provided the information that the inhibition is of mixed type. Scanning electron microscopy (SEM) and Atomic force microscopy (AFM) assured the formation of protective inhibitor film on mild steel surface [187].

Verma *et al.*[188] have investigated D-glucose derivatives of dihydropyrido-[2,3-d:6,5-d']-dipyrimidine-2, 4, 6, 8(1H,3H, 5H,7H)-tetraone (GPHs) as corrosion inhibitors for mild steel in 1M HCl solution. The order of inhibition efficiency was GPH-3 > GPH-2 > GPH-1. The results further showed that the inhibitor molecules with electron releasing (-OH, -OCH_3) substituents exhibited higher efficiency than the parent molecule without any substituents. Polarization study suggested that the studied compounds were mixed-type but exhibited predominantly cathodic inhibitive effect. The adsorption of these compounds on mild steel surface obeyed the Langmuir adsorption isotherm. SEM, EDX and AFM analyses confirmed the inhibitive actions of the molecules on mild steel surface. Quantum chemical (QC) calculations and Monte Carlo (MC) simulations studies well supported the experimental results.

The corrosion inhibition activity of adenosine on mild steel in 1 mol dm^{-3} HCl solution was tested based on the weight loss method and electrochemical methods. Adenosine was found to have inhibition efficiency of 78.88 % at concentration of 1×10^{-3} mol dm^{-3} by the weight loss study. In the electrochemical studies, adenosine was shown to be a mixed-type inhibitor that inhibited both the anodic and cathodic reaction. The corrosion inhibition effect was observed to be weakened in hydrodynamic condition. Adenosine was shown to adsorb by mixed-type adsorption (via a physisorption and chemisorption process) based on the values of calculated Gibbs free energy. The surface morphology of mild steel in 1 mol dm^{-3} HCl with adenosine showed improvement compared with mild steel in 1 mol dm^{-3} HCl without adenosine [189].

Corrosion inhibition performance of an environmentally benign compound, gelatin on X60 steel in 15% hydrochloric acid (HCl) at 25 °C, which simulate oil well acidizing environment was investigated by using various experimental methods. Both the weight loss and the electrochemical results showed that the gelatin exhibited high inhibition efficiency and the inhibition efficiency increased with increasing gelatin concentration. The addition of low concentration of potassium iodide improved the inhibition efficiency of gelatin considerably. The ATR-FTIR and SEM/EDX surface morphology analyses provided evidence of formation of protective gelatin film on the metal surface. The gelatin molecules are predicted to get adsorbed on the metal surface through an interaction between the nitrogen and oxygen atoms of gelatin and the metal surface to form a metal/gelatin complex on the metal surface [190]. The adsorption behavior of gelatin molecule is shown in the following Fig.1.24.

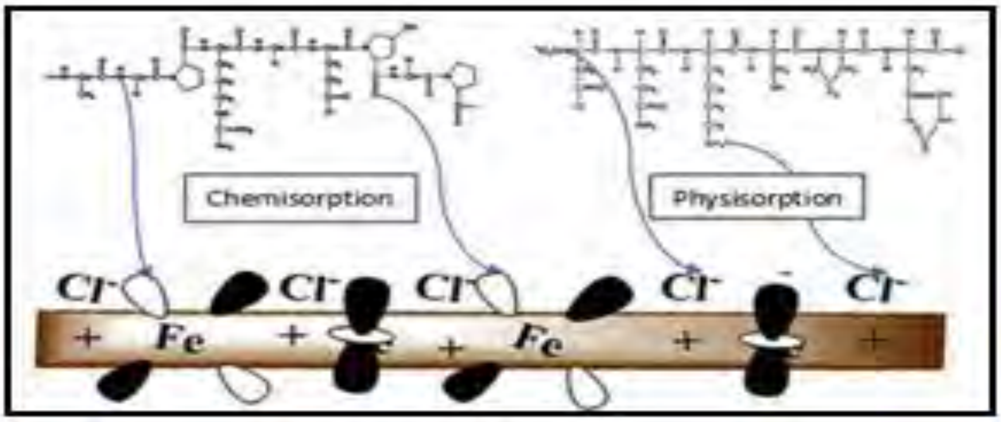

Fig.1.24: Adsorption of the gelatin molecules on the metal surface

Organic dyes are compounds with promising corrosion inhibition characteristics. The presence of π-electron systems and heteroatoms in their molecules which is responsible for their colouration also suggests their high propensity to adsorb on metal surface and other adsorbents. There are different kinds of dyes and over a hundred thousand of dyes are commercially available.

7.9 Dyes as Corrosion Inhibitors

The inhibition effect of acid violet 6B (AV6B) on the corrosion of cold rolled steel (CRS) in 1.0–5.0 M HCl solution was studied for the first time by Deng *et al.*[191] using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods. The results showed that AV6B acted as a very good inhibitor in 1.0 M HCl, and the adsorption of AV6B on CRS surface obeyed Langmuir adsorption isotherm. Polarization curves revealed that AV6B behaved as a mixed-type inhibitor. EIS spectra exhibited one capacitive loop and confirmed the inhibitive ability**.**

Corrosion inhibition properties of some organic dyes, namely Sunset Yellow (SS), Amaranth (AM), Allura Red (AR), Tartrazine (TZ) and Fast Green (FG), for mild steel corrosion in 0.5 M HCl solution, has been investigated [192]. The results showed that the studied dyes were good corrosion inhibitors with enhanced inhibition efficiencies. The inhibition efficiency of all the studied dyes increased with increase in concentration, and decreased with increase in temperature. The results showed that the inhibition efficiency of the dyes increased in the presence of KI due to synergistic interactions of the dye molecules with iodide (I−) ions. Potentiodynamic polarization results revealed that the studied dyes acted as mixed-type inhibitors both in the absence and presence of KI. The adsorption of the studied dyes on mild steel surface, with and without KI, obeyed the Langmuir adsorption isotherm and involved physical adsorption mechanism. Quantum chemical calculations revealed that the most likely sites in the dye molecules for interactions with mild steel were the S, O, and N heteroatoms.

7.10 Hydrazide Derivatives as Corrosion Inhibitors

Hydrazide derivatives are the type of organic compounds containing a nitrogen-nitrogen covalent bond with one of the substituents being an acyl group. Hydrazides and their derivatives have gained prominence because of their antibacterial, anti-inflammatory, anticancer, antiplatelet, antimalarial, analgesic and antioxidant activity. In addition to this they are also employed as potential inhibitors for controlling corrosion of many metals including mild steel.

Two hydrazide derivatives namely *N′*-(4-Hydroxybezylidene) nicotinic hydrazone (HBNH) and *N′*-(4-methylybezylidene) nicotinic hydrazone (MBNH) have been investigated as corrosion inhibitors for mild steel in 1 M HCl. Both the inhibitors showed good corrosion inhibition efficiency; with the inhibition efficiency of MBNH being higher than that of HBNH. The polarization results indicated that both the inhibitors acted as mixed type inhibitors and followed Langmuir adsorption isotherm. Interaction energies derived from molecular dynamics simulation were in agreement with experimental results [193].

The Corrosion inhibition of mild steel in 15% HCl solutions by newly synthesized acetohydrazides namely, *N′*-[(1*Z*)-phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and *N′*-[(1*Z*)-4-chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA), has been investigated. It was shown that PQA and CPQA acted as good corrosion inhibitor for mild steel protection. It was concluded that the inhibition efficiencies increased with increase in the concentrations of the inhibitor. Tafel polarization studies showed that both the studied inhibitors acted as mixed type inhibitor. The high inhibition efficiencies were attributed to the simple blocking effect by adsorption of inhibitor molecules on the steel surface. Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM) and Energy Dispersion X-ray Spectroscopy (EDX) observations confirmed the existence of an adsorbed protective film on the metal surface. The density functional theory (DFT) was employed for theoretical calculations and the obtained results were found to be consistent with the experimental findings [194].

Preethi *et al.* [195] have studied the influence of an aromatic hydrazide derivative, 2-(3,4,5-trimethoxybenzylidene) hydrazinecarbothioamide (TMBHC) as corrosion inhibitor on mild steel in 1 M hydrochloric acid. The results showed that the inhibition efficiency (% *IE*) of TMBHC increased with increasing inhibitor concentrations and also with increase in temperatures. TMBHC acted as a mixed type of inhibitor and its adsorption on mild steel surface was found to follow Langmuir's adsorption isotherm. The evaluation of thermodynamic and activation parameters indicated that the adsorption of TMBHC took place through chemisorption. The formation of protective film was further confirmed by scanning electron microscopy (SEM).

The anticorrosion properties of azelaic acid dihydrazide for mild steel in 1 M HCl solution was evaluated experimentally [196]. Potentiodynamic polarization studies indicated that azelaic acid dihydrazide acted as mixed-type inhibitor. The inhibition efficiency increased with increased inhibitor concentration and reached its maximum of 93% at 5×10^{-3}M. The adsorption of the inhibitor on a mild steel surface obeyed Langmuir's adsorption isotherm.

7.11 Imidazoline and its Derivatives as Corrosion Inhibitors

Nitrogen-based organic compounds, such as imidazoline and its derivatives, have been used successfully to protect mild steel in oil and gas wells and pipelines from carbon dioxide (CO_2) and hydrogen sulfide (H_2S) corrosion. These organic compounds inhibit the corrosion of mild steel by adsorption on the metal-solution interface thereby creating a barrier that prevents the active ions in the corrosion reactions to get to the surface. However, despite extensive use of imidazoline corrosion inhibitors the mechanism of inhibition remains poorly understood. Therefore, in order to develop more cost-effective inhibitors, a better understanding of the mechanism of inhibition of current and new inhibitors is needed.

Two novel imidazoline derivatives, 2-(2-trifluoromethyl-4,5-dihydro-imidazol-1-yl)-ethylamine (1-IM) and 2-(2-trichloromethyl-4,5-dihydro-imidazol-1-

yl)-ethylamine (2-IM), has been tested as corrosion inhibitors for mild steel in 0.5 M HCl solution by using various methods. The surface morphology of sample was presented through scanning electron microscopy (SEM) and the inhibition mechanism was elucidated by measuring the potential of zero charge (E_{pzc}) at the solid/liquid interface. Potentiodynamic polarization measurements revealed that they acted as mixed-type inhibitors with predominant anodic action. The EIS measurements confirmed that imidazole derivatives were adsorbed on mild steel surface to isolate the metal from aggressive environment. The formation of protective layer formed on the mild steel surface was further confirmed by SEM study.Results of theoretical calculation further confirmed that the chloride-substituted compound showed better inhibitive performance than the fluoride-substituted one [197].

A novel imidazoline derivative, 2-methyl-4-phenyl-1-tosyl-4, 5-dihydro-1H-imidazole (IMI), was prepared and investigated as corrosion inhibitor for P110 carbon steel in 1.0 M HCl solution. Experimental results revealed that IMI acted as excellent inhibitor for P110 carbon steel in 1.0 M HCl solution at 60 °C and the efficiency increased with the increasing concentration of inhibitor. According to the polarization measurements, IMI inhibitor could be classified as an excellent mixed-type inhibitor. Concluded from the weight loss measurements, the adsorption behaviour of IMI inhibitor on metal surface obeyed the Langmuir adsorption model. The SEM analysis indicated that the addition of IMI into the aggressive solution can remarkably protect carbon steel material from a macroscopic perspective [198]. The adsorption behavior of IMI inhibitor in shown in following Fig.1.25.

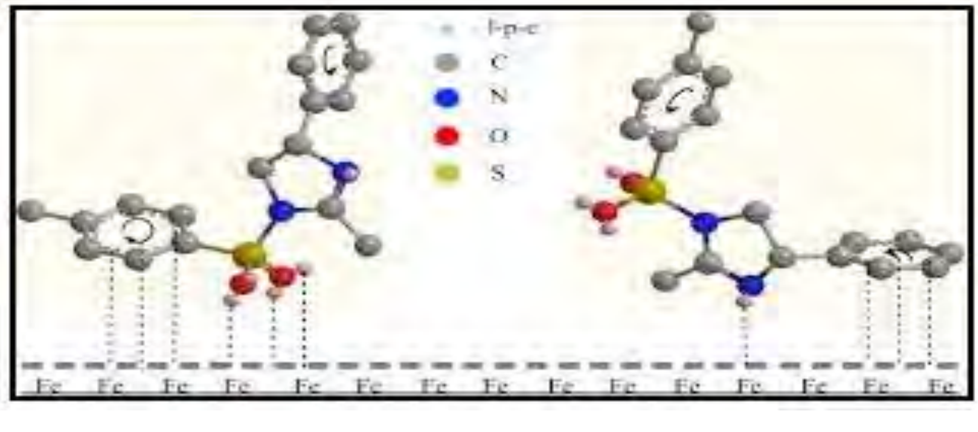

Fig. 1.25: Adsorption of the IMI molecules on the metal surface

Potentiodynamic polarization, electrochemical impedance spectroscopy, and weight loss methods were used to study the inhibition of the corrosion of X70 and

Q235 steels in CO_2-saturated 3 wt% NaCl solution with various concentrations of imidazoline-based inhibitor. The inhibition efficiencies for X70 and Q235 reached 97.8% and 98.6%, respectively, with sufficient concentration of inhibitor. The results indicated that, the inhibition efficiencies for X70 and Q235 were dramatically different with low concentration of inhibitor. Compared with X70, Q235 exhibited higher inhibition efficiency and stronger adsorption ability because of the larger amount and more homogeneous distribution of carbides. The adsorption of the inhibitor on the metal surface consisted of a mixture of physisorption and chemisorption and was observed to followed the Langmuir adsorption isotherm [199].

An imidazoline-based compound was synthesized, characterized and tested as a corrosion inhibitor for low alloy steel in CO_2-saturated 3 wt. % NaCl solution at 60 °C. The influence of pre-corrosion treatment on inhibition efficiency of the inhibitor was evaluated. The results showed that the inhibitor had excellent inhibition effectiveness on freshly abraded samples, with an inhibition efficiency of 98.7% in the presence of 2.4390×10^{-5} mol/l inhibitor. The adsorption of the inhibitor on the steel surface was found to obeyed Langmuir's adsorption isotherm and chemisorption. Pre-corrosion had a detrimental effect on the inhibitor performance, significant localized corrosion was observed on the pre-corroded samples with 1.2195×10^{-5} mol/l inhibitor after 96 h immersion. The differences in inhibition efficiency of the inhibitor for samples pre-corroded for different time were related to the different corrosion products and the increase of surface area after pre-corrosion [200].

Zhang *et al.*[201] have also analyzed CO_2 corrosion behaviour of carbon steel with different microstructures (H steel: coarse laminar pearlite; T steel: globular and shot rod shaped pearlite) in 3 wt.% NaCl solution at 60 °C with imidazoline-based inhibitor. Electrochemical measurements showed that, compared to H steel, the inhibitor film adsorbed on T steel had a higher pitting corrosion resistance and the inhibition efficiency for T steel was larger at each concentration of inhibitor. Weight loss results exhibited that both steels suffered general corrosion in absence of inhibitor; however, localized corrosion was observed on the samples with insufficient concentration of inhibitor. H steel suffered more severe localized corrosion than T steel. It was related to the fact that H steel had a higher density of dislocations in the pearlite area and the larger driving force for galvanic corrosion. The localized corrosion on H steel mainly distributed on the laminar pearlite area.

The effects of thioureidoimidazoline and $NaNO_2$ on passivation and pitting corrosion of X70 steel in acidic NaCl solution were studied by using experimental techniques. The experimental results revealed that the addition of thioureidoimidazoline promoted passivation of the steel in the NaCl-$NaNO_2$ solution, but the pitting potential decreased, which was attributed to the preferential adsorption of residue thiourea monomers in the inhibitor. With longer immersion time, the pitting potential in solution with thioureidoimidazoline + $NaNO_2$ increased to the value with only $NaNO_2$. A multi-layer film formed with thiourea rich in inner and imidazoline rich in outer formed on the surface.It is further observed that Inhibition effects of $NaNO_2$ and TAI on steel are both superimposed and interactive [202].

7.12 Pyrazole Derivatives as Corrosion Inhibitors

The effectiveness of **pyrazole derivatives** as a corrosion inhibitors for mild steel in hydrochloric acid media has been reported.A comparative study of three new corrosion inhibitors namely ethyl 6-amino-3-methyl-4-(*p*-tolyl)-2,4-dihydropyrano-[2,3,C]pyrazole-5-carboxylate (EPP-1), ethyl 6-amino-3-methyl-4(phenyl)-2,4-dihydro pyrano [2,3,C] pyrazole-5-carboxylate (EPP-2), ethyl 6-amino-3-methyl-4-(3-nitrophenyl)-2,4-dihydropyrano[2,3,C]pyrazole-5-carboxylate (EPP-3) as inhibitors for mild steel corrosion in 0.1 M HCl solution at 20 ºC was carried out. The studies have shown that EPP-1 was the most efficient inhibitor reaching the values of inhibition efficiency up to 98.9 % at the concentration of 100 mg/L. Tafel slopes obtained from potentiodynamic polarization indicated mixed nature of inhibitors. Impedance method indicated that all inhibitors adsorbed on mild steel surface by increasing charge transfer resistance and decreasing the double layer capacitance. It is also found that all three inhibitors followed the Langmuir adsorption isotherm. AFM and SEM studies further confirmed the formation of adsorbed film on the metal surface. A good relationship was obtained between theoretical and experimental results [203].

Newly synthesized compounds, namely methyl 5-(4-Chlorobenzoyloxy)-1-phenyl-1*H*-pyrazole-3-carboxylate (MCPPC) and 5-(4-methoxyphenyl)-3-(4-methylphenyl)4,5-dihydro-1H-pyrazol-1-yl-(pyridin-4-yl)methanone (MMDPPM) were investigated as corrosion inhibitor for mild steel (MS) in 15% HCl solution. Inhibition efficiency was found concentration-dependent and increased by increasing the concentration of MCPPC and MMDPPM. Both of inhibitors were efficient even at a very low concentration of 25 ppm. The inhibitors MCPPC and MMDPPM showed inhibition efficiency of 67.1 and 76.8%, respectively, at 25 ppm, whereas it was 92.0 and 95.9%, respectively, at 250 ppm concentration at 303 K. The potentiodynamic polarization curves showed that MCPPC and MMDPPM act as mixed-type inhibitor in 15% HCl solution. The Nyquist plots showed that charge transfer resistance increase and double-layer capacitance decrease on increasing the concentration of studied inhibitors due to adsorption of inhibitor molecules on MS surface. The adsorption of each inhibitor on MS surface obeyed Langmuir adsorption isotherm. On the basis of thermodynamic adsorption parameters, mixed-type adsorption (physisorption and chemisorption) for the studied inhibitors on MS surface was suggested. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and atomic force microscopy (AFM) analyses confirmed the existence of a protective film of the inhibitor on MS surface. The density functional theory was employed for theoretical calculations, and the obtained results were found to be consistent with the experimental findings [204].

7.13 Surfactants as Corrosion Inhibitors

Surfactants have been commonly used as corrosion inhibitors for the protection of metallic materials against corrosion. The amphiphilic nature of surfactant molecules creates an affinity for adsorption at interfaces such as metal/metal oxide–water interface.

Hegazy *et al.*[205] have evaluated series of cationic surfactants namely: 1-dodecyl-2-(phenethylimino)-1-methylpyrrolidin-1-iumbromide (A), 1-dodecyl-2-((2-hydroxyethyl) imino)-1-methylpyrrolidin-1-ium bromide (B) and 1-dodecyl-2-((4-hydroxy phenyl) imino)-1-methylpyrrolidin-1-ium bromide (C), as corrosion inhibitors for carbon steel pipelines in oil and gas wells applications. Surface parameters of the cationic surfactants were determined using surface tension and conductivity techniques. The results of the surface tension measurements showed good surface behaviour of these compounds in their aqueous solutions. The prepared cationic surfactants showed a good ability to be acted as corrosion inhibitors for the tested system. It was found that the inhibition efficiency increased by increasing the inhibitor concentration, exposure time and temperature. Inhibition efficiency of three cationic surfactants follows the order: C > A > B. All the Inhibitors acted as mixed-type inhibitor and their adsorption obeyed Langmuir isotherm.

Four novel cationic gemini surfactants with a spacer functionalised by an oxygen atom were synthesised, characterized using FTIR and ^{1}H NMR spectroscopy and tested as corrosion inhibitors for stainless steel in 3 M HCl solution [206]. Experimental results revealed that, in the presence of the inhibitors, the open circuit potential of the AISI 304 stainless steel is shifted towards more positive values when compared to that of the potential of the blank sample (no inhibitor).Further The addition of inhibitors to the HCl shifted both the cathodic and anodic curves towards lower current densities, which suggested that the inhibitors acted as mixed type inhibitors; reducing the anodic dissolution of stainless steel and retarding the cathodic hydrogen evolution reaction.EIS measurement results indicated that the resistance of the stainless steel electrode reached the highest values around the surfactant's CMC values. The decrease of the electrochemical double layer capacitance of the tested surfactants may be attributed to the replacement of the water molecules at the electrode surface by the inhibitor molecules of lower dielectric constant through the adsorption process. The adsorption of cationic gemini surfactants on the SS surface from hydrochloric acid solutions obeyed the Langmuir adsorption isotherm model. For three of them (12-O-12, 12-MOH-O-MOH-12 and 18-MOH-O-MOH-18) the adsorption process involved chemisorption and physisorption and for 18-O-18 involved typical chemisorption. Experimental results appeared to be in good agreement with the theoretical calculations.

Organic compounds are well qualified to play more protection for steel corrosion. Many organic compounds have been reported as effective corrosion inhibitors for steel in acidic media. Methyl substituted phenyl containing dithiocarbamate compound acted as effective corrosion inhibitor against steel corrosion in 1 M HCl solution. The inhibitor (namely ammonium (2,4-dimethylphenyl)-dithiocarbamate) offeredextra stability and higher inhibition efficiency when compared to previously reported dithiocarbamate family inhibitors against steel corrosion. The inhibitor is able to get adsorbed on surface, by both physical and chemical means, while the methyl functionalized benzene ring produced hydrophobicity against the aqueous corrosive environment [207].

Three new isatin derivatives namely 5-bromo-1[2-(diethylamino)ethyl]-1H-indole-2,3-dione (5-BEI), 1-[2-(diethylamino)ethyl]- 1H-indole-2,3-dione (5-HEI), and 5-fluro-1[2-(diethylamino)ethyl]-1H-indole-2,3-dione (5-FEI) as corrosion inhibitor for carbon steel in hydrochloric acid medium has been tested. The detailed study of 5-BEI is given using gravimetric measurements and electrochemical methods (DC and AC techniques). Results showed that this new isatin is an efficient corrosion inhibitor for carbon steel in 1 M HCl and an inhibition efficiency of 95.2% was exhibited by 5-BEI at 1 mM concentration of 5-BEI after 6 h of immersion at 303 K. Polarization curves suggested that the 5-BEI acted as mixed type inhibitor. Electrochemical impedance spectroscopy showed that increased inhibitor (5-BEI, 5-HEI and 5-FEI) concentration leads to an increase in the values of the charge transfer resistance. Adsorption of 5-BEI, 5-HEI and 5-FEI molecules on the steel surface obeyed Langmuir adsorption isotherm model. X-Ray Photoelectron Spectroscopy (XPS) analyses revealed that the corrosion inhibition mechanism of 5-BEI is mainly controlled by a chemisorption process. The comparative study of inhibitive performance of the three isatin derivatives (5-BEI, 5-HEI and 5-FEI) using density functional theory (DFT) calculations of orbital energies and reactivity indices suggested that the trend of inhibition potentials of the compounds depend on the effect of substituent atoms (—Br, —F, and —H) on the electron donating and/or accepting ability of the molecules. The trend of reactivity of the molecules was 5-BEI > 5-FEI > 5-HEI. Theoretical Monte Carlo simulation studies also corroborated experimental findings [208].

The effect of keto-enol derivatives namely (Z)-3-hydroxy-1-(pyridin-2-yl)but-2-en-1-one (KE-1) and (Z)-1-(1,5-dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(pyridin-2-yl)prop-2-en-1-one (KE-2) on the inhibition of carbon steel (CS) corrosion in 1 M HCl solution has been investigated by Salhi *et al.*[209] Weight loss measurements indicated that these compounds reduced the corrosion rate of carbon steel in acidic solution and the inhibition effect increased with the inhibitors concentration but decreased with temperature. The electrochemical polarization study revealed that the tested Keto-enol derivatives are mixed type. EIS showed that the KE-1 and KE-2 formed an adsorptive layer on the metallic surface. The adsorption of the KEs on the carbon steel surface obeyed the Langmuir adsorption isotherm. The results of quantum chemical calculations and Monte Carlo simulation studies were in good agreement with experimental results.

The corrosion inhibition action of two new organo-silicon compounds; di-triethanolaminesiloxane and bis (dithioaminetriethanolamine) siloxane on carbon steel in 1 M HCl solution were analyzed by using chemical, electrochemical and surface analytical methods..The synthesized compounds showed good inhibition efficiency and it has been found that the efficiency increased with the increase in inhibitor concentration. Polarization curves stated that the two compounds acted as mixed type inhibitors and their adsorption on the metal surface followed Langmuir's adsorption isotherm. Furthure SEM and EDX analyses supported the formation of protective film on carbon steel in presence of inhibitors [210].

The inhibition ability of N,N′-bis(4-formylphenol)-1,2-Diaminocyclohexane (4-HCD) on the carbon steel in 1 M hydrochloric acid solution was examined by using experimental techniques. Experimental results revealed that4-HCD inhibited steel corrosion in 1 M HCl solution significantly and the inhibition efficiency increased with 4-HCD concentration. It was also observed that after 5 h, this inhibitor has a maximum percentage inhibition efficiency of approximately 71% in the presence of 2 mM inhibitor and the adsorption of the inhibitor was followed Langmuir adsorption isotherm with the standard adsorption free energy of $-25.66\ \text{kJ mol}^{-1}$[211].

The inhibition effect of $N^1,N^{1'}$-(1,4-phenylene)bis(N^4-(4-nitrobenzylidene) benzene-1,4-diamine) SB-I, $N^1,N^{1'}$-(1,4-phenylene)bis(N^4-benzylidenebenzene-1,4-diamine) SB-II, $N^1,N^{1'}$-(1,4-phenylene) bis(N^4-(4-methyl benzylidene) benzene-1,4-diamine)SB-III and $N^1,N^{1'}$-(1,4-phenylene) bis(N^4-(4-methoxy benzylidene)benzene-1,4-diamine) SB-IV for corrosion of mild steel in 1 M HCl solution was investigated[212]. The obtained results showed that the corrosion inhibition efficiency of SBs for mild steel are 71.42% (SB-I), 89.52 (SB-II), 92.85 (SB-III), 96.19 (SB-IV) respectively. Tafel polarization further revealed that all the SBs behaved as mixed-type inhibitor but predominantly of cathodic type and followed Langmuir adsorption isotherms. EIS measurements showed the charge transfer process in SBs. The protective film formed on metal surface was also confirmed by SEM and AFM techniques.

Ma *et al.* [213] have investigated the inhibition of corrosion of mild steel in 1 M HCl by new corrosion inhibitor acrylamide methyl ether (AAME) from *N*-Methylol acrylamide (N-MAM) using different chemical and electrochemical techniques. Protection efficiency up to 96.2% was obtained with small amount

AAME. From the polarization results it can be concluded that both the compounds acted as mixed inhibitors which impeded both anodic and cathodic reactions. The inhibition efficiency values found from weight loss method was in good agreement with electrochemical finding.

New 1*H*-pyrrole-2,5-dione derivatives, namely 1-phenyl-1*H*-pyrrole-2,5-dione (PPD) and 1-(4-methylphenyl)-1*H*-pyrrole-2,5-dione (MPPD) were synthesized and their inhibitive action against the corrosion of carbon steel in 1 M HCl solution were investigated at 308 K.The results showed that the investigated 1*H*-pyrrole-2,5-dione derivatives acted as good corrosion inhibitors for carbon steel in 1 M HCl medium. Their inhibition efficiency increased with inhibitor concentration, and MPPD was slightly more effective than PPD. Potentiostatic polarization study showed that PPD and MPPD are mixed-type inhibitors in 1 M HCl. Impedance experimental data revealed a frequency distribution of the capacitance, simulated as constant phase element. The results obtained from electrochemical and weight loss studies were in reasonable agreement. The adsorption of MPPD and PPD on steel surface obeyed Langmuir's adsorption isotherm. Thermodynamic data and XPS analysis clearly indicated that the adsorption mechanism of 1*H*-pyrrole-2, 5-dione derivatives on carbon steel surface in 1 M HCl solution is mainly controlled by a chemisorption process. Quantum chemical parameters were in good agreement with experimental finding [214].

The corrosion inhibition effect of1-[3-(4-methylphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Me-4-PQPB), 1-(3-(4-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl)butan-1-one (Mt-4-PQPB), 1-[3-(3-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Mt-3-PQPB) and 1-[3-(2H-1,3-benzodioxol-5-yl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Oxo-1,3-PQPB) for mild steel corrosion in 1 M HCl has been investigated [215]. The results of both potentiodynamic polarization and electrochemical impedance spectroscopic studies revealed that these compounds are mixed-type inhibitors and the order of corrosion inhibition efficiency at 100 ppm is Me-4-PQPB>Mt-3-PQPB>Oxo-1,3-PQPB>Mt-4-PQPB. Fourier transform infrared (FTIR) and ultraviolet–visible (UV–vis) spectroscopic analyses confirmed the presence of chemical interactions between the inhibitors and mild steel surface. The adsorption of the inhibitor molecules on mild steel surface was found to be both physisorption and chemisorption but predominantly chemisorption. The experimental data obeyed Langmuir adsorption isotherm. Scanning electron microscopy studies revealed the formation of protective films of the inhibitors on mild steel surface.

Quantum chemical parameters obtained from density functional theory (DFT) calculations supported experimental results.

The anticorrosion effect of 5-hydroxytryptophan (5-HTP) on mild steel (MS) was investigated by gravimetric and electrochemical techniques. Two different concentrations (1 M and 15%) of hydrochloric acid were used to simulate well-acidizing fluid. The results showed that 10 × 10−5 M 5-HTP is 96.1% efficient in 1 M HCl and 78.1% efficient in 15% HCl at 30^0C. The efficiency decreased as the temperature increased, reaching 66.9% and 39.8% in 1 M and 15% HCl, respectively, at 90^0C. When 5-HTP is blended with potassium iodide and glutathione, the efficiency increased to above 88% and 78% in 1 M and 15% HCl, respectively, at 90^0C. Increasing the 5-HTP concentration decreased the double-layer capacitance and increased the charge-transfer resistance. 5-HTP behaved as a mixed-type corrosion inhibitor with anodic predominance and is spontaneously adsorbed on the steel surface. Physisorption of 5-HTP is best described by the Langmuir adsorption model and was also exothermic with a resultant decrease in the entropy of the bulk solution. The results of SEM/EDAX, FTIR and UV–VIS studies supported the hypothesis that a protective film of 5-HTP formed on MS facilitated by O, N and C -C functionalities [216].

1-(4-Nitrophenylo-imino)-1-(phenylhydrazono)-propan-2-one (NO_2AM) was evaluated as a corrosion inhibitor for mild steel in 1 M HCl solution. The inhibition efficiency was found to increased with increasing inhibitor concentration and to decreased with increasing temperature. The adsorption of the inhibitor on the mild steel surface obeyed the Langmuir adsorption isotherm. Polarization studies showed that the inhibitor behaved as a mixed-type inhibitor. SEM studies revealed that the corrosion of mild steel in 1M HCl was diminished by the addition of inhibitor. The results obtained from experimental measurements and those from theoretical calculations were in good agreement [217].

Bichalcophene series namely 4-(2,2′-bithiophene-5-yl) benzamidine (MA-0944) and 6-(2,2′-bithiophene-5-yl) nicotinamidine (MA-0949) were tested as corrosion inhibitors for carbon steel (CS) in 1 M HCl using non electrochemical and electrochemical techniques. The results revealed that the tested compounds were efficient corrosion inhibitors and their inhibition percentage (η %) reached 98.3% at

18×10^{-6} M. The tested compounds were classified as mixed-type inhibitors. The adsorption of the investigated compounds followed Langmuir adsorption isotherm. AFM and ATR-IR analysis showed that there was some improvement in the surface morphology of inhibited mild steel compared to uninhibited mild steel. The theoretical data supported the experimental results [218].

(1-Benzyl-1H-1,2,3-triazole-4-yl)methanol (BTM) and (1-(pyridin-4-ylmethyl)-1H-1,2,3- triazole-4-yl)methanol (PTM) were prepared and investigated as corrosion inhibitors for mild steel in 1.0 M HCl solution. It is found that PTM acted as more effective inhibitor than BTM in the concentration range of 0.2 −1.0 mM. Computational chemistry studies showed that the triazole derivatives adsorbed on the mild steel surface by sharing the lone pair electrons of N atoms with iron atoms or by accepting electrons from iron surfaces. Due to its strong interaction with the mild steel surface in aqueous system, the pyridine segment should be responsible for the higher inhibition efficiency of PTM [219].

The corrosion inhibition performance of Poly(vinyl alcohol-cysteine) (PVAC) on mild steel in 1M hydrochloric acid solution was investigated by weight loss and electrochemical methods. A maximum inhibition efficiency of 94% was observed in the presence of 0.6 wt% of the inhibitor. Poly(vinyl alcohol-cysteine) acted as a good inhibitor for the corrosion of mild steel in 1 M HCl. Potentiodynamic curves revealed the mixed mode of inhibition of PVAC. Results obtained from different methods were in good agreement. The inhibition efficiency increased with an increase in concentration and immersion time. The activation energy of corrosion process of the inhibited solution was greater than the uninhibited solution. The enthalpy of activation reflected the endothermic metal dissolution and the entropy of activation reflected the decrease in rate of metal dissolution. The adsorption of PVAC followed the El-Awady isotherm. The thermodynamic parameters of adsorption suggested the spontaneity and physical nature of the process. The SEM images of mild steel revealed the formation of adsorbed film of PVAC [220].

Aouniti *et al.* [221] have studied the adsorption and corrosion inhibition behaviour of (*E*)-2-methyl-N-(thiophen-2-ylmethylidene) aniline (**T**) at steel/1.0 M HCl interface using gravimetric and electrochemical methods at 308 K. (*E*)-2-methyl-N-(thiophen-2-ylmethylidene)aniline showed good inhibitive properties for mild steel corrosion in 1.0 M HCl solution and the inhibition efficiency increased with increasing the concentration of the inhibitor. The results of potentiodynamic polarization measurements demonstrated Thiophene derivative behaved as a mixed type inhibitor and could suppress both anodic metal dissolution and cathodic hydrogen evolution reactions. (*E*)-2-methyl-N-(thiophen-2-ylmethylidene) aniline on the metal surface obeyed Langmuir adsorption isotherm. The value of the adsorption equilibrium constant showed that inhibitor is strongly adsorbed on the metal surface.

4-(N,N-dimethylamino) benzaldehyde nicotinic acid hydrazone was prepared and investigated as corrosion inhibitor for mild steel in 1 M HCl by using various techniques [222]. The inhibition efficiency increased with increasing inhibitor concentration. The polarisation study indicated that it acted as a mixed type corrosion inhibitor. The adsorption of inhibitor was spontaneous and obeyed the Langmuir's adsorption isotherm. The FE-SEM images and AFM images of mild steel supported strong adsorption and high inhibition efficiency of the inhibitor. Quantum chemical parameters were also in agreement with experimental obtained efficiency.

The inhibition effect of 3-(4-Hydroxyphenylamino) propanenitrile (Para) and 3-(2-Hydroxyphenylamino) propanenitrile (ortho) on the corrosion of mild steel 1M HCl solution has been evaluated. The results revealed that corrosion rate depend on the molecular structure and the concentration of inhibitors. It is also found that the Para Hydroxyphenylamino propanenitrile was a good inhibitor and with efficiency reached to 85% in 10^{-3} M. Polarization studies through electrochemical curves and spectroscopy of electrochemical impedance clearly showed that 3-(4-Hydroxyphenylamino) propanenitrile was a mixed inhibitor. The adsorption of ortho and para inhibitors on the mild steel surface obeyed Langmuir isotherm. The quantum chemical parameters calculated using DFT theory showed a good correlation to the inhibition efficiency. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), the separation energy (ΔE) and the dipole moment (μ) from the inhibitor to the metal surface explained well experimental data [223].

The effect of electron withdrawing nitro ($-NO_2$) and electron releasing hydroxyl (–OH) groups on corrosion inhibition potentials of 5-arylaminomethylenepyrimidine-2,4,6-trione (AMP) had been studied by Verma *et al.*[224]. Four AMPs tagged AMP-1, AMP-2, AMP-3 and AMP-4 were studied for their ability to inhibit mild steel corrosion in 1 M HCl using experimental and theoretical methods. Gravimetric results showed that inhibition efficiency of the studied inhibitors increased with increasing concentration. The results further revealed that that electron withdrawing nitro (–NO_2) group decreased the inhibition efficiency of AMP, while electron donating hydroxyl (–OH) group increased the inhibition efficiency of AMP. SEM and AFM studies showed that the studied compounds inhibited mild steel corrosion by adsorbing at the metal/electrolyte interface and their adsorption obeyed the Temkin adsorption isotherm. Potentiodynamic polarization study revealed that studied inhibitors acted as mixed type inhibitors with predominant effect on cathodic reaction. The inhibitive strength of the compounds might have direct relationship with electron donating ability of the molecules as revealed by quantum chemical parameters. The order of interaction energies derived from Monte Carlo simulations was AMP-4 > AMP-3 > AMP-2 > AMP-1, which was in agreement with the order of inhibition efficiencies obtained from experimental measurements.

The corrosion inhibition efficiency of (*E*)-3-phenyl-2-(1H-tetrazole-5-yl) acrylonitrile,(PTA),(*E*)-3-(4-nitrophenyl)-2-(1H-tetrazole-5-yl)acrylonitrile (NTA), and (*E*)-3-(4-hydroxyphenyl)-2-(1H-tetrazole-5-yl) acrylonitrile (HTA) on mild steel in 1 M HCl has been examined [225].The results showed that the inhibition efficiency increased with the increasing concentration, and maximum values were obtained at a 40 mg L^{-1} concentration. The inhibition efficiency of the studied inhibitors followed the order HTA (98.69%) > NTA (96.60%) > PTA (93.99%). The adsorption of tetrazoles on the mild steel surface obeyed the Langmuir adsorption isotherm.

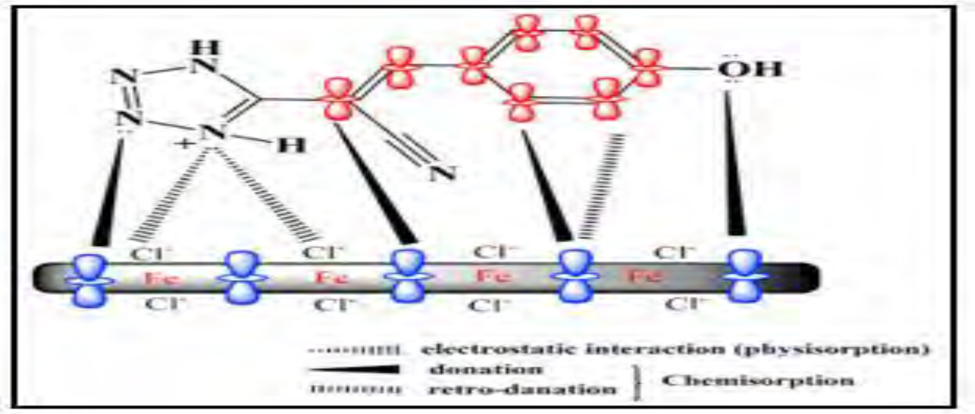

Fig.1.26: Pictorial representation of the adsorption behavior of the tetrazoles on mild steel in 1 M HCl

The values of the activation energy (E_a) showed that tetrazoles inhibited mild steel corrosion by forming an energy barrier to the corrosion process. The values of the Gibbs free energy suggested that the tetrazoles had a strong tendency to get adsorbed spontaneously on the mild steel surface. Polarization studies showed that tetrazoles acted as cathodic inhibitors. EIS measurements indicated that the thickness of the electric double layer increased due to the adsorption of tetrazoles at the metal/electrolyte interface. SEM and EDX studies indicated that the tetrazoles form a protective surface covering. A good correlation has been found between quantum chemical calculations and the results obtained experimentally.

The inhibition effect of aryl sulfonamidomethylphosphonates on mild steel corrosion in 1 M HCl is described by verma *et al.* [226]. Experimental results showed that aryl sulfonamidomethylphosphonates acted as good corrosion inhibitors for mild steel in 1 M HCl and their inhibition efficiency increased with concentration. Potentiodynamic polarization studies showed that studied inhibitor acted as mixed type and their adsorption on mild steel surface obeyed the Langmuir's adsorption isotherm. EIS plots showed that the inhibitive performance depended on the adsorption of the molecule on the metal surface. The SEM analysis supported the weight loss, EIS and polarization results. Quantum chemical calculations provided good support to the experimental results.

The corrosion inhibition performance of soluble self-doped copolymers of aniline and 4-amino-3-hydroxy-naphthalene-1-sulfonic acid, synthesized by chemical oxidative polymerization method for mild steel in 1.0 M HCl was evaluated using Tafel extrapolation method, electrochemical impedance spectroscopy (EIS) and surface analytical techniques. Results showed that the copolymer film exhibited the significant shifting in the corrosion potential and greater charge transfer resistance. The corrosion inhibition efficiency was found to increase from 50% to 90% by increasing the concentration of copolymer from 10 to 70 mg/l in HCl medium. Moreover, the copolymer showed the larger degree of surface coverage onto the iron surface, reflecting the higher inhibition for corrosion of the iron in highly acidic medium [227].

The inhibition effect of three diheteroaryl thioethers (DHATs) namely 5,5’-thiobis (4-phenylthiazol-2amine) (DHAT-1), 4,4’-(5,5’-thiobis(2-aminothiozole-5,4-diyl)) diphenol (DHAT-2) and 4,4’-(5,5’-thiobis(2-aminothiazole-5,4-diyl))bis (benzene-1,3-diol) (DHAT-3) on mild steel corrosion in 1 M HCl solution has been examined. Among the studied compounds DHAT-3 exhibited maximum inhibition efficiency (η%) of 96.99% at 11.2×10^{-5} mol/L concentration. The potentiodynamic studies revealed that investigated DHATs acted as mixed type inhibitors. Adsorption of the DHATs on the mild steel surface in 1 M HCl obeyed the Langmuir adsorption isotherm. The results of SEM and AFM suggested that DHATs inhibited mild steel corrosion by adsorption method. The experimental results were well supported by theoretical calculations [228].

4-hydroxybenzylideneaminomethyl-5-ethyl-1,3,4-thiadiazol has been synthesized and tested as corrosion inhibitor for a mild steel (MS) sample in 1 M hydrochloric acid solution (HCl). The obtained results indicated that 4-hydroxybenzylideneaminomethyl-5-ethyl-1, 3, 4-thiadiazol acted as a good corrosion inhibitor for mild steel sample in HCl solution with efficiency above 90%. It also showed that 4-hydroxybenzylideneaminomethyl-5-ethyl-1, 3, 4-thiadiazol corrosion inhibitors were effective in helping to reduce and slow down the corrosion process that occurs on mild steel surface in hydrochloric acid solution. Increase of corrosion inhibitor concentration provided a protective layer of mild steel. However, this protective layer becomes weak when the temperature of the solution increased [229]. The asortion behavior of Thiadiazole in shown in the following Fig.1.27

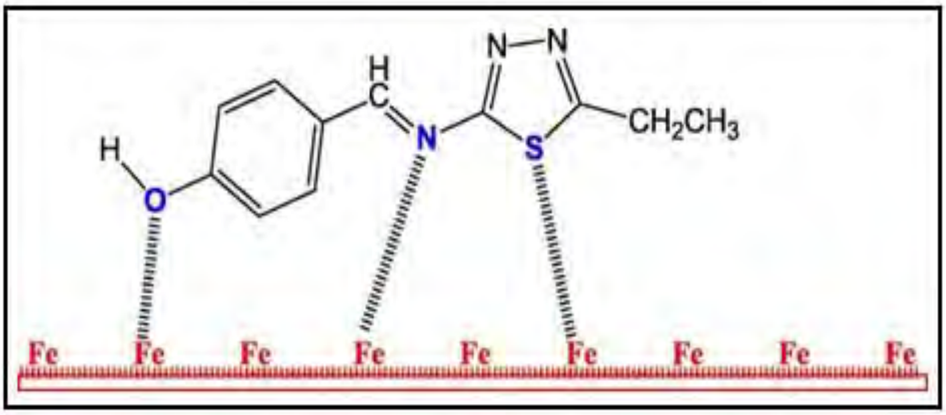

Fig.1.27: Pictorial representation of the adsorption behavior of the thiadiazole on mild steel in 1 M HCl.

The synthesis and characterization of a novel organic corrosion inhibitor (4-(3-mercapto-5,6,7,8-tetrahydro-[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazin-6-yl)phenol), for mild steel in 1 M hydrochloric acid (HCl) has been successfully reported for the first time by Mohammed *et al.*[230]. The inhibitor evaluated as corrosion inhibitor for mild steel in 1 M of Hydrochloric acid solution using electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM) measurement techniques. Changes in the impedance parameters suggested an adsorption of the inhibitor onto the mild steel surface, leading to the formation of protective films. The results showed that the inhibition efficiencies increased with increasing the concentrations of the inhibitors and decreased with increasing temperature. The maximum inhibition efficiency up to 67% at the maximum concentration 0.5 mM. This showed that those inhibitors were effective in helping to reduce and slowing down the corrosion process that occurs to mild steel with a hydrochloric acid solution by providing an organic inhibitor for the mild steel that could be weakened by increasing the temperature. Further it was confirmed that the adsorption process of the synthesized organic inhibitor depended on its electronic characteristics in addition to steric effects and the nature of metal surface, temperature degree and the varying degrees of surface-site activity. The synthesized inhibitor molecules were absorbed by metal surface and followed Langmuir isotherms.

The anticorrosion ability of a synthesized coumarin, namely 2-(coumarin-4-yloxy)acetohydrazide (EFCI), for mild steel (MS) in 1 M hydrochloric acid solution was tested using a weight loss method. The results of the present study revealed that the new coumarin derivative 2-(coumarin-4- yloxy)acetohydrazide functioned as a good corrosion inhibitor for MS in 1 M HCl solution in a concentration-dependent mode and maximum inhibition efficiency was up to 94.7% at 0.5 mM inhibitor concentration. The new corrosion inhibitor was adsorbed over a MS surface obeyed the Langmuir isotherm. The new inhibitor was proved as an efficient organic inhibitor having good inhibitive properties due to presence of nitrogen and oxygen atoms. SEM measurements supported the formation of a protective layer by new corrosion inhibitor on the MS surface. The anticorrosion study of the new corrosion inhibitor clearly revealed its role in the protection of mild steel in acid media [231].

The electrochemical performance of a novel organic corrosion inhibitor 6-(4-hydroxyphenyl)-3-mercapto-7,8-dihydro-[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine [HT3], for mild steel in 1 M hydrochloric acid was evaluated . The experimental results showed that the investigated inhibitor [HT3], effectively retarded the corrosion process that occurred to mild steel with a hydrochloric acid solution by providing a protective coating for the mild steel that could be weakened by increasing the temperature. Furthermore, the inhibition efficiency of [HT3] increased with increasing the concentrations of the inhibitors and decreased with increasing temperature [232].

Deyab *et al.* [233] have studied the adsorption and inhibition effect of Ascorbylpalmitate (AP) on carbon steel in ethanol blended gasoline containing water as a contaminant (GE10 + 1%water) by weight loss and electrochemical impedance spectroscopic (EIS) techniques. The results showed that the addition of ethanol and water to gasoline increase the corrosion rate of carbon steel. AP inhibited the corrosion of carbon steel in (GE10 + 1% water) solution to a remarkable extent. Efficiency more than 96% was obtained with 120 mg l^{-1} AP at 298 K. The adsorption of AP on the carbon steel surface was found to obey the Langmuir adsorption isotherm model.

Corrosion inhibition potentials of two imidazole derivatives namely, vinylimidazole (VI) and allylimidazole (AI) for carbon steel in 1 M HCl at 25 °C were predicted theoretically using quantum chemical calculations and molecular dynamics (MD) simulations. DFT calculations indicated that VI was more reactive towards steel surface than AI. Equilibruim adsorption behaviour of VI and AI molecules on Fe_2O_3 (0 1 0) surface was investigated using molecular dynamics (MD) simulations and it is revealed that the equilibrium adsorption energy followed the order: VI > AI. . Polarization study revealed that both inhibitors acted as mixed type.EIS studies clearly indicated that the both the inhibitors formed a protective surface film at metal/electrolyte interfaces. Excellent agreement existed between theoretical and experimental results as inhibition efficiency of VI > AI. The adsorption of corrosion inhibitor on the carbon steel was well supported by SEM/ AFM studies [234].

New chalcone derivatives namely (E)-(1-(5-(4-(3-(4-methylphenyl)-3-oxoprop-1-enyl)phenoxy)pentyl)-1H-1,2,3-triazol-4-yl)methyl acrylate (CH-5), (E)-(1-(5-(4-(3-(4-methylphenyl)-3-oxoprop-1-enyl)phenoxy)hexyl)-1H-1,2,3-triazol-4-yl)methyl acrylate (CH-6) and (E)-(1-(5-(4-(3-(4-methylphenyl)-3-oxoprop-1-enyl)phenoxy)decyl)-1H-1,2,3-triazol-4-yl) methyl acrylate (CH-10) were synthesized, characterized and tested as corrosion inhibitors for mild steel in 1M HCl solution. Potentiodynamic polarization measurements showed that both the intact and photo-cross-linked chalcones are mixed-type corrosion inhibitors for mild steel in aqueous hydrochloric acid. The EIS results showed an increase in charge transfer resistance with increasing concentration of the inhibitors. The chalcone derivatives adsorbed spontaneously on the mild steel surface and their adsorption obeyed the Langmuir adsorption isotherm. The adsorption mode revealed the possibility of competitive physisorption and chemisorption mechanisms. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) analyses confirmed that the chalcones formed a protective film on the mild steel surface. The overall results showed that the photo-cross-linked chalcones are better corrosion inhibitors than the intact chalcones. The results of quantum chemical calculations and Monte Carlo simulation studies are in good agreement with experimental results [235].

A new corrosion inhibitor namely, 2-amino-3-((4-((*S*)-2-amino-2-carboxyethyl)-1H-imidazol-2-yl)thio)propionic acid (AIPA) has been synthesized and its inhibition action on corrosion of mild steel in 1 M HCl were evaluated experimentally[236]. The results obtained reveal that AIPA acted as excellent inhibitor. It gave maximum inhibition efficiency of 96.52% at 0.456 mM/L (125 ppm; 125 mg L^{-1}) and inhibited corrosion by adsorbing at the mild steel surface. Polarization study suggested that AIPA acted as mixed type inhibitor with some cathodic predominance. SEM and AFM analyses showed improved morphology of the mild steel surface in presence AIPA. Quantum chemical analysis further supported experimental results.

Azzouzi *et al.* [237] have investigated the inhibition of mild steel corrosion in 1.0 M HCl by some hydrazine derivatives namely: (1E,2E)-1,2-bis(thiophen-2-ylmethylene) hydrazine (PP2) and (1E,2E)-1,2-bis(1H-pyrrol-2-ylmethylene)hydrazine (PP3).The results showed that PP3 was the best corrosion inhibitor among the three compounds studied and the inhibition efficiency increased with increase in concentration for all the inhibitors. The adsorption of inhibitor molecules on mild steel surface was found to be spontaneous and obeyed the Langmuir adsorption isotherm. Potentiodynamic polarization investigations indicated that the studied inhibitors were mixed type inhibitors. Electrochemical Impedance Spectroscopic measurements showed that the inhibitors formed an adsorptive layer on the metallic surface. Experimental study further established the correlation between quantum chemical parameters and inhibition action of inhibitor.

The influence of ring and ring size of three 3-amino alkylated indoles (AAIs) namely, N-((1H-indol-3-yl)(phenyl) methyl)-N-ethylethanamine (AAI-1), 3-(phenyl (pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) and 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3) on mild steel corrosion in 1M HCl using various techniques has been studied[238]. Both experimental and theoretical results showed that the 3-amino alkylated indoles with cyclic amino groups exhibited higher inhibition efficiency compared to the one with opened-chain amino group. The results further suggested that the inhibition efficiency increased with increasing ring size of the amino group such that the piperidine-containing (6-membered ring) 3-amino alkylated indole showed higher inhibition performance than the pyrrolidine-containing (five membered) 3-amino alkylated indole. Experimental esults revealed that the inhibition efficiency increased with increasing concentration of the inhibitors. Maximum inhibition efficiencies of 94.34% for AAI-1, 96.08% for AAI-2 and 96.95% for AAI-3 were obtained at 0.862 mM concentration. EIS measurements showed that the studied compounds inhibited mild steel corrosion by adsorbing on the steel surface. Polarization studies revealed that the compounds were cathodic type inhibitors. The adsorption of the studied compounds obeyed the Langmuir adsorption isotherm. SEM and AFM surface morphology analyses also provided evidence of formation of adsorbed film of the AAIs on the steel surface. Theoretical parameters such as E_{HOMO} and electronegativity derived from quantum chemical calculations as well as binding energy derived from molecular dynamics simulations studies adequately corroborate the trend of experimental inhibition efficiencies of the studied inhibitors.

Verma *et al.* [239] tested the inhibition property of benzo 1,3-diazol 2-(4-{[4-Methyl-6-(1-methyl-1*H*-1,3-benzodiazol-2-yl)-2-propyl-1*H*-1,3-benzodiazol-1-yl]- methyl} phenyl) benzoic acid (Telmisartan, Cresar-H) on mild steel corrosion in 1 M HCl Results showed that the corrosion inhibition efficiency (η%) increased with increasing telmisartan concentration and attained the maximum value of 97.39% at 125 mg L^{-1} concentration. Polarization studies revealed that telmisartan acted as cathodic type inhibitor. Electrochemical impedance spectroscopy (EIS) studies suggested that the telmisartan inhibited mild steel corrosion by becoming adsorbate at the metallic/electrolyte surfaces. Among the several tested isotherms, adsorption of the telmisartan on mild steel surface obeyed the Temkin adsorption isotherm. The values of the apparent activation energy (E_a) suggested that Telmisartan inhibited metallic corrosion by creating energy barrier for corrosion process. Further the adsorption of corrosion inhibition was well supported by SEM/EDX and AFM studies.

Two pyranopyrazole derivatives namely, 6-amino-4-(4-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (AMPC) and 6-amino-4-(4-

chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (ACPC) were synthesized and investigated as an inhibitor for mild steel corrosion in 15% HCl solution.The experimental results showed that the inhibition efficiency of studied inhibitors increased with increasing inhibitor concentration whereas decreased with an increase in temperature. Corrosion inhibition efficiency of 96.1 and 94.6 was obtained with 300 ppm of AMPC and ACPC, respectively, at 303 K. Potentiodynamic polarization studies showed that both studied inhibitors were mixed type in nature and the adsorption of both inhibitors on mild steel surface obeyed Langmuir adsorption isotherm. Electrochemical impedance spectroscopic study proved that pyranopyrazoles could adsorb on mild steel surface and impart high charge-transfer resistance. SEM/EDX and AFM results further showed that presence of pyranopyrazole derivatives decreased the surface roughness of mild steel sample [240].

2-Methyl-4H-benzo[*d*][1,3]oxazin-4-one (BZ1) and 3-amino-2-methylquinazolin-4(3H)-one (BZ2) were evaluated for their corrosion inhibition properties on mild steel (MS) in hydrochloric acid solution. Results showed that the inhibition efficiency values depend on the amount of nitrogen in the inhibitor and both the inhibitors exhibited excellent corrosion inhibition performances. The maximum inhibition efficiencies of 89% and 65% were observed for BZ2 and BZ1, respectively at an inhibitor concentration. The inhibition efficiency increased with increasing inhibitor concentration whereas it decreased with increasing temperature. The SEM images showed that BZ1 and BZ2 might form a protective film on the MS surface [241].

The corrosion inhibition performance of synthesized amino acid compounds, namely, (Z)-2-(2-oxoindolin-3-ylideneamino)acetic acid (OYAA) and 2-(2-oxoindolin-3-ylideneamino)-3-phenylpropanoic acid (OYPA) on mild steel in 15-% HCl solution were evaluated by means of various experimental techniques. Potentiodynamic polarization studies showed that both studied inhibitors were mixed types in nature and adsorption of inhibitors on the mild steel surface obeyed Langmuir's adsorption isotherm.EIS measurements showed that the studied compounds inhibited mild steel corrosion by adsorbing on the mild steel surface.SEM, EDX and AFM results further confirmed that the presence of inhibitors increased surface smoothness of mild steel [242].

Inhibition effect of newly synthesized heterocyclic aromatic compounds, 3-(cyano-dimethyl-methyl)-benzoic acid thiophen-2-ylmethylene-hydrazide (CBTH) and 3-(cyano-dimethyl-methyl)-benzoic acid furan-2-ylmethylene-hydrazide (CBFH) on mild steel corrosion in hydrochloric acid medium has been evaluated [243]. Synthesized hydrazone derivatives showed good inhibition property against MS corrosion in 0.5 M HCl medium. Hydrazones proved efficient at lower temperatures than higher temperature. The adsorption behavior of both hydrazones followed Langmuir isotherm. Polarization study revealed that the hydrazones acted as cathodic and anodic inhibitors. Nyquist plots, Bode plots and morphological studies (SEM and EDX) confirmed the presence of protective inhibitory film. Quantum chemical studies proved that electronic interaction of CBTH was better than that of CBFH.

The effect of novel synthesized 4-(pyridin-2yl)-N-p-tolylpiperazine-1-carboxamide(PTC) on corrosion of mild steel in 1 M HCl was tested using using chemical and electrochemical methods. The synthesized 4-(pyridin-2yl)-N-p-tolylpiperazine-1-carboxamide(PTC) showed good inhibition efficiency for the corrosion of mild steel in 1M HCl solution and the inhibition efficiency increased with increase in the concentration of inhibitor and decreased with temperature. The maximum inhibition efficiency observed in weight loss method was 98.45% in 1M HCl for PTC at 303K.. The optimum inhibition efficiency was achieved at the concentration of 900ppm for all the studies. The negative value of ΔG_{ads} indicated that the adsorption is spontaneous and physical in nature.The adsorption of this inhibitor followed Langmuir adsorption isotherm. Potentiodynamic polarization studies suggested that the inhibitor exhibited mixed type nature.EIS measurements showed that charge transfer resistance (Rct) increased and double layer capacitance (Cdl) decreased in the presence of inhibitors which suggested the adsorption of the inhibitor molecule on the surface of mild steel. The SEM proved the formation of a protective film of the inhibitor. FT-IR analysis of the surface film indicated the formation of Fe-PTC complex which retarded the corrosion process [244].

The anti corrosive performance of synthesized Naphthalen-2-yl Naphthalene-2-Carboxammide (NNC) in 1 N HCl solution as corrosion inhibitor on carbon steel was studied at room temperature by Kanan *et al.* [245]. Potentiodynamic polarization study revealed the mixed behavior of the inhibitor NNC along with inhibition efficiency. The inhibition efficiency of NNC increased with increasing inhibitor concentration. The electrochemical noise analysis (ENA) and electrochemical impedance spectroscopy (EIS) studies have showed that noise resistance (R_n) and charge transfer resistance (R_{ct}) values were increased with addition of inhibitor concentrations. The adsorption isotherm explored that the adsorption of NNC obeyed Langmuir adsorption to bond with metal surface at carbon steel/HCl solution interface. Atomic force microscopic (AFM) study showed a less corroded and roughness surface morphology, which is due to the formation of protective film layer on the surface..The study revealed that the adsorption nature of inhibitor had both physisorption and chemisorption phenomena.

The corrosion inhibition behavior of AHEC on mild steel in 1M HCl has been studied. Results obtained in weight loss method showed that inhibition efficiency increased with increase in concentration of AHEC. The adsorption of the inhibitor on metal surface followed Frumkin isotherm. Polarization studies revealed that the AHEC inhibits through mixed mode. SEM and EDX studied also confirmed formation of protective inhibitor layer on mild steel surface [246].

Lotto *et al.* [247] have evaluated the inhibition performance of thiocarbanilide on the electrochemical corrosion behaviour of high carbon steel in 1 M H_2SO_4 and HCl solutions through weight loss method and potentiodynamic polarization test. Data obtained showed that the organic compound performed effectively in acid solutions at all concentrations with an average thiocarbanilide inhibition efficiency above 70% in H_2SO_4 and 80% in HCl from weight loss and potentiodynamic polarization test respectively. Results from corrosion thermodynamic calculations showed that the adsorption of thiocarbanilide onto the steel was through chemisorption mechanism whereby the redox electrochemical process responsible for corrosion and the electrolytic transport of corrosive anions were simultaneously suppressed. Statistical derivations through ANOVA analysis confirmed that the influences of both the inhibitor concentration and exposure time on inhibition efficiency values were negligible. Adsorption of the compound was determined to obey the Langmuir and Frumkin isotherm model.

The electrochemical behaviour of low carbon steel in 1 M H_2SO_4 and HCl was studied in the presence of 4-hydroxy-3-methoxybenzaldehyde (HMD) as the inhibiting organic compound. Results showed HMD has strong corrosion inhibition effects on the steel in the acid solution. HMD performed excellently at all concentrations studied with optimal inhibition efficiency of 96.6 and 92.5% from weight loss analysis and 88.81 and 91.35% for potentiodynamic polarization tests in H2 SO4 and HCl. The compound showed mixed inhibition properties in both solutions. Data from statistical analysis through ANOVA showed the overwhelming influence of inhibitor concentration in H2 SO4 and exposure time in HCl on the inhibition efficiency of the organic compound. Adsorption of the compound obeyed the Langmuir isotherm. Thermodynamic calculations showed strong physiochemical interactions and spontaneous adsorption mechanism [248].

1,5-Dimethyl-4-((2-methylbenzylidene)amino)-2-phenyl-1H-pyrazol-3(2H)-one (DMPO) was synthesized and evaluated as a corrosion inhibitor for mild steel in 1M HCl solution [249]. The results showed that DMPO inhibited mild steel corrosion in acid solution and indicated that the inhibition efficiency increased with increasing inhibitor concentration. Changes in the impedance parameters suggested an adsorption of DMPO onto the mild steel surface, leading to the formation of protective films. Calculation of electronic properties such as highest occupied molecular orbital energy, lowest unoccupied molecular orbital energy (E_{HOMO} and E_{LUMO}, respectively) and dipole moment (μ) showed that the corrosion inhibition efficiency increased with an increase in the E_{HOMO} values but with a decrease in the E_{LUMO} value.

The corrosion inhibitory effects of new synthesized compound namely 5,5'-((1Z,1'Z)-(1,4-phenylenebis(methanylylidene)bis(azanylylidene))bis(1,3,4-thiadiazole-2-thiol) (PBB) on mild steel in 1.0 M HCl evaluated at different temperatures. Results showed that PBB inhibited mild steel corrosion in acid solution and indicated that the inhibition efficiencies increased with the concentration of inhibitor, but decreased proportionally with temperature. Changes in impedance parameters suggested the adsorption of PBB on the mild steel surface, leading to the formation of protective films [250].

The acid corrosion inhibition process of mild steel in 1 M HCl by 4-[(2-amino-1, 3, 4-thiadiazol-5-yl) methoxy] coumarin (ATC), has been investigated [251]. Experimental results showed that the synthesized macromolecule represented an excellent inhibitor for materials in acidic solutions. Inhibition efficiencies were enhanced with an increase in concentration of inhibitor and decreased with a rise in temperature..The efficiency of this macromolecule had maximum inhibition efficiency up to 96 % at 0.5 mM and diminishes with a higher temperature degree, which is revealing of chemical adsorption. An inhibitor molecule were absorbed by metal surface and followed Langmuir isotherms .Quantum chemical calculations results showed that the corrosion inhibition efficiency increased with an increase in both the E_{HOMO} and μ values but with a decreased in the E_{LUMO} value.

The corrosion inhibition performance of 2-hydrazino-4,6-dimethoxy-1,3,5-tirazine (DMeHT), 2,4-dihydrazino-6-methoxy-1,3,5-triaizine (DHMeT), and 2,4,6-tridydrazino-1,3,5-triaizne (TH_3) on steel corrosion in acidic media was examined using electrochemical techniques. The results showed 2,4-Ddihydrazino-6-methoxy-1,3,5-triaizine (DHMeT) gave the best corrosion protection performance among the other hydrazino derivatives even at a low concentration of 25 ppm (95%). The number of hydrazino groups played an important role in the corrosion inhibition, where the two hydrazine groups increased the electrostatic interactions between the protonated tested compounds, the negatively charged steel surface resulted from the adsorption of the chloride anions, and the presence of the methoxy group made the compound morereliable for formation of film protection on the surface of steel through the lone pair of oxygen atoms. Electrochemical Impedance Spectroscopy (EIS) measurements suggested that the corrosion processes of steel in presence of the hydrazino-s-triazine derivatives (TH_3, DMeHT and DHMeT) were being controlled by the charge transfer reaction. Polarization curves indicated that the examined TH_3, DMeHT and DHMeT behaved as mixed type inhibitors [252].

A new corrosion inhibitor namely, 2-amino-3-((4-((*S*)-2-amino-2-carboxyethyl)-1H-imidazol-2-yl)thio)propionic acid (AIPA) has been synthesized and its inhibition action on corrosion of mild steel in 1 M HCl has been investigated by Haque *et al.*[253].It is concluded that the investigated compound acted as a good corrosion inhibitor for mild steel in acid solution and its inhibition efficiency increased with increasing concentration. Maximum inhibition efficiency of 96.52% was obtained at 0.456 mM/L concentration. Adsorption of the compound on mild steel surface obeyed the Langmuir adsorption isotherm. Potentiodynamic polarization study revealed the AIPA acted as a mixed type inhibitor with cathodic predominance. EIS results showed that the presence of inhibitor molecule decreased the value of Cdl and increased the value of Rct which indicated its adsorption over the metal/electrolyte interface. SEM and AFM analysis showed the existence of protective film of inhibitor molecule over the metallic surface. Quantum chemical study confirmed the experimental results and showed that the investigated inhibitor has a strong tendency of adsorption over the metallic surface.

The influence of two pyridazine derivatives, namely, 6-phenyl-3(2H)-pyridazinone (P1) and 3-chloro-6-phenylpyrazine (P2) as corrosion inhibitor for mild steel in 0.5 M HCl were investigated by Lukman *et al.*[254].P1 was found to accelerate corrosion at low concentrations but exhibited inhibitive action at higher concentrations, attaining 61%inhibition efficiency at 1.25 mM. The inhibitive action of P2 increased with increasing concentration from 88% at 0.1 mM to 96% at 1.25 mM as deduced from EIS measurements. Both compounds are mixed type inhibitors. P2 seems to display chiefly anodic inhibitive effects. The adsorption of P2 on mild steel surface obeyed the Langmuir adsorption isotherm and involved competitive physisorption and chemisorption mechanisms. Scanning electron microscopy analysis of steel surfaces in acid-inhibitor solutions showed that both compounds protected mild steel surface effectively at 1.25 mM. FTIR and UV–vis spectroscopic analyses revealed that N-H, C=O, and C-N functional groups of the pyridazine derivatives were actively involved in adsorption of the molecules onto steel surface. Quantum chemical parameters showed that the higher inhibition efficiency of P2 compared to P1 might be related to better electron acceptance ability of P2.

Two N(4)-substituted thiosemicarbazones, anisoin- and furoin N(4)-methyl(phenyl) thiosemicarbazone (AMPTSC and FMPTSC, respectively) have been tested as inhibitors on the corrosion of mild steel in 1 M HCl solution [255]. Polarization measurements revealed the mixed type inhibitor character. The inhibiting action of these molecules was discussed in terms of blocking the electrode surface by the adsorption of inhibitor molecules obeying Langmuir isotherm. The lowest corrosion rate was obtained with FMPTSC. Surface morphological studies also gave unfailing results.

The inhibition influence of 5-amino 1,3,4-thiadiazole-2-thiol (5-ATT) on the corrosion of mild steel in 1 M HCl solution was studied at 303 K practicing weight loss, electrochemical electrochemical (AC and DC) studies and X-ray photoelectron spectroscopy (XPS) methods. The obtained results showed that 5-ATT was an effective inhibitor in HCl medium. The inhibition efficiency, η(%), increased with the increase in concentration inhibitor but the temperature has almost no effect on the inhibition efficiency of 5-ATT. Thermodynamic data and XPS analysis clearly showed that the adsorption mechanism of 5-ATT on the mild steel surface in 1 M HCl solution was mainly electrostatic-adsorption. Tafel curves revealed that 5-ATT behaved as a mixed-type inhibitor with cathodic predominance and obeyed Langmuir adsorption isotherm. EIS measurement results indicated that the resistance of the carbon steel electrode increased greatly and its capacitance decreased by increasing the inhibitor concentration [256].

Umoren *et al.* [257] have studied the effect of Polypropylene glycol (PPG) as a corrosion inhibitor for typical X60 pipeline steel in 15% HCl solution. Results obtained showed that polypropylene glycol acted as a good corrosion inhibitor for X60 pipeline steel in the strong acid environment. Inhibition efficiency increased with an increase in PPG concentration and temperature up to 55 °C but decreased as immersion time was prolonged. Optimum inhibition efficiency of 90.5% was obtained at 55 °C with 1000 ppm PPG concentration from weight loss method. Potentiodynamic polarization studies revealed that PPG functioned as a mixed-type inhibitor. The corrosion inhibition effect of PPG could be related to the adsorption of PPG molecules on the metal surface which followed Langmuir adsorption isotherm model and a protective film formation.

The inhibition efficiency of the stearamidopropyl dimethyl amine (SAPDA) surfactant for the corrosion of API X120 steel in a 0.5 M HCl solution at different temperatures was investigated using different electrochemical and microscopy techniques. The overall results showed that SAPDA significantly decreased the corrosion rate of API X120 steel with an inhibition efficiency of approximately 99% at an inhibitor concentration of 136 μmol L^{-1}. It was revealed that the adsorption of the SAPDA surfactant on the API X120 steel surface followed Langmuir's adsorption isotherm. Polarization studies indicated that SAPDA was chemi/physisorbed on the steel surface. Quantum chemical calculations, using the density functional theory, further supported the relationship between the inhibitor efficiency and its molecular structure [258].

The inhibitive effect of the hexamethylenediamine tetra(methylene phosphonic acid) (HMDTMPA) on the corrosion of carbon steel in 1.0 M HCl solution has been investigated by Laamari *et al.*[259]. The presence of (HMDTMPA) reduced remarkably the corrosion rate of carbon steel in acidic solution. Results clearly revealed that the (HMDTMPA) behaved as a mixed type corrosion inhibitor with the highest inhibition at 4×10^{-3} M. The adsorption of HMDTMPA on the carbon steel surface obeyed to the Langmuir's adsorption isotherm. Surface analysis via scanning electron microscope (SEM) showed a significant improvement on the surface morphology of the carbon steel plate.

The corrosion inhibition behaviour of (E)-N-((E)-3-phenylallylidene)-2-(phenylthio) aniline (2-PTA) as corrosion inhibitor for low carbon steel (LCS) in hydrochloric acid solution was investigated using electrochemical techniques for a wide temperature range. The results revealed that 2-PTA inhibited the corrosion of LCS by adsorbing to a great extent, even at high temperatures and exhibited 98% inhibition efficiency at 60 °C in 1.0 M HCl medium. Polarization study showed that the inhibitor is mixed type inhibitor with predominant cathodic control and the adsorption of 2-PTA is more than an electrostatic adsorption. The potential and time dependent stability tests of 2-PTA film verified that 2-PTA is an effective inhibitor for the acid corrosion of LCS [260].

4(N,N-dimethylamino) benzaldehyde nicotinic acid hydrazone is prepared and investigated as corrosion inhibitor for mild steel in 1 M HCl using various experimental methods[261].The inhibition efficiency increased with increasing inhibitor concentration. The polarisation study indicated that it acts as a mixed type corrosion inhibitor. The adsorption of inhibitor is spontaneous and obeyed the Langmuir's adsorption isotherm. The FE-SEM images and AFM images of mild steel supported strong adsorption and high inhibition efficiency of the inhibitor. Quantum chemical parameters were also in good agreement with experimentally obtained efficiency.

The effect of newly synthesized amine derivative 1, 3, 5-tris (4-amino phenoxy) benzene (TAPOB) as corrosion inhibitor for mild steel has been evaluated. The inhibition efficiency of TAPOB was as high as 95% determined by gravitational method. Information based on potentiodynamic polarization indicated that TAPOB was a mixed-type inhibitor. Electrochemical impedance spectroscopic study proved that TAPOB could adsorbed on mild steel surface and impart high charge-transfer resistance. The thermodynamic results demonstrated that the adsorption process of TAPOB on mild steel surface obeyed Langmuir adsorption isotherm and involved both physical and chemical adsorption. The surface analysis of mild steel further suggested that TAPOB exist on the metal surface to form a protective film by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) technique. The relationship between the inhibition efficiency and molecular structure was discussed via theoretical calculation, which was in a good agreement with the experiment results. All these evidence revealed that TAPOB was an effective and potential amine-typed corrosion inhibitor [262].

The corrosion inhibition of mild steel in 0.1M HCl solution by 4-hydrobenzoic acid has been studied at temperature range 303, 313, 323 and 333 K. The results obtained at 303 K indicated that the studied inhibitor had established >88% inhibition efficiency at an optimum concentration of 0.10 M. The adsorption of 4-hydrobenzoic acid took place according to Langmuir`s adsorption isotherm. Potentiodynamic polarization studies indicated that 4-hydrobenzoic acid acted as a mixed type of inhibitor. Data collected from EIS studies has been analyzed to model the appropriate equivalent circuit for better explanation of corrosion inhibition process. The surface analysis study using SEM confirmed the corrosion of the mild steel and its inhibition by the inhibitor. FTIR spectra of the inhibitor and the corrosion product of mild steel (in the presence of the inhibitor) revealed that there was shifts in frequencies of adsorption suggesting that some functional groups were used in adsorption and some new bonds were formed [263].

8. References

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Chapter 2

MATERIAL AND METHODS

Chapter 2

MATERIAL AND METHODS

2.1 Introduction

It is often necessary to predict the performance of specific material in particular environment to determine the inherent corrosivity of system. Predicting corrosivity is especially important when designing equipment, most of which extremely challenging to repair or replace once it installed. Corrosion testing is widely use method of evaluating a material's ability to withstand specific environment condition. In general corrosion testing is conducted by exposing sample of a material to desired environment for relatively short period of time, than evaluating the type and severity of corrosion in order to selected material or chemical that will maximizes the life of the material.

2.2 Metals and Alloys

Mild steel refers to low carbon steel which is usually used for structural applications in oil and gas industries. Commercial grade sheets of mild steel were used for the present investigation. It purchased from the local market and analyzed by using X-ray diffractometer for its composition (C- 0.16%, Si- 0.10%, Mn-0.40%, P-0.013%, S- 0.02% and remaining as iron).

2.3 Chemicals

2.3.1 Inhibitors

New inhibitors were synthesized, purified and characterized by FTIR spectroscopic technique. Inhibitors were dissolved in 1M HCl to prepare stock solution of 1000 ppm concentration. Desired concentration was obtained by diluting the stock solution with 1M HCl solution.

2.3.2 Chemicals and solutions

All chemicals used in the present investigation were of AR grade and procured from different chemical companies. The aggressive solution was prepared from AR grade hydrochloric acid obtained from Merck. One molar solution of hydrochloric acid was prepared with double distilled water. Different concentrations (100 – 500 ppm) of inhibitors in 1M hydrochloric acid were prepared to study their inhibition efficiency on mild steel. All the materials were used as received without any further treatment.

Figure 2.1: Fourier-transform infrared spectroscopy (FTIR)

2.4 Sample Preparation

For weight loss experiments, rectangular shaped coupons (3 cm x 1 cm x 0.1 cm) were sheared from sheets of mild steel. Specimens with 1 cm2 working area were used for electrochemical experiments. The surface of specimens was prepared by sequential polishing with 1/0,2/0,3/0 and 4/0 grade Emery paper (John Okay).

After polishing the surface by lower grade of emery paper, it was polished with the next higher grade in a direction right angle to the first. After polishing all specimens were washed with triple distilled water, and degreased with 95% ethyl alcohol. Specimens were dried and stored over silica gel in vacuum desiccators. Specimens were weighed on an electronic balance (CONTECH, Model No.CBS-50, least count 0.001g).

2.5 Corrosion measurement

2.5.1 Gravimetric Experiments

Due to reliability and simplicity of weight loss method, it is preferably the starting method for corrosion testing. After initial weighing, the specimens were immersed in beakers which contained 100ml of 1M HCl in the absence and presence of different concentration of inhibitor. Themostatic water bath used to maintain temperature during immersion period. After 24 h, the specimens were taken out, washed, dried and weighed accurately. Mean corrosion rate (CR) in mg cm2 h-1 with respect to acid and inhibitors was calculated. The experiment was repeated at 298-328k. The corrosion rate (CR) was calculated from following equation:

$$CR = \Delta W / At \qquad (1)$$

Where CR is corrosion rate (mg cm2h-1), ΔW is the weight loss (mg),A is surface area and t is immersion time in h. The inhibition efficiency (η%) of inhibitor on corrosion of mild steel was calculated as follows,

$$\eta\,\% = \frac{W_0 - W}{W_0} \times 100 \qquad (2)$$

Where, W_0 and W are corrosion rate of mild steel in the absence and presence of inhibitors, respectively.

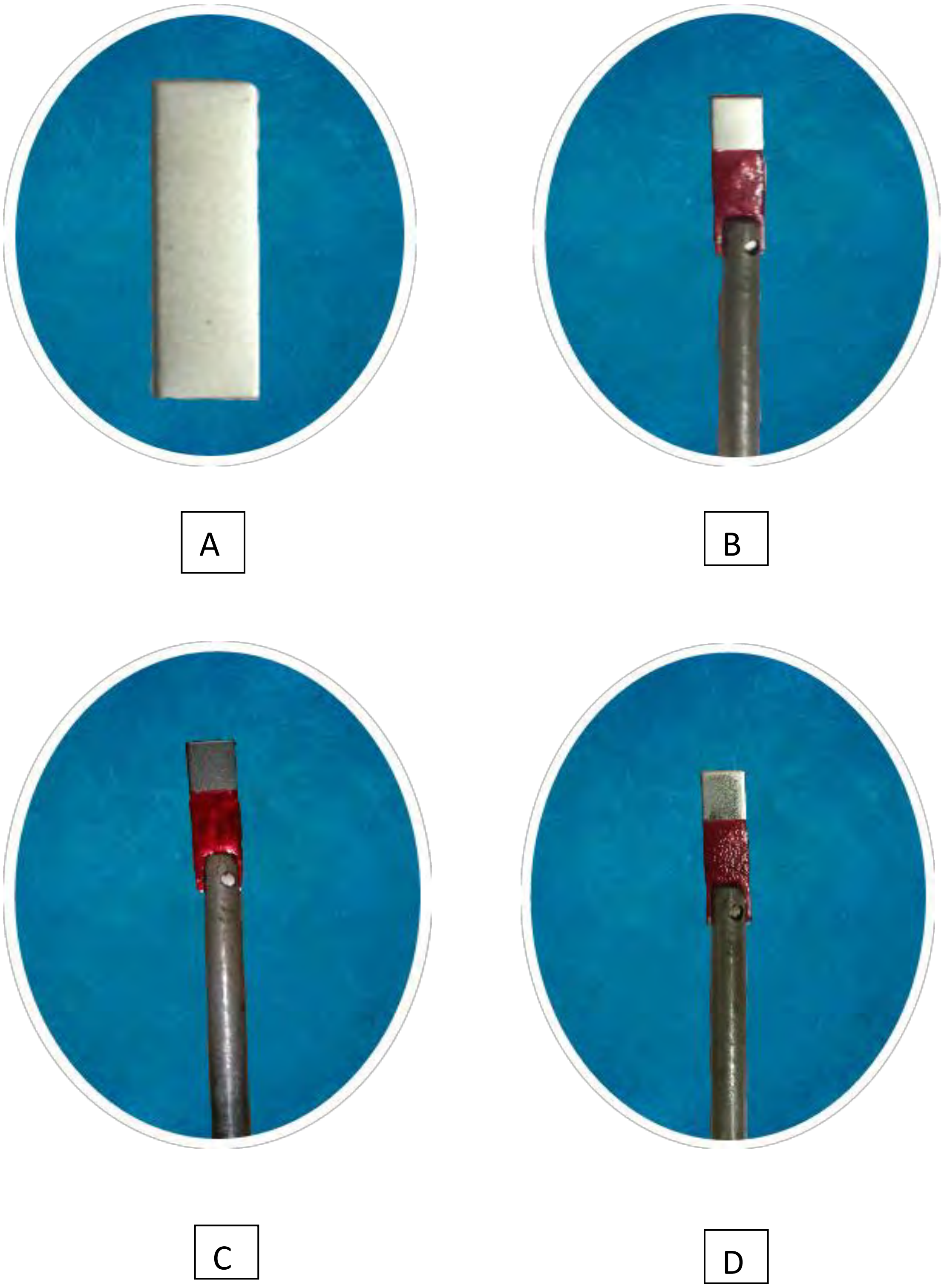


Figure 2.2: (A) coupon size 3cm x 1cm x 0.1cm, (B) Polished mild steel coupen coated with enamel lacquer having 1cm working area, (C) mild steel coupon after exposure to 1M HCl, (D) mild steel coupon after exposure to inhibitor.

2.5.2 Measurement of Open Circuit Potential

The variation of corrosion potential of mild steel in 1 M HCl was measured against saturated calomel electrode (SCE) in absence and presence of various concentrations of inhibitors. The time dependence of OCP for different experiments was recorded for 1 hour exposure period. Sample period was 1 second and sample area was 1 square centimeter. Then same sample which was used for OCP measurement was used for potentiodynamic polarization experiments. The polarization studies were carried out in unstirred solutions.

2.5.3 Electrochemical Polarization

Electrochemical Measurement System, DC 105,containing software of DC corrosion techniques from M/S Gamry Instruments Inc., (No. 23-25) 734, Louis Drive, Warminster, PA-18974, USA has been used for performing corrosion potential and polarization experiments.The electrochemical studies were performed in a three electrodes Pyrex glass vessel with mild steel coupon as working electrode, saturated calomel electrode as reference electrode and spectroscopic grade graphite rod as counter electrode.The potentiodynamic polarization study was performed in the absence and presence of optimum concentrations of inhibitors. For potentiodynamic study potential was swept between -0.5V to 0.5V at the scan rate of 5mV/second. The different electrochemical parameters and corrosion rate of mild steel in 1 M HCl with and without inhibitors were calculated with the help of inbuilt Tafel formula in the Gamry instruments software.

Different electrochemical results obtained from potentiodynamic polarization are reported in respective chapters.

The corrosion inhibition efficiency was calculated by using the following equation:

Inhibition efficiency (IE%) = $100(i_o – i)/i_o$ (3)

Where i_o and i are the corrosion current densities in the absence and presence of inhibitor in the solution respectively.

The complete experimental set up used throughout the present investigation is shown in fig 2.3.

Figure 2.3: Electrochemical Measurement System, DC-105, DC corrosion techniques M/S Gamry instruments, Inc, USA.

For electrochemical polarization studies (corrosion potential, and potentiodynamic polarization) rectangular specimens of 3 cm x 1 cm x 0.1 cm were cut from the mild steel sheet. These samples were polished as described earlier. One side with working area 1cm2 was exposed to corrosive medium and the other side was used to provide electrical contact. Its surface was coated with enamel lacquer including side edges, leaving an area of 1cm2 on both sides. One side about 50 cm3 of the corrosive medium was taken in a mini corrosion testing electrochemical cell. This volume was appropriate to permit desired immersion of electrodes. The three electrode cell system consisting of working electrode, reference electrode (saturated calomel electrode) and counter electrode (graphite rod) was used throughout the electrochemical measurements.

The PC4/750(mA) Potentiostat/Galvanostat uses the PC4 potentiostat to perturb the equilibrium corrosion process. Corrosion rate is obtained by selecting the Tafel analysis and potentiodynamic data. The software of EMS-750 performs a sophisticated numerical fit to the Stern-Geary equation. The measured data is fitted to Stern-Geary equation by adjusting the values of Ecorr, Icorr, β_a and β_c.

Assembly of the electrochemical cell used in the present investigation is shown in the Fig.2.4.

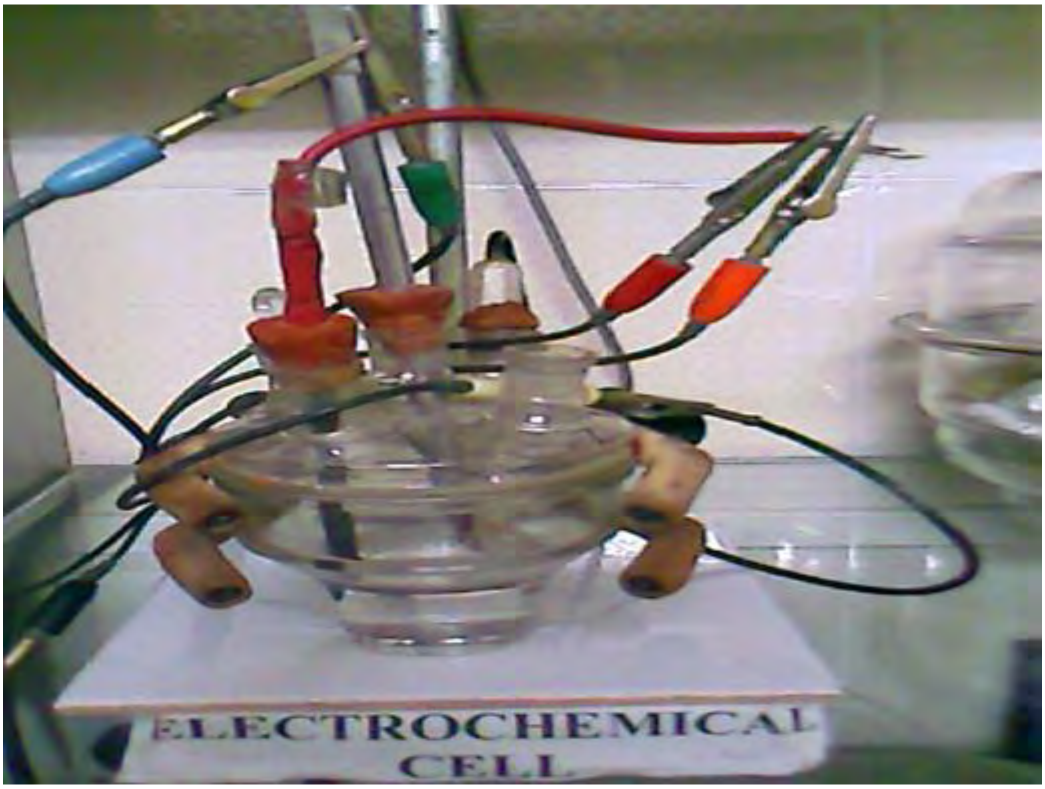


Figure 2.4: Three electrodes pyrex glass vessel

It is a four port cell. The fourth port, which holds a gas dispensing tube, is not shown in the interest of clarity. Assembly of the cell starts with the cell tops onto the cell bottom. The cell clamp holds the top and bottom together. The three contain the Luggin capillary containing saturated calomel electrode (SCE) as reference electrode, graphite counter electrode, and the working electrode (reserved in the central port). The counter electrode is the rod of very high density graphite of spectroscopic grade. The reference electrode is inserted into the wide opening at the upper end of the Luggin capillary. It contacts the test solution that has risen into the tube. The Saturated Calomel Electrode (SCE) is a single junction device, utilizing a porous Vycor tip to isolate the saturated KCl in the electrode from test solution.

2.6 Scanning Electron Microscopy and Energy Dispersive X-ray analysis

The surface film formed on the metal specimen was evaluated by SEM-EDX analysis. This was carried out by SEM/EDX model PHENOM PROX from the Netherlands. The spectra were recorded for specimens exposed to 1M HCl for a period of 24 hours in the absence and presence of 500 ppm inhibitors. The energy of acceleration beam employed was 20 kv.

Figure 2.5: Scanning Electron Mcroscope (SEM) with Energy Dispersive X-ray (EDX)

Chapter 3

CORROSION INHIBITION OF MILD STEEL USED IN OIL AND NATURAL GAS INDUSTRIES USING 5-(4-CHLOROPHENYL) TETRAZOLE, 5-PHENYL TETRAZOLE AND, 5-AMINOTETRAZOLE IN 1M HCl

Chapter 3

CORROSION INHIBITION OF MILD STEEL USED IN OIL AND NATURAL GAS INDUSTRIES USING 5-(4-CHLOROPHENYL) TETRAZOLE, 5-PHENYL TETRAZOLE AND , 5-AMINOTETRAZOLE IN 1M HCl

3.1 Introduction

Corrosion is naturally occurring phenomena defined as the deterioration in quality of materials (usually metal) or its properties because of the reaction of material with its environment. Corrosion of material is inevitable due to the fundamental need of lowering of Gibbs free energy [1-2].Mild steel has been used extensively in the oil, gas and chemical industries because of its outstanding mechanical properties. The use of steel is also one of the effective strategies to maximize profit and reduce cost as compared to expensive corrosion resistant alloys. In many industrial applications related to oil and gas processing such as pipeline cleaning, pipeline/acid descaling and oil well acidizing, the use of mineral acids (usually hydrochloric acid) is still an effective method for improving productivity. This process however endangers the life of steel structures as a result of acid driven corrosion. In order to prevent this undesirable reaction, corrosion inhibitors are often added to the acid solution during acidification process [3-10].Organic compounds, containing functional electronegative groups and π-electron in triple or conjugated double bonds are usually good inhibitors [11]. Heteroatoms, such as sulphur, phosphorus, nitrogen and oxygen, together with aromatic rings in their structure are the major adsorption centres [12]. The planarity (g) and the lonely electron pairs in the heteroatoms are important features that determine the adsorption of these molecules on the metallic surface [13]. The use of corrosion inhibitor is one of the most effective measures for protecting metal surfaces against corrosion in acid environments.

Some organic compounds are found to be effective corrosion inhibitors for many metals and alloys. Generally, inhibitor molecules may physically or chemically adsorb on a corroding metal surface [14]. In any case, adsorption is generally over the metal surface forming an adsorbed layer that functions as a barrier protecting the metal from the corrosion [15]. It has been commonly recognized that an organic inhibitor usually promotes formation of a chelate-metal complex on a metal surface, by transferring electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption. In this way, the metal acts as an electrophile ; and the nucleophile centres of inhibitor molecule are normally heteroatoms with free electron pairs that are readily available for sharing, to form a bond. The power of the inhibition depends on the molecular structure of the inhibitor [16-18].

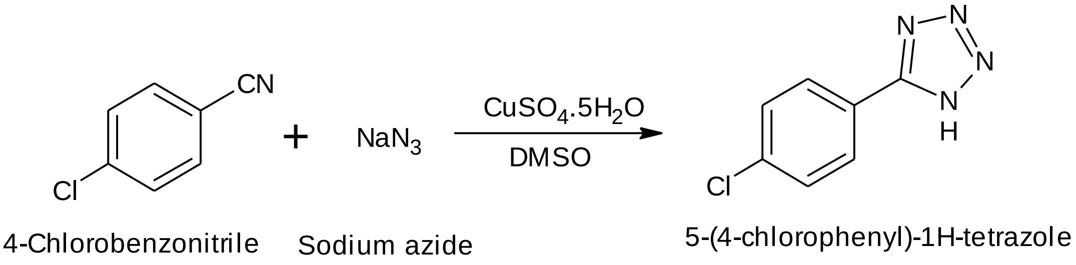
Tetrazoles are one of the most stable nitrogen rich heterocyclic compounds among other heterocyclic systems. Due to their higher nitrogen content they show the exciting acidity, basicity, and complex formation constants. Tetrazole containing molecules have several applications in the field of organic synthesis, coordination chemistry, material science, and medicinal chemistry. Recently, the tetrazole ring, particularly, the 5-substituted-1H-tetrazole, that is, commonly referred as tetrazolic acid, has been widely employed in corrosion science as a corrosion inhibitors for protection of metals.

The present study was undertaken to investigate the inhibition of corrosion of mild steel in 1M hydrochloric acid by tetrazoles namely 5-aminotetrazole(ATZ),5-phenyl tetrazole(PTZ) and 5-(4-chlorophenyl) tetrazole(Cl-PTZ). The study was conducted by using gravimetric analysis, electrochemical technique such as Open circuit potential, potentiodynamic polarization and surface analytical techniques such as Scanning electron microscope (SEM) studies and Energy Dispersive X-ray spectroscopy (EDX) studies. The nature of inhibitor adsorption process was also studied and discussed.

3.2 Synthesis

3.2.1 5-(4-chlorophenyl) tetrazole

Sodium azide (0.0650 g) and cupric sulphate pentahydrate (0.0050 g) were added to a solution of 4-chloro benzonitrile (0.1031 g) in DMSO (2 mL) with stirring at room temperature. The reaction temperature was raised up to 140 °C for 1 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled and treated with 10 mL HCl (4 mol L^{-1}) and then with 10 mL ethyl acetate. The resultant organic layer was separated, washed with 2×10 mL distilled water, dried over anhydrous sodium sulphate, and concentrated to give the crude solid 5-phenyl-1H-tetrazole (1). The crude product was recrystallized from n-hexane: ethylacetate (1:1) .The melting point of pure compound is around 262^0C [19].



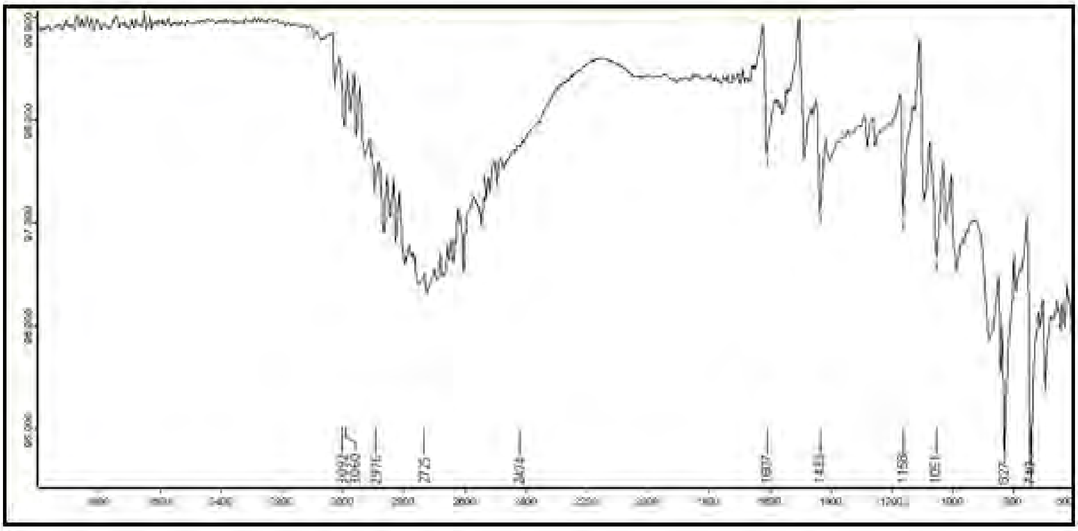
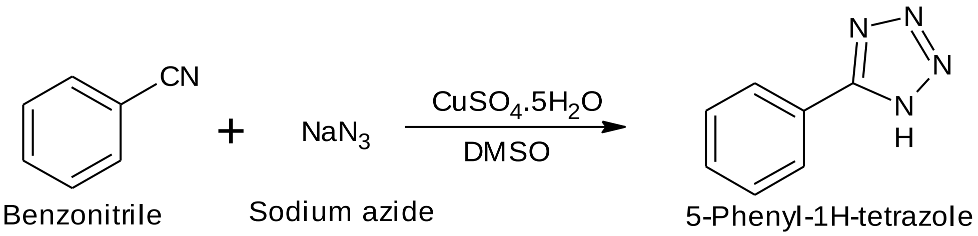


Figure 3.1: FTIR spectrum of synthesized 5-(4-chlorophenyl) tetrazole

The FTIR spectrum of 5-(4-chlorophenyl) tetrazole is shown in Figure 3.1.Aromatic C-H stretching is observed at around 3060 cm^{-1} to 3092 cm^{-1} ,C=C stretching occurs around 1433 cm^{-1} to 1607 cm^{-1}, C=N stretching occurs at around 1550 cm^{-1} to 1650 cm^{-1}, C-N stretching occurs around 1061 cm^{-1} to 1158cm^{-1}, C-Cl stretching is observed at around 740cm^{-1} to 827cm^{-1}.

3.2.2 5-Phenyl tetrazole

Sodium azide (0.0650 g) and cupric sulphate pentahydrate (0.0050 g) were added to a solution of benzonitrile (0.1031 g) in DMSO (2 mL) with stirring at room temperature. The reaction temperature was raised up to 140 °C for 1 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled and treated with 10 mL HCl (4 mol L^{-1}) and then with 10 mL ethyl acetate. The resultant organic layer was separated, washed with 2×10 mL distilled water, dried over anhydrous sodium sulphate, and concentrated to give the crude solid 5-phenyl-1H-tetrazole (1). The crude product was recrystallized from n-hexane:ethylacetate (1:1).Pure 5-phenyl tetrazole melts at 215^0c [19].



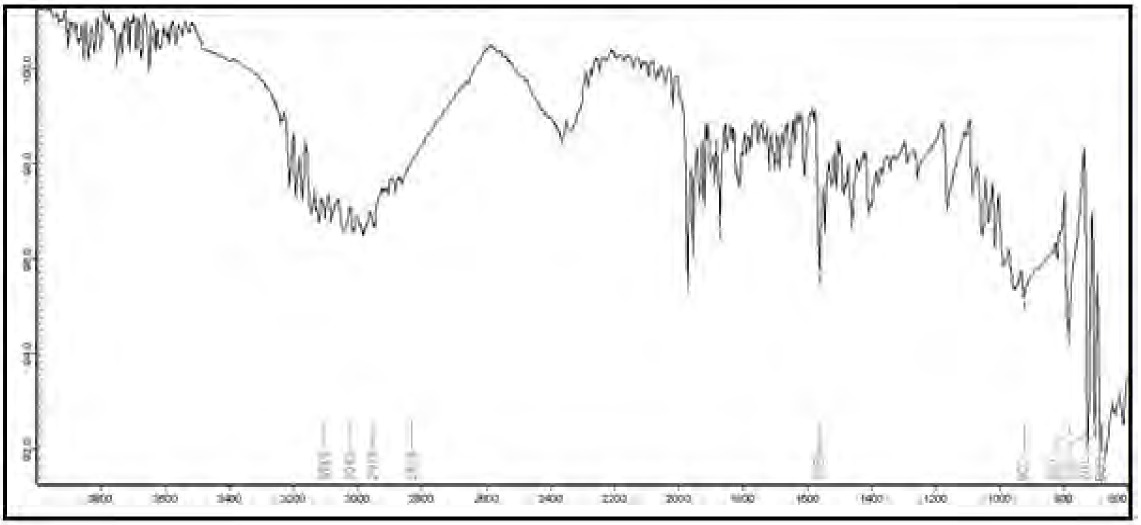


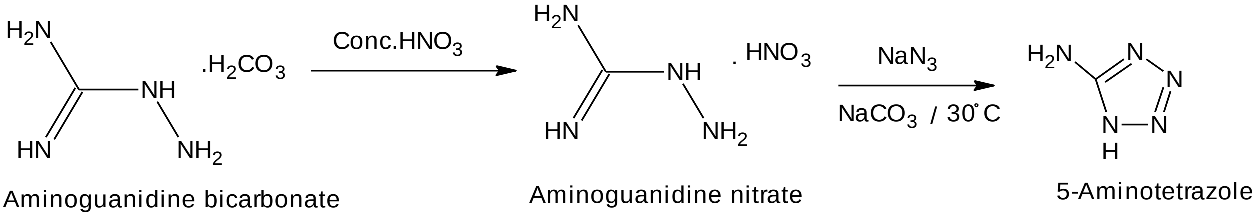
Figure 3.2: FTIR spectrum of synthesized 5-phenyl tetrazole

The FTIR spectrum of 5-phenyl tetrazole is shown in figure 3.2.Aromatic C-H stretching is observed at around 3045 cm^{-1} to 3125 cm^{-1} ,C=C Stretching occurs around 1400 cm^{-1} to 1600 cm^{-1}, C=N stretching occurs at around 1559, C-N stretching occurs around 1450 cm^{-1}.

3.2.3 5-Aminotetrazole

11 grams of amino guanidine bicarbonate are slowly added with stirring to a solution of 34 ml of 32% nitric acid. Neutralization reaction takes place and carbon dioxide is evolved. To the prepared amino guanidine nitrate solution slowly 20 ml

35% of sodium nitrite solution drop-wise are added. During the addition of sodium nitrite the temperature should not exceed 30-35° C. At the end of diazotization solution colour changes to the brow-red. Then to the reaction mixture while stirring 10 grams of sodium carbonate are added portion-wise. The flask is connected to reflux condenser and the reaction mixture is heated 4 hours. The hot solution is neutralized with 30% sulphuric acid and on cooling 5-aminotetrazole crystallizes. The obtained 5-aminotetrazole crystals are washed with small amount of water and recrystallized from hot water, or water and ethanol mixture. Pure 5-aminotetrazole melts at 199-201°C [19].



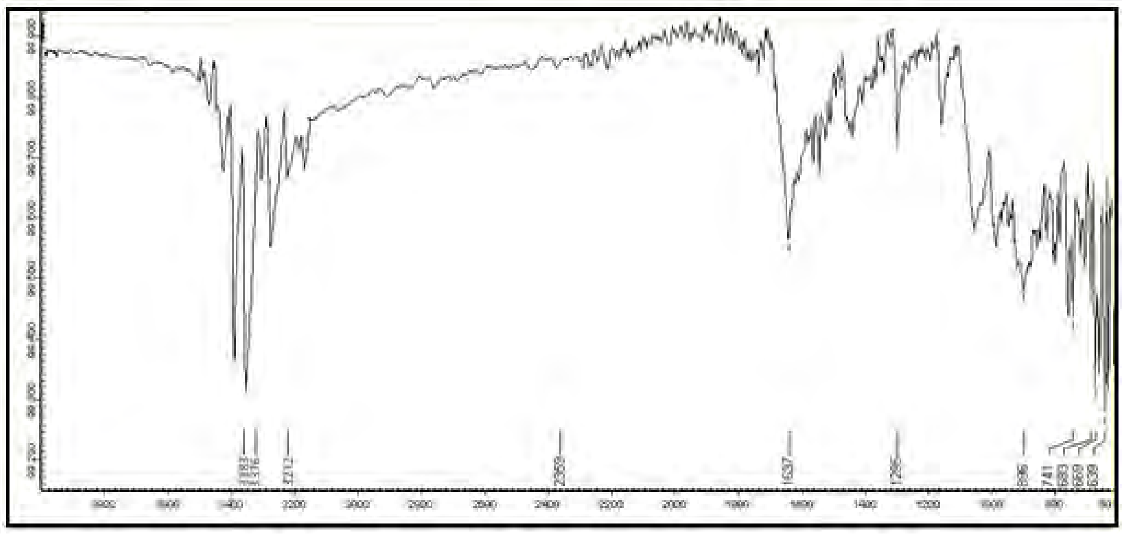


Figure 3.3: FTIR spectrum of synthesized 5-aminotetrazole

The FTIR spectrum of 5-aminotetrazole is shown in figure 3.3.Aromatic C-H stretching is observed at around 3150 cm^{-1} to 3212 cm^{-1} ,C=C Stretching occurs around 1400 cm^{-1} to 1637 cm^{-1}, C=N stretching occurs at around 1550 cm^{-1} to 1650 cm^{-1}, C-N stretching occurs around 1080-1296 cm^{-1},N-H bending observed around 1600 and N-H stretching observed around 3376 to 3383cm^{-1}.

3.3 Results and Discussion

3.3.1 Weight loss Measurement

Weight loss data of mild steel in 1M HCI in the absence and presence of various concentrations of inhibitors were obtained and are given in table 3.1. Inhibitors efficiencies were calculated according to following equation.

$$E\,\% = \frac{W_0 - W}{W_0} \times 100 \qquad (1)$$

W and W_0 are weight loss of mild steel in presence and absence of inhibitors respectively.

The results show that the percentage inhibition efficiency increases upon increasing the tetrazole concentrations, and maximum values of percentage inhibition efficiency for all studied tetrazoles were obtained at 500 ppm. A further increase in concentration did not cause any significant change in the inhibition performance. The percentage inhibition efficiency of the three studied tetrazoles follows the order: 5-(4-chlorophenyl) tetrazole>5-amino tetrazole>5-phenyl tetrazole [20-23].

Inhibitor	Concentration (ppm)	Weight loss (mg)	Corrosion rate (mg cm^{-2}h^{-1})	Surface coverage	E (%)
Blank	0.00	168	23.33	-	-
	100	40	5.556	0.7619	76.19
	200	29	4.027	0.8273	82.73
Cl-PTZ	300	24	3.334	0.8571	85.71
	400	15	2.083	0.9107	91.07
	500	10	1.388	0.9404	94.07
	100	52	7.222	0.6904	69.04
	200	47	6.522	0.7202	72.02
ATZ	300	34	4.722	0.7976	79.76
	400	30	4.166	0.8214	82.14
	500	27	3.750	0.8392	83.92
	100	87	12.083	0.4821	48.21
	200	81	11.250	0.6250	62.50
PTZ	300	54	7.500	0.6785	67.85
	400	44	6.111	0.7280	72.80
	500	32	4.444	0.8095	80.95

Table 3.1: The weight loss parameter obtained for mild steel in 1M HCl containing different concentration of tetrazoles at 298K

3.3.2 Kinetic –thermodynamic corrosion parameters

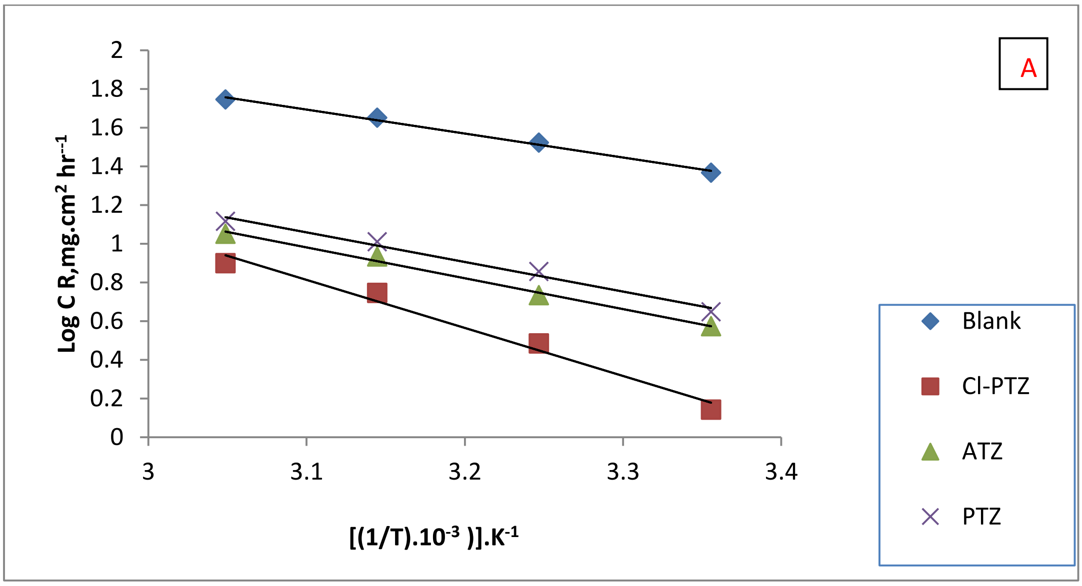
The effect of temperature on both corrosion and corrosion inhibition of mid steel in 1 M HCl solution in the absence and presence of tetrazoles at 500 ppm concentration for 24 h immersion time and at different temperatures ranging from 298K to 328K was studied using weight loss measurements. The results obtained are shown in table 3.2.The data in table 3.2 reveal that the corrosion rate increases with increasing temperature both in uninhibited and inhibited acid [24-26]. The apparent activation energy (E_a) for the corrosion process can be calculated from Arrhenius-type equation:

$$\log CR = \frac{-E_a}{2.303RT} + \log A \qquad (2)$$

where E_a is the apparent activation corrosion energy, R is the universal gas constant (8.314 $JK^{-1}mol^{-1}$), T is the absolute temperature (in K) and A is the Arrhenius pre-exponential factor. Values of apparent activation energy of corrosion for mild steel in 1 M HCl ($-E_a$ = (slope) x 2.303 x R) shown in Table 3.3, without and with optimum concentration of tetrazoles determined from the slope of log (CR) versus 1/T plots are shown in Figure 3.4(A).

Inhibitors	**Tempearture K**	**Corrosion rate (mg cm^{-2} h^{-1})**	**E (%)**
1M HCl	298	23.33	-
	308	33.34	-
	318	44.86	-
	328	55.59	-
	298	1.387	94.04
Cl-PTZ	308	3.055	86.90
	318	5.556	76.19
	328	7.917	66.07
	298	3.750	83.92
ATZ	308	5.417	76.78
	318	8.611	63.09
	328	11.25	51.78
	298	4.444	80.95
PTZ	308	7.222	69.04
	318	10.287	55.95
	328	13.055	44.04

Table 3.2: Effect of tetrazole concentration on corrosion rate and inhibition efficiency for mild steel in 1M HCl at different Temperature



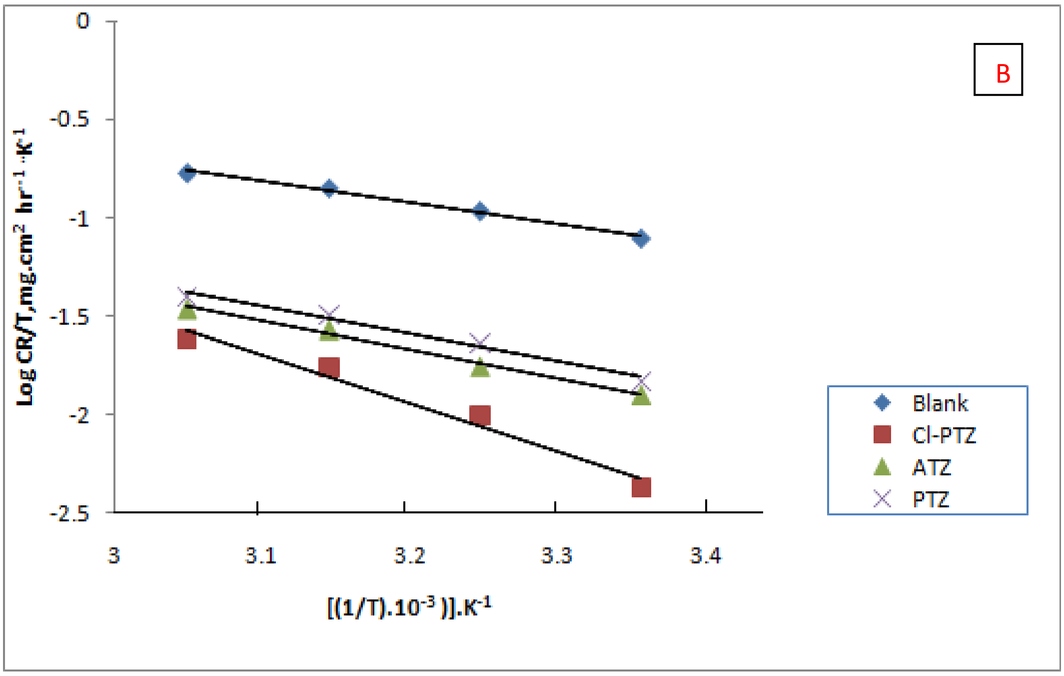


Figure 3.4: Arrhenius plots of (A) log CR vs. 1000/T and (B) Transition state plots of log (CR/T) vs. 1000/T for mild steel in 1M HCl solution in the absence and presence of 500ppm of Cl-PTZ, ATZ and PTZ.

Inspection of the data shows that the activation energy is higher in the presence of inhibitors than in its absence. The alternative formulation of transition state equation is shown in Eq. (3):

$$CR = \frac{\mathrm{RT}}{\mathrm{Nh}} \exp\left(\frac{\Delta \mathrm{S}}{\mathrm{R}}\right) \exp\left(-\frac{\Delta \mathrm{H}}{\mathrm{RT}}\right) \quad (3)$$

Where CR is the rate of metal dissolution, h is Planck's constant, N is Avogadro's number, ΔS is the entropy of activation and ΔH is the enthalpy of activation. Figure 3.4 (B) shows a plot of log (CR/T) against (1/T) in the case of tetrazoles in 1 M HCl. Straight lines are obtained with a slopes equal to (-ΔH /2.303R) and intercepts are [log (R/Nh + ΔS /2.303R)] are calculated and presented in Table 3.3.[27-35].

The increase in E_a with increase in inhibitor concentration is typical of physical adsorption. The positive signs of the enthalpies (ΔH) reflect the endothermic nature of the mild steel dissolution process. Value of entropies (ΔS) imply that the activated complex at the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [36-40].

Inhibitors	**E_a (kJ mol^{-1})**	**ΔH(kJ mol^{-1})**	**ΔS (J mol^{-1} K^{-1})**
1M HCl	23.62	20.99	-148.14
Cl-PTZ	29.256	26.69	-142.55
ATZ	30.558	27.86	-140.478
PTZ	47.56	47.19	-83.649

Table 3.3: Thermodynamic activation parameter for mild steel in 1M HCl in absence and presence of optimum concentration (500 ppm) of Cl-PTZ, ATZ and PTZ

3.3.3 Adsorption Isotherm

In corrosion field Adsorption isotherm provides basics information regarding interaction between the inhibitors molecules and metal surface [41].To find suitable adsorption isotherm in the present study, several commonly used isotherms were tested, among which Langmuir adsorption isotherms were found to fit well with experimental data. Assumption of Langmuir relates the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage (θ) according to equation:

$$C/\theta = 1/K + C \tag{4}$$

where K is equilibrium constant of adsorption. The graph of C/θ vs C obtained straight line with R^2 value obtained varied close to unity confirming the validity of this approach as shown in figure 3.5.The slop of the straight line was almost close to unity, suggesting that adsorbed molecule formed monolayer on mild steel surface [42-44].

Free energy of the adsorption (ΔG^0_{ads}) can be calculated by using the following equation:

$$\Delta G^0_{ads} = -RT \ln(55.5\, k_{ads}) \tag{5}$$

Where R is the universal gas constant, T is the absolute temperature in K, and the numerical value 55.5 represents the molar concentration of water in the acid solution. The calculated values of K_{ads} and ΔG^0_{ads} at 298 K are given in table 3.4. Generally, a high value of K_{ads} is associated with high adsorption efficiency. In our present case, the values of K_{ads} follow the order PTZ < ATZ < Cl-PTZ, which is consistent with the order of the inhibition efficiency.

Inhibitors	**slope**	**K_{ads} (M^{-1})**	**Regression coefficient**	**ΔG^0_{ads} (kJ.mol^{-1})**
5-(4-chlorophenyl) tetrazole	0.998	5000	0.998	-31.03
5-Phenyl tetrazole	1.00	4000	0.998	-30.52
5-Aminotetrazole	1.00	1052	0.999	-27.21

Table 3.4: Slope, equilibrium constant, regression coefficient and free enthalpy of adsorption of in 5-(4-chlorophenyl) tetrazole, 5-phenyl tetrazole and 5-amino tetrazole in 1 M HCl.

Generally, value of ΔG^0_{ads} up to -20 kjmol^{-1} are associated with physisorption while those around -40 kjmol^{-1} or higher are associated with chemisorption. In present case the value of ΔG^0_{ads} were found to be between -27.21to -31.03,which was lower than -40 kj mol^{-1} but higher than -20 kj mol^{-1} indicating that the adsorption was neither typical physisorption nor chemisorption but it was complex mixed typed. Thus in the present case adsorption of inhibitor molecule on the mild steel involved both physisorption and chemisorption but physisorption was the predominant mode of adsorption. The negative value of ΔG^0_{ads} indicated the spontaneous adsorption of tetrazoles on the surface of the metal [45-50].

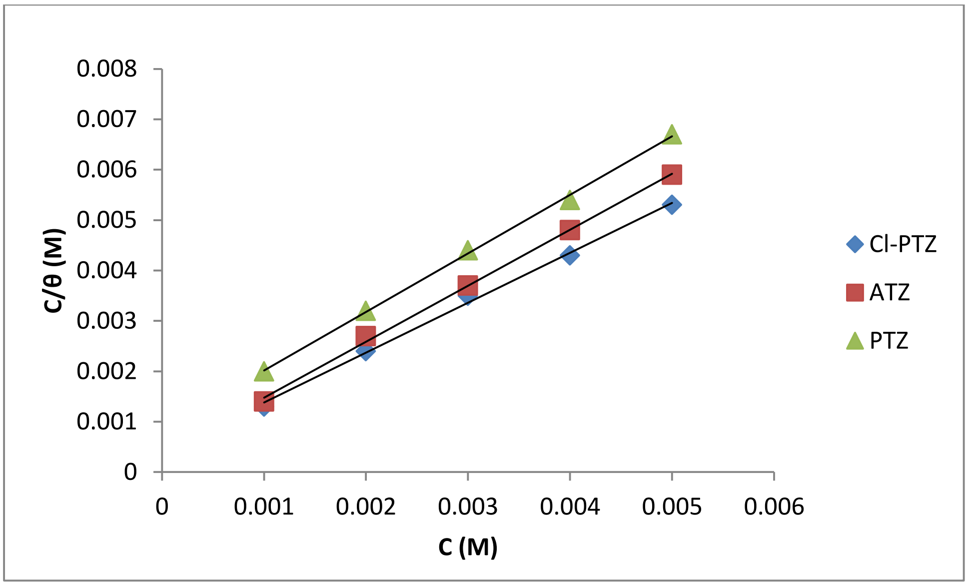


Figure 3.5: Langmuir adsorption isotherm plot for the adsorption of tetrazole derivatives on the mild steel surface in 1M HCl solution

3.4 Electrochemical Measurements

3.4.1 Open Circuit Potential (OCP) Curves

The potential developed on the mild steel electrode relative to the potential of the reference electrode is termed as open circuit potential. The stabilization of OCP is essential before performing electrochemical measurement .The variation of OCP of the working electrodes with respect to time in 1M HCl in absence and presence of various concentrations of tetrazoles is shown in figure 3.6 to 3.8. The OCP curves gives straight line in absence and presence of inhibitors, indicating that steady state potential has been established after 30 min. immersion. It can be observed from OCP curves that in presence of tetrazoles , the steady state potential (E_{corr}) shifted towards more positive direction without changing common feature of the OCP vs. time curves indicative that a physical barrier form between metal and inhibitors[51].

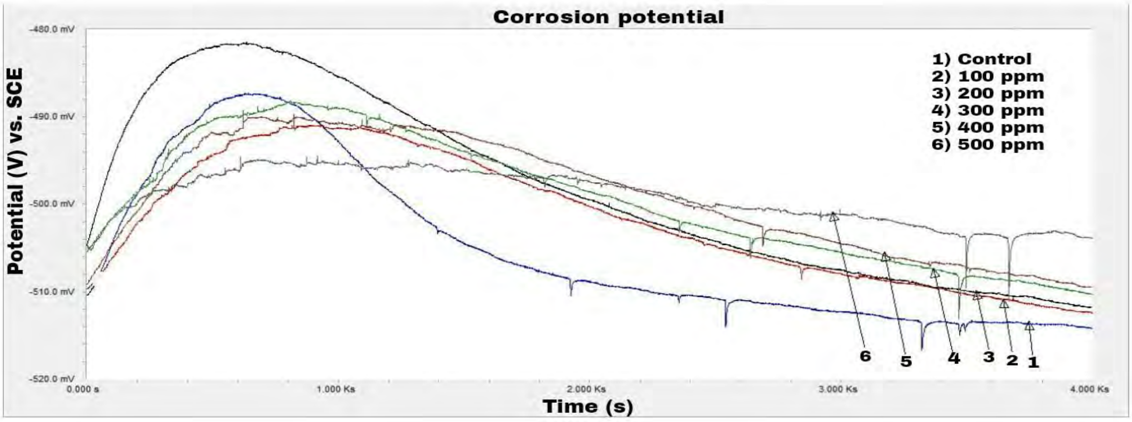


Figure 3.6: Open circuit potential of mild steel without and with different concentration of Cl-PTZ inhibitor in 1M HCl

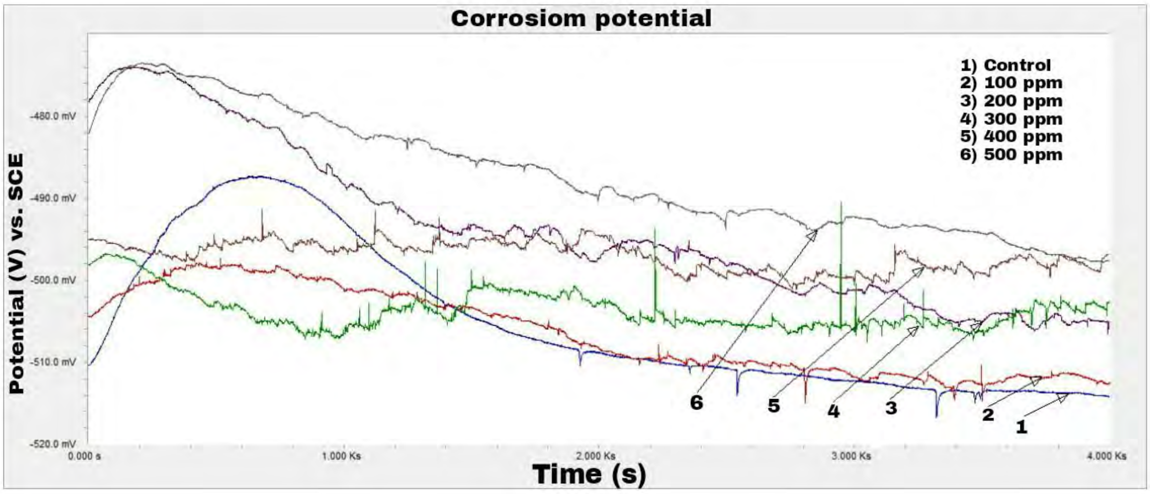


Figure 3.7: Open circuit potential of mild steel without and with different concentration of ATZ inhibitor in 1M HCl

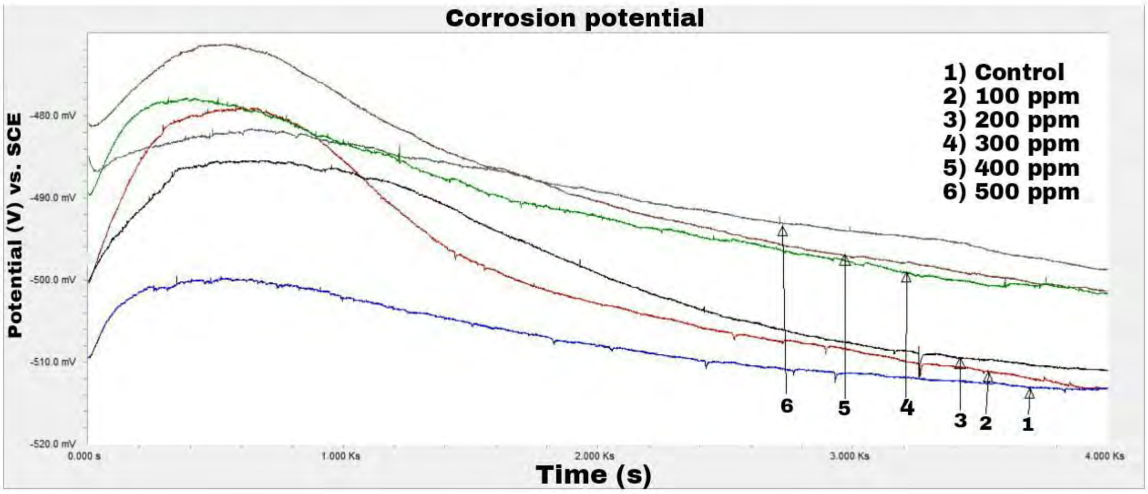


Figure 3.8: Open circuit potential of mild steel without and with different concentration of PTZ inhibitor in 1M HCl.

3.4.2 Potentiodynamic Polarisation Studies

In order to know the kinetics of anodic and cathodic reactions, polarization experiments were carried out potentiodynamically in unstirred 1 M HCl solution in the absence and presence of different concentration of tetrazoles and the obtained polarization curves are shown in Figures 3.9 to 3.11. Electrochemical parameters such as corrosion current (i_{corr}), corrosion potential (E_{corr}), and Tafel slope constant β_a and β_c calculated from Tafel plots are given in table 3.5. From the evaluated i_{corr} value, η% can be calculated using the relation

$$\eta\% = \frac{i_0 - i_{corr}}{i_0} \qquad (6)$$

Where i_0 and i_{corr} are the corrosion current densities in the absence and presence of inhibitors. From the table and figure, it is clear that in the presence of tetrazoles, there was remarkable decrease in i_{corr} value by shifting both anodic and cathodic Tafel slopes towards low current densities [52]. It was further confirmed that the shape of polarization curves were similar in absence and presence of inhibitors, suggesting that tetrazoles inhibited mild steel corrosion by simply adsorbing on the mild steel surface without changing the mechanism of mild steel dissolution[53]. An inhibitor can be classified as anodic, cathodic or mix type depending upon the displacement in E_{corr} value. If the displacement in E_{corr} for the inhibited and uninhibited solution is more than 85 mV it can be classified as cathodic or anodic type. But if the displacement in E_{corr} is less than 85 mV then it can be classified as mix type. However, in the present study, the largest displacement exhibited by the inhibitors was less than 85 mV, from which it can be concluded that all the inhibitors act as mixed type inhibitors.[54-56].

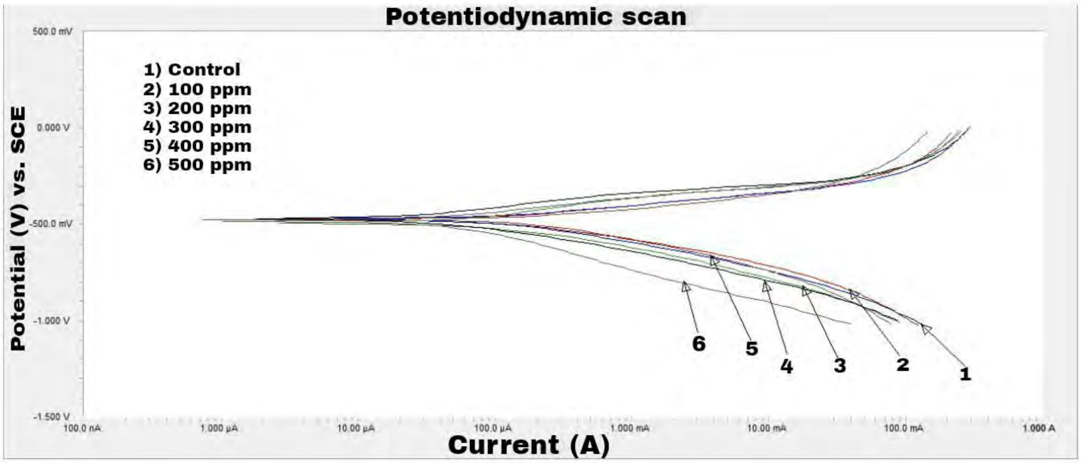


Figure 3.9: Potentiodynamic polarization of mild steel without and with different concentration of Cl-PTZ in 1M HCl

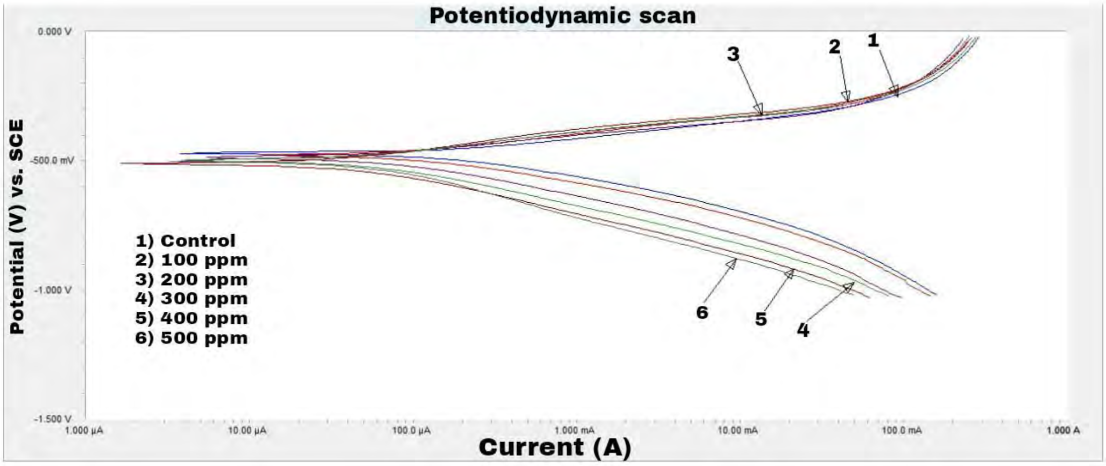


Figure 3.10: Potentiodynamic polarization of mild steel without and with different concentration of ATZ in 1M HCl

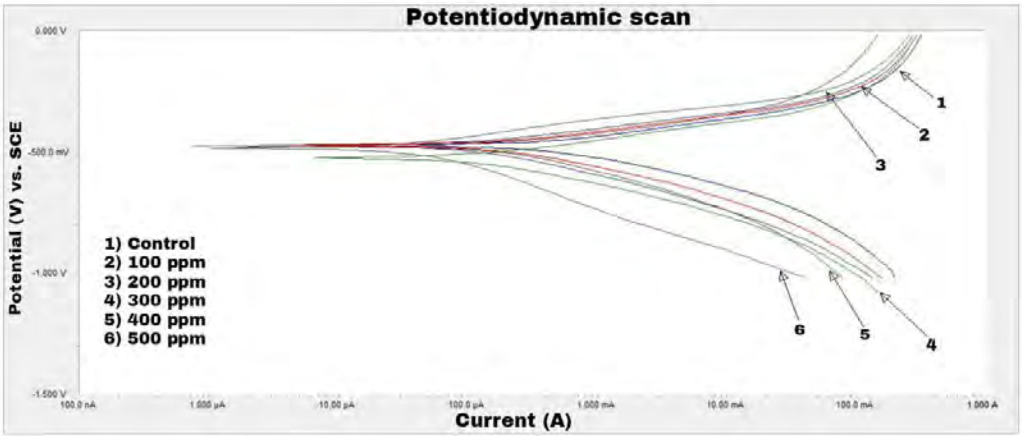


Figure 3.11: Potentiodynamic polarization of mild steel without and with different concentration of ATZ in 1M HCl.

Concentration of Inhibitors (ppm)	$-E_{corr}$ (mv)	I_{corr} ($\mu A/cm^2$)	β_a (v/dec)	β_c (v/dec)	η %
1M HCl	-470	548	87.70 e^{-3}	164.4 e^{-3}	-
Cl-PTZ					
100	-466.0	133.0	68.20 e^{-3}	133.9 e^{-3}	75.73
200	-462.0	71.00	61.20 e^{-3}	129.1 e^{-3}	87.04
300	-488.0	67.30	67.40 e^{-3}	156.8 e^{-3}	87.72
400	-491.0	41.70	74.50 e^{-3}	171.1 e^{-3}	92.39
500	-491.0	36.90	66.80 e^{-3}	164.8 e^{-3}	93.27
ATZ					
100	-497.0	164.00	64.14 e^{-3}	123.3 e^{-3}	70.07
200	-498.0	148.10	65.33 e^{-3}	122.5 e^{-3}	72.97
300	-498.0	121.08	72.54 e^{-3}	121.1 e^{-3}	77.90
400	-496.0	104.20	82.33 e^{-3}	120.4 e^{-3}	80.98
500	-497.0	99.00	80.11 e^{-3}	123.2 e^{-3}	81.93
PTZ					
100	-495.0	274.08	76.21 e^{-3}	149.1 e^{-3}	49.98
200	-485.0	214.00	80.11 e^{-3}	159.3 e^{-3}	60.94
300	-489.0	175.10	59.34 e^{-3}	144.8 e^{-3}	68.05
400	-476.0	153.21	72.65 e^{-3}	116.6 e^{-3}	72.04
500	-482.0	110.01	82.30 e^{-3}	123.5 e^{-3}	79.92

Table 3.5: Polarization curves for corrosion of mild steel in 1 M HCl in the absence and presence of different concentration of (a) Cl-PTZ, (b) ATZ, (c)PTZ.

3.5 Surface Studies

3.5.1 Scanning Electron Microscopic (SEM) Analysis

Tetrazoles form protective film on surface of mild steel which is further supported by SEM micrographs of the mild steel surface obtained after immersion in 1M HCl for 24 hours in absence and presence of 500ppm concentration of tetrazole. Figure

3.12[A] represents the surface of mild steel without any addition. From figure 3.12 [B] it can be visualized that the specimen surface was rough and strongly damaged in the presence of acid solution. Figure 3.12 [C-E] shows SEM micrograph of the mild steel surface immersed in1M HCl containing 500 ppm of tetrazoles. It can be concluded that extent of damage to the mild steel surface was small and rate of corrosion was greatly reduced in presence of tetrazoles. This is due to formation of protective surface film on mild steel, which act as barrier and was responsible for inhibition of corrosion.

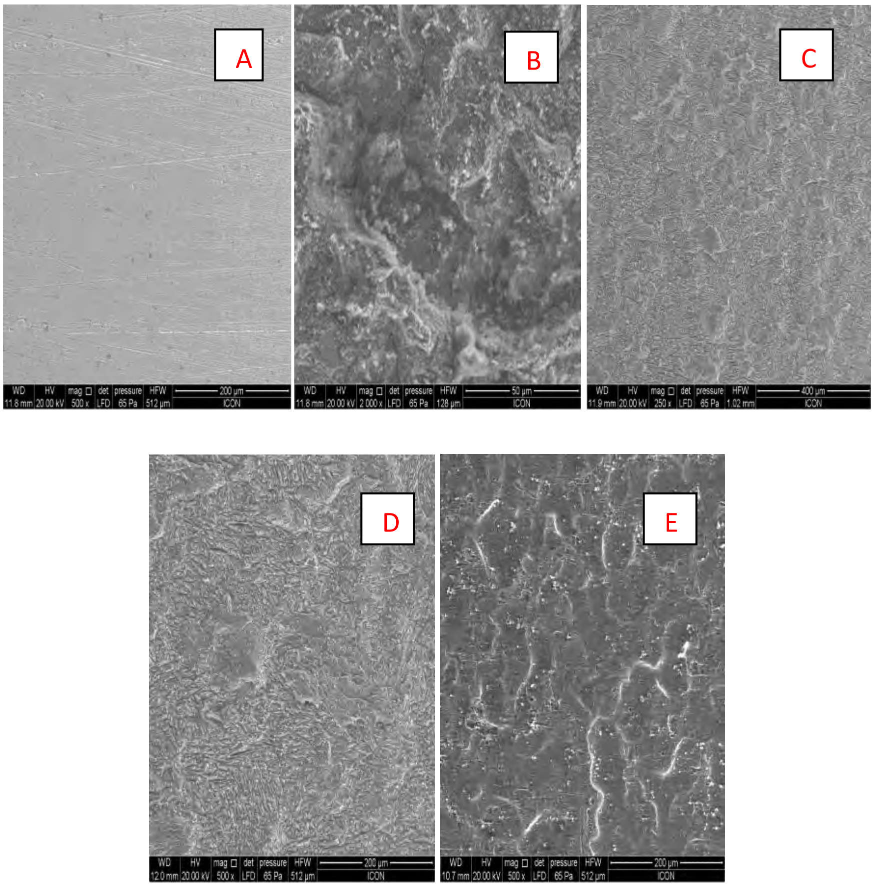
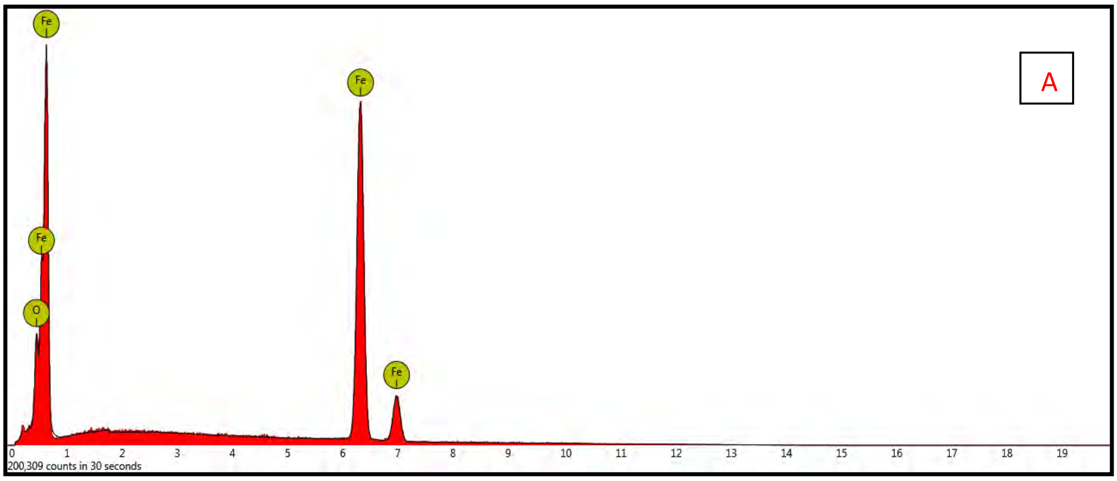


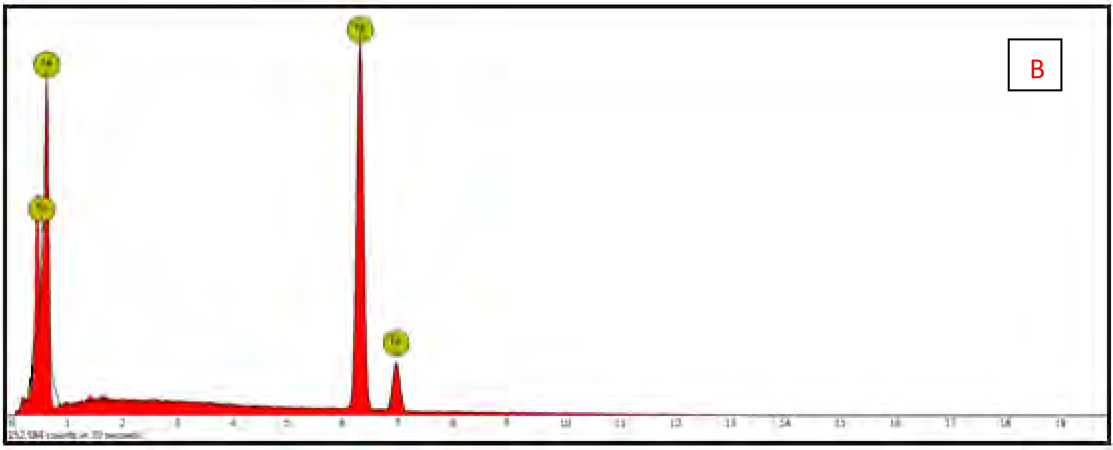
Figure 3.12: SEM of mild steel with (A) Polished, (B) 1M HCl, (C) 500 ppm of Cl-PTZ, (D) 500 ppm of ATZ and (E) 500 ppm of PTZ.

3.5.2 Energy-dispersive X-ray spectroscopy (EDX)

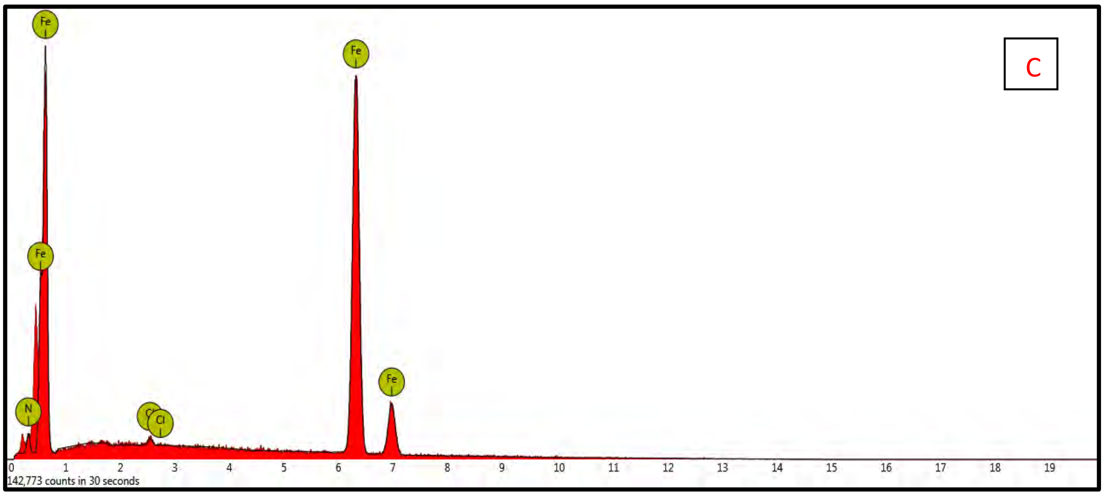
To support weight loss and electrochemical studies, EDX spectra were obtained from mild steel in the presence and absence of 500 ppm inhibitors. Figure 3.13 [A] shows EDX spectra of polished mild steel surface with the characteristic peak for Fe and oxygen. From figure 3.13[B] it is clear that the EDX spectra in absence of tetrazole shows characteristic signal for Fe only as peak for oxygen disappear due to breaking of air formed oxide film in presence of 1 M HCl. However in presence of tetrazoles the EDX spectra shown in figure 3.13[C-E] indicates some additional peaks for nitrogen and chlorine confirming the presence of these elements on surface, which could be due to adsorption of studied inhibitors on mild steel surface. One can also observe that the damage caused by 1M HCl is curtailed by inhibitors.



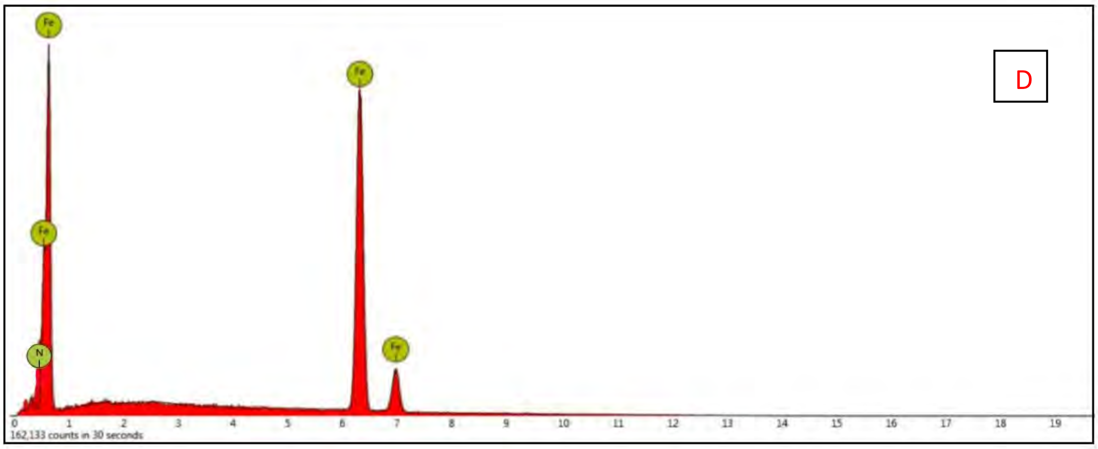
A) Polished sample



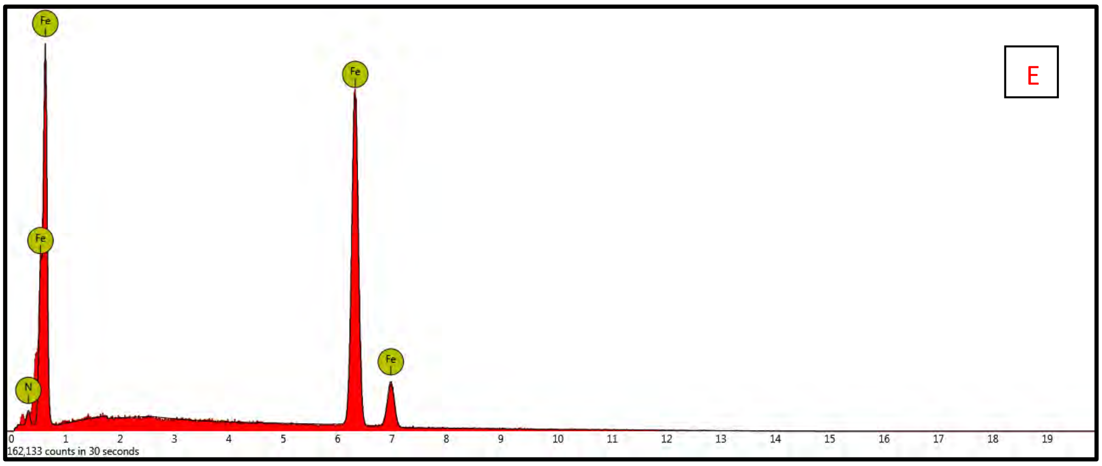
B) Control (1M HCl)



C) 1M HCl+500 ppm Cl-PTZ



D) 1M HCl+500 ppm ATZ



E) 1M HCl+500 ppm PTZ

Figure 3.13:EDX of mild steel with: (A)Polished, (B) 1M HCl, (C) 500 ppm of Cl-PTZ, (D) 500 ppm of ATZ and (E) 500 ppm PTZ.

3.6. Mechanism of Inhibition

The inhibition effect of tetrazole derivatives on corrosion of mild steel in 1 M HCI solution may be attributed to the adsorption of this compound to the metal solution interface. The extent of adsorption of the inhibitors depends on the nature of metal, chemical structure of inhibitors, nature of electrolyte and temperature. Adsorption on the metal surface was suggested to be via the active center present on inhibitors molecule and relies on their charge density [57-60].

In case of tetrazole, the inhibition effect is due to interaction of π electron of phenyl and tetrazole ring as well as the presence of electron donor nitrogen through which it forms a bond with vacant d- orbital of the atom of the metal at the interface.

Generally, two modes of adsorption are considered on the metal surface in acid media. In first mode, the neutral molecules may be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the hetero atoms and iron [61]. The inhibitor molecules can also get adsorbed on the mild steel surface on the basis of donor–acceptor interactions between their π-electrons and vacant d-orbitals of surface iron. In second mode, since it is well known that it is difficult for the protonated molecules to approach the positively charged mild steel surface due to the electrostatic repulsion. Since Cl have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favour more adsorption of the positively charged inhibitor molecules, the protonated inhibitors adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus, there is a synergism between adsorbed Cl ions and protonated inhibitors [62-64].

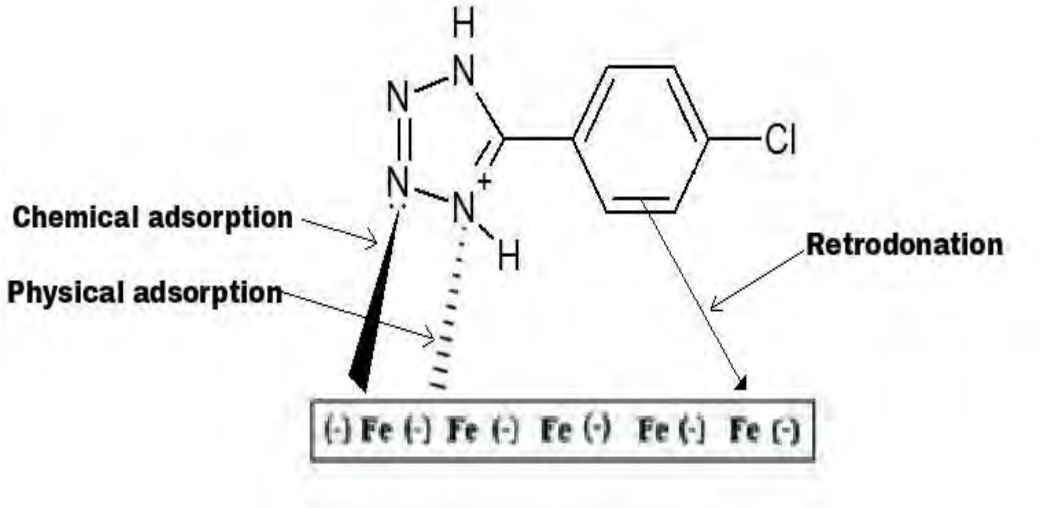


Figure 3.14: Pictorial representation of adsorption of one of the tetrazole Derivative on MS surface in 1M HCl

In the present study, the efficiency of the studied tetrazoles follows the order 5-(4-chlorophenyl) tetrazole>5-amino tetrazole>5-phenyl tetrazole. The best performance of Cl-PT as corrosion inhibitors over ATZ and PTZ may be attributed to the presence of –Cl group in Cl-PT. The nucleophilic (electron releasing) character of –Cl group is higher than the electron withdrawing. ATZ possess electron donating substituent (-NH_2) hence exhibit higher corrosion inhibition efficiency as compared to PTZ [65].

3.7. Conclusion

The corrosion behaviour of mild steel in 1 M HCI in absence and presence of tetrazole compounds was investigated using the weight loss, open circuit potential and potentiodynamic polarization techniques and surface analytical techniques. From the result obtained the following conclusion can be drawn:

1. The investigated compounds are good inhibitors and act as mixed type inhibitors for mild steel corrosion in 1 M HCl.

2. Reasonably good agreement was observed between the values of IE obtained by the weight loss and electrochemical measurements. The order of % IE of these

investigated compounds was in the following order: 5-(4-chlorophenyl) tetrazole>5-amino tetrazole>5-phenyl tetrazole.

3 The data obtained from weight loss technique for the studied inhibitors fit well in to Langmuir adsorption isotherm.

4. Polarization studies showed that all studied tetrazoles act as mixed inhibitor.

5. The thermodynamic parameters revealed that the inhibition of corrosion by investigated compounds is due to the formation of a physically adsorbed film on the metal surface.

6. The negative values of ΔG^0_{ads} indicate spontaneous adsorption of the inhibitors on the mild steel surface.

7. The surface morphology techniques showed that the mild steel specimen had smoother surfaces in the presence of inhibitors due to formation of protective film of adsorbed inhibitors on the metal surface which prevented corrosion.

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Chapter 4

A THEMODYNAMICAL, ELECTROCHEMICAL, AND SURFACE STUDIES FOR CORROSION INHIBITION OF MILD STEEL BY BENZOTRIAZOLE, 1-ACETYL-1H-BENZOTRIAZOLE AND 1-BENZOYL-1H-BENZOTRIAZOLE IN 1M HCl

Chapter 4

A THEMODYNAMICAL, ELECTROCHEMICAL, AND SURFACE STUDIES FOR CORROSION INHIBITION OF MILD STEEL BY BENZOTRIAZOLE, 1-ACETYL-1H-BENZOTRIAZOLE AND 1-BENZOYL-1H-BENZOTRIAZOLE IN 1M HCl SOLUTION.

4.1 INTRODUCTION

Mild steel is the most common choice of material which is extensively used in the production and transportation of crude oil in the oil and natural gas industry [1].The main problem concerning mild steel application is its relatively low corrosion resistance in acidic solutions [2]. Hydrochloric acid solutions are widely used for acid cleaning, industry acid pickling, oil well acidizing and acid descaling [3].The strong acid medium can cause structural damage to mild steel . Therefore, the use of inhibitors is one of the most practical methods for the protection of metal against corrosion in acid media [4].

The corrosion inhibition in oil and gas field is complicated and requires specialty inhibitors depending on the area of application such as in refineries, wells, recovery units, pipelines etc. Combating corrosion in oil and gas industry is paramount since the economic loss in these industries due to corrosion is extremely high. Among the various methods to combat corrosion in oil and gas industry, the use of corrosion inhibitor is one of the best and economic methods. There are many types of corrosion inhibitors, broadly classified in to anodic, cathodic and mixed corrosion inhibitor. They protect the surface of the metal either by merging with them or reacting with the impurities in the environment that may cause corrosion. Corrosion inhibitors may act in a number of ways: It may restrict rate of anodic process or cathodic process by simply blocking active sites on metal surface. Alternatively it may act by increasing the potential of metal surface so that the metal enters in passivation region where the natural oxide film is formed. A further mode of action of some inhibitors is that the inhibiting compounds contribute to the formation of a thin layer on the surface which prevents the metal surface [5-7]. Factor to be considered before using a corrosion inhibitor in the oil and gas industry include toxicity, environmental friendliness, and cost. Organic corrosion inhibitors are more effective than inorganic compounds. Many of the commercial corrosion inhibitors used in oil and natural gas industry are unique mixtures that may contain surfactant, film enhancer, demulsifier or oxygen scavengers in addition to inhibitor moiety [8-10].A variety of organic compounds act as corrosion inhibitors for mild steel during the acidizing procedure in the presence of HCl, including acetylenic alcohols, aromatic aldehydes, amines, amides, nitrogen (N) containing heterocylics, nitriles, triazoles ,tetrazoles, pyridine and its derivatives, thiourea derivatives and quinoline derivatives[11-14] . In order to use corrosion inhibitors in oil and natural gas industry, the inhibitor must be compatible with the expected environment, economical and not only provide great protection to metal but also should not cause any significant undesirable side effects which might affect the operation/ process[15-17] .

Nitrogen-based organic compounds, such as imidazoline and its derivatives, have been used successfully to protect mild steel in oil and gas wells and pipelines from carbon dioxide (CO_2) and hydrogen sulfide (H_2S) corrosion. These organic compounds inhibit the corrosion of mild steel by adsorption on the metal-solution interface thereby creating a barrier that prevents the active ions in the corrosion reactions to get to the surface. However, despite extensive use of imidazoline corrosion inhibitors the mechanism of inhibition remains poorly understood. Therefore, in order to develop more cost-effective inhibitors, a better understanding of the mechanism of inhibition of current and new inhibitors is needed [18].

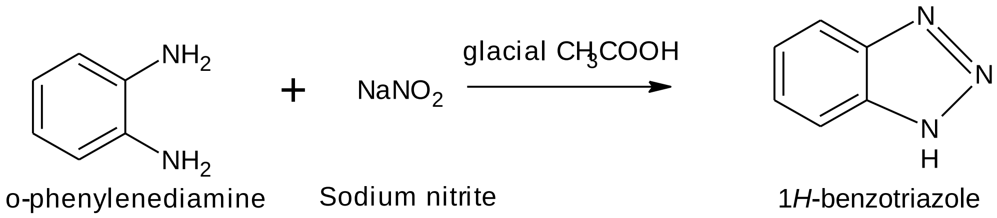
The purpose of this study is to evaluate benzotriazole (BTZ) and its derivatives i.e 1-acetyl-1H-benzotriazole (ABTZ) and 1-benzoyl-1H-benzotriazole (BBTZ) as corrosion inhibitors for mild steel in 1M HCl solution. The inhibitory mechanism of these organic compounds was discussed based on the analysis of the Langmuir adsorption isotherm, weight loss, thermodynamic, polarization and surface studies.

4.2 Synthesis

4.2.1Benzotriazole

10.8 gm of o-phenylenediamine was added to a mixture of 12 gm (11.5 ml) of glacial acetic acid and 30 ml of water, which was cooled to 15^0C. Solution of 7.5 gm of sodium nitrite in 15 ml water was added all at ones, the mixture being stirred with the glass rod or by slow mechanical stirrer .The temperature increased slowly to

85^0C and then cooled slowly. When temperature was 45^0C the mixture was chilled in an ice bath for 30 minutes. A pale brown solid separated by filtration. Recystallisation was done using benzene as the solvent [19].



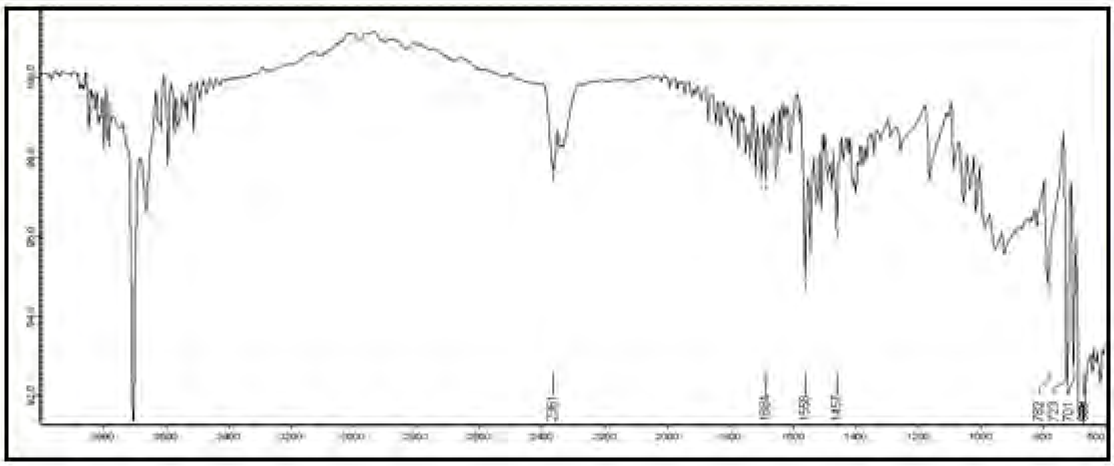
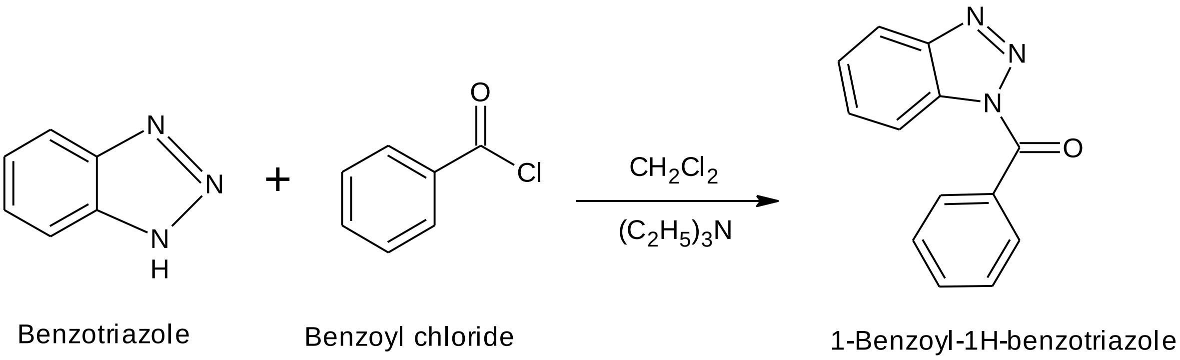


Figure 4.1: FTIR spectrum of synthesized Benzotriazole

The FTIR spectrum of Benzotriazole is shown in figure 4.1. In the spectrum the peaks appeared at around 3500 cm^{-1} to 3900 cm^{-1} corresponds to N-H stretching vibration. The band appeared at around 1457 cm^{-1} to 1604 cm^{-1} corresponds to C=C stretching vibration. The peak at around 1559 cm^{-1} belongs to C=N stretching vibration. The peaks at around 1080 cm^{1} to 1296cm^{-1}contributes to C-N stretching vibration and absorption peak at around 1600 cm^{-1}belongs to N-H bending vibration.

4.2.2 1-Benzoyl-1H-benzotriazole

To a solution of benzotriazole (11.9 g ,0.1 mole) in anhydrous dichloromethane (200 ml) at 0^0 C under nitrogen, triethyl amine (17 ml ,0.12 mol) was added drop wise, followed by addition of benzoyl chloride (0.11 mol).The resulting mixture was stirred at room temperature for 1-2 hours. The reaction was quenched at this temperature with hydrochloric acid (2 N,200mL), and the organic phase was separated with hydrochloric acid (2N,2x50 mi) and water (50 ml) sequentially .The organic extract were dried over anhydrous magnesium sulphate , filtered and evaporated to dryness to give a white powdery solid which was purified by recrystallisation from water[20].



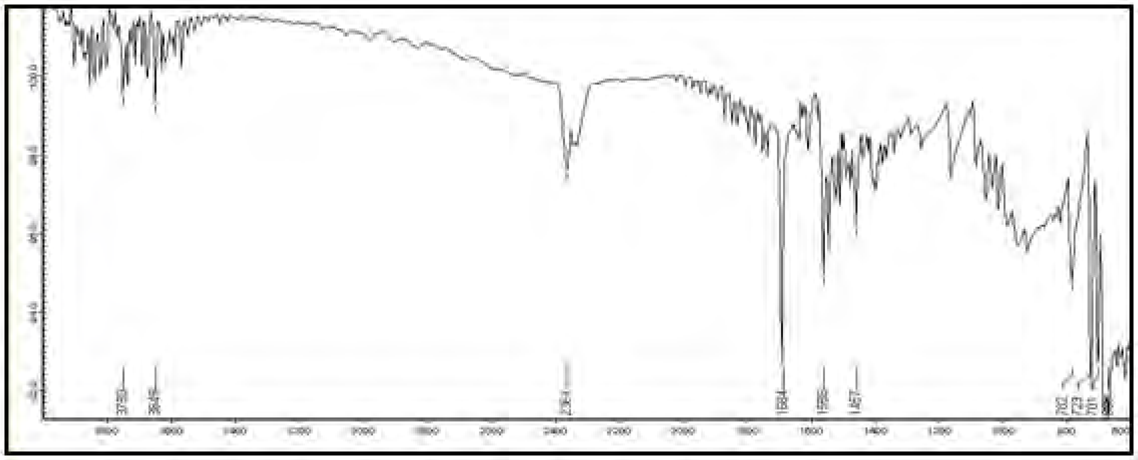
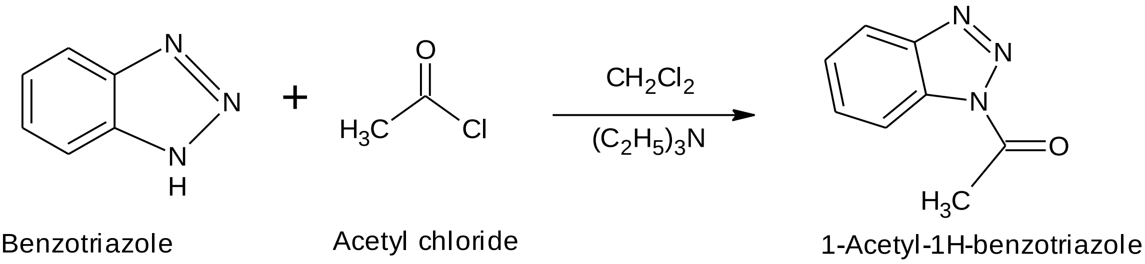


Figure 4.2: FTIR spectrum of synthesized 1-Benzoyl-1H- benzotriazole

The FTIR spectrum of 1-benzoyl-1H-benzotriazole is shown in figure 4.2.The peaks at around 3649 $cm^{-1}$to 3750 cm^{-1} belongs to N-H stretching vibration. The absorption peaks at 1400cm^{-1} to1600 cm^{-1} prove the existence of benzene ring. The absorption peak at 1684cm^{-1}contributes to C=O stretching vibration. The peak at 1558 $cm^{-1}$and 1200 are C-N-H bending vibration absorption and C-N stretching vibration respectively, and the absorption at 1457 cm-1 contributes to N=N bending vibration. The peaks at around 723 cm^{-1} and 782 cm^{-1} belong to C-H rocking and bending vibration.

4.3.3 1-Acetyl-1H-benzotriazole

To a solution of benzotriazole (11.9 g ,0.1 mole) in anhydrous dichloromethane (200 ml) at 0^0 C under nitrogen, triethyl amine (17 ml ,0.12 mol) was added drop wise, followed by addition of acetyl chloride (0.11 mol).The resulting mixture was stirred at room temperature for 1-2 hours. The reaction was quenched at this temperature with hydrochloric acid (2 N,200ml), and the organic phase was separated with hydrochloric acid (2N,2x50 mi) and water (50 ml) sequentially .The organic extract were dried over anhydrous magnesium sulphate , filtered and evaporated to dryness to give a white powdery solid which was purified by recrystallisation from water[20].



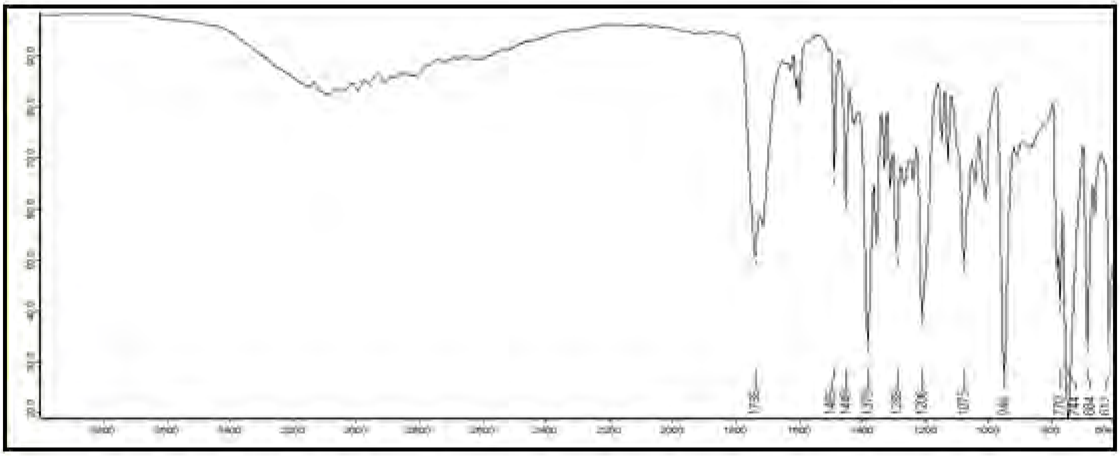


Figure 4.3: FTIR spectrum of synthesized 1-Acetyl-1H-benzotiazole

The FTIR spectrum of 1-Acetyl-1H-benzotriazole is shown in figure 4.3.The absorption peak at 1736cm^{-1} belongs to C-O stretching vibration. The absorption peaks around 1400 cm^{-1} to 1600 cm^{-1} corresponds to C=C stretching vibration. The absorption at 1449 cm^{-1}contributes to N-H bending vibration and the band appeared at around 1075cm^{-1} to 1206 cm^{-1} corresponds to C-N stretching vibration. The peaks at 600 cm^{-1} to 700 cm^{-1}corresponds to C-H rocking and bending vibration.

4.3. Result and Discussion

4.3.1 Weight loss Measurement

The loss in the weight of mild steel coupons in 1M HCl in absence and presence of different concentration of triazoles was determined after 24 hours immersion at 298 K. The percentage inhibition efficiency (%E) and degree of surface coverage (θ) were calculated and presented in Table.4.1 It can be observed from the table that the inhibition efficiency increased with increase in concentration of inhibitors and the compounds acted as very good corrosion inhibitors for corrosion of mild steel in 1M HCl. The maximum efficiency for each compound was achieved at 500 ppm concentration. The parameter (θ) which represents the part of the metal surface covered by the inhibitors molecules increased as the inhibitors concentration increased. The corrosion inhibition can be attributed to the adsorption of inhibitors at the metal /acid interface [21-22].

Inhibitor	**Concentration (ppm)**	**Weight loss (mg)**	**Corrosion rate ($mgcm^{-2}h^{-1}$)**	**Surface coverage (θ)**	**E (%)**
Blank	0.00	235	32.638	-	-
BTZ	100	184	25.555	0.2170	21.70
	200	136	18.889	0.4190	41.90
	300	92	12.778	0.6080	60.80
	400	51	7.083	0.7840	78.40
	500	12	1.667	0.9490	94.90
BBTZ	100	104	14.444	0.5574	55.74
	200	74	10.277	0.6851	68.51
	300	56	7.778	0.7617	76.17
	400	48	6.667	0.7957	79.57
	500	35	4.861	0.8510	85.10
ABTZ	100	122	16.944	0.480	48.00
	200	113	15.694	0.519	51.90
	300	78	10.833	0.6680	66.80
	400	63	8.750	0.732	73.20
	500	52	7.222	0.778	77.80

Table 4.1: The weight loss parameter obtained for mild steel in 1M HCl containing different concentration of triazoles at 298K

4.3.2 Effect of Temperature

Effect of temperature and thermodynamic activation parameters to elucidate the mechanism of inhibition and to determine the thermodynamic parameters of the corrosion process weight loss measurements were performed at 298, 308,318,and 328K in absence and presence of inhibitors at 500 ppm concentration. The corresponding data are shown in Table 4.2.

Inhibitors	Tempearture K	Corrosion rate ($mgcm^{-2}h^{-1}$)	E (%)
1 M HCl	298	32.638	-
	308	43.055	-
	318	54.861	-
	328	66.388	-
	298	1.667	94.89
BTZ	308	4.722	85.50
	318	9.167	71.93
	328	13.055	59.60
	298	4.8611	85.10
BBTZ	308	8.4722	74.20
	318	12.222	62.70
	338	17.947	45.10
	298	7.222	77.87
ABTZ	308	11.388	65.20
	318	15.277	53.18
	328	18.888	42.20

Table 4.2: Effect of triazoles concentration on corrosion rate and inhibition efficiency for mild steel in 1M HCl at different temperature

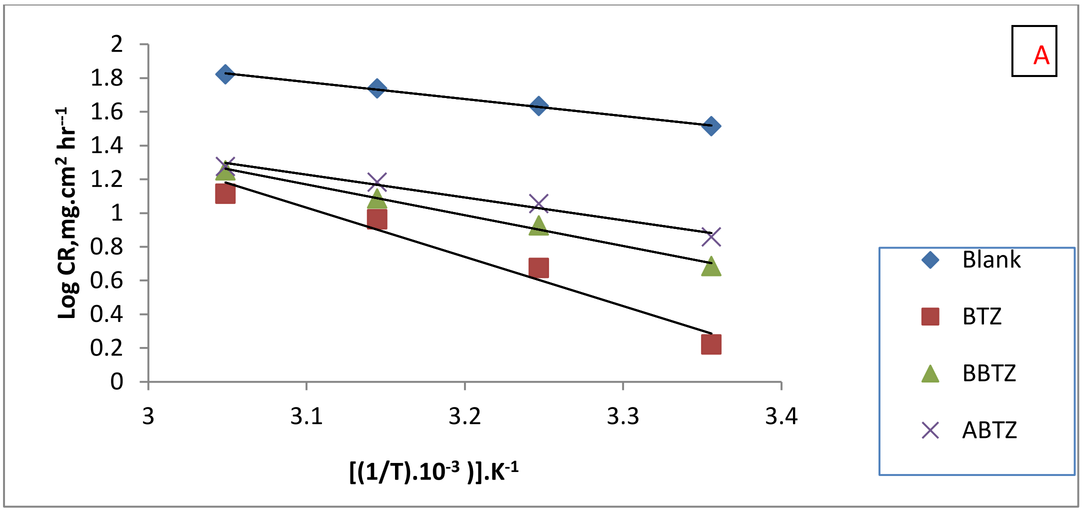
Inspection of Table 4.2 showed that corrosion rate increased with increasing temperature both in uninhibited and inhibited solutions while the inhibition efficiency of inhibitors decreased with temperature. A decrease in inhibition efficiencies with the increase in temperature in the presence of the compounds might be due to weakening of physical adsorption. In order to calculate activation parameters for the corrosion process, Arrhenius Eq. (1) and transition state Eq. (2) were used [23]:

$$logCR = \frac{-\mathrm{E_a}}{2.303\mathrm{RT}} + \log \mathrm{A} \quad (1)$$

An alternative formulation of the Arrhenius equation is,

$$CR = \frac{\mathrm{RT}}{\mathrm{Nh}} \exp\left(\frac{\Delta \mathrm{S}}{\mathrm{R}}\right) \exp\left(-\frac{\Delta \mathrm{H}}{\mathrm{RT}}\right) \tag{2}$$

Where CR is the corrosion rate, R the gas constant, T the absolute temperature, A the pre exponential factor, h the Plank's constant and N is Avogadro's number, E_a the activation energy for corrosion process , ΔH the enthalpy of activation and ΔS the entropy of activation. The apparent activation energy (E_a) at 500 ppm concentration of inhibitors were determined by linear regression between Log of CR and 1/T (Fig.4.4 (A)) and the result is shown in table 4.3. The linear regression coefficient was close to 1, indicating that the steel corrosion in hydrochloric acid can be elucidated using the kinetic model. Inspection of table 4. 3 showed that the value of Ea determined in 1M HCl containing inhibitors is higher (25.93 kJ mol^{-1} for BTZ, 34.89 kJ mol^{-1} for BBTZ and 55.89kJ mol^{-1} for ABTZ) than that for uninhibited solution (19.28 kJ mol-1). The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage [24]. Szauer and Brand explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with increase in temperature. As adsorption decreases more desorption of inhibitor molecules occurs because these two opposite processes are in equilibrium. Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of steel comes in contact with aggressive environment, resulting in increased corrosion rates with increase in temperature[25]. Fig.4.4(B) showed a plot of Log of (CR/T) versus 1/T. The straight lines are obtained with a slope (-ΔH /2.303R) and an intercept of [log (R/Nh + ΔS /2.303R)] from which the values of the values of Δ H and a ΔS are calculated and are given in Table 4.3. Inspection of these data revealed that the thermodynamic parameters (ΔH and ΔS) for dissolution reaction of steel in 1M HCl in the presence of inhibitors is higher than that of in the absence of inhibitors. The positive sign of ΔH reflect the endothermic nature of the steel dissolution process suggesting that the dissolution of steel is slow in the presence of inhibitor [26-30]. Also, the value of entropy of activation is negative. The negative value of entropy imply that the activated complex in the rate determining step represents an association rather than dissociation, means that decrease in the disorder of the system due to adsorption of inhibitors molecules on to the metal surface [31-34].



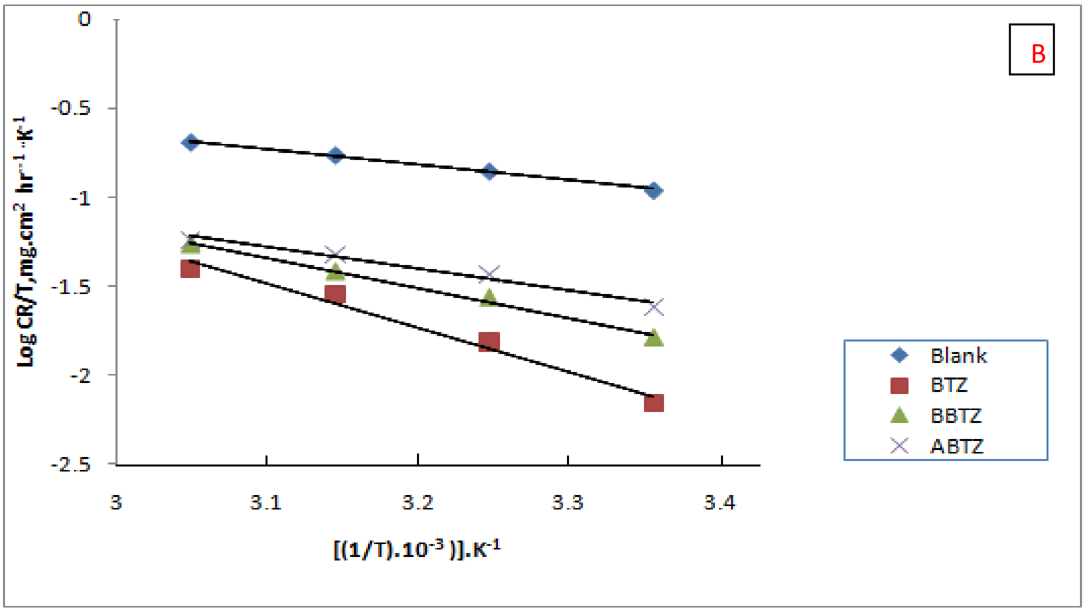


Figure 4.4: Arrhenius plots of (A) log CR vs. 1000/T and (B) Transition state plots of (b) log (CR/T) vs. 1000/T for mild steel in 1.0M HCl solution in the absence and presence 500ppm of BTZ, BBTZ and ABTZ.

Inhibitors	E_a (kJ mol^{-1})	ΔH(kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
1.0M HCl	19.28	16.69	-159.81
BTZ	25.93	21.44	-148.94
BBTZ	34.89	32.28	-123.11
ABTZ	55.89	47.71	-78.001

Table 4.3: Thermodynamic activation parameter for mild steel in 1M HCl in absence and presence of optimum concentration (500 ppm) of BTZ, BBTZ and ABTZ.

4.3.3. Adsorption Isotherm

Adsorption isotherms are often used to demonstrate the performance of organic adsorbent type inhibitors and important in determining the mechanisms of organic electrochemical reactions. The most frequently used adsorption isotherms are Langmuir, Temkin and Frumkin isotherms which describes relation between surface coverage θ and bulk concentration [35]. The values of surface coverage θ were evaluated using the value of %IE resulted from weight loss experiment in 1M HCl. Figure 4.5 shows a plot C/θ v/s C gave a straight line with a coefficient $(R)^2$ value very close to unity. It indicates that corrosion control take place via adsorption. The adsorption of inhibitors molecules on mild steel surface obeys Langmuir adsorption isotherm. The equation can be represented as:

$$K_{ads} = \frac{\theta}{C(1-\theta)} \tag{3}$$

The equation can be rearranged to

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \tag{4}$$

Where, C_{Inh} is the concentration of inhibitor, θ is surface coverage and K_{ads} is the equilibrium constant for adsorption-desorption process. The K_{ads} is related to standard free energy (ΔG^0_{ads}) of adsorption by following relation.

Free energy of adsorption: $(\Delta G^0_{ads}) = -2.303RT \log (55.5\, K_{ads})$. (5)

Where R is the universal gas constant, T is the absolute temperature in K, and the numerical value 55.5 represent the molar concentration of water in acid solution.The calculated values of K_{ads} and $\Delta G^0{}_{ads}$ at studied temperature is listed in Table 4.4.

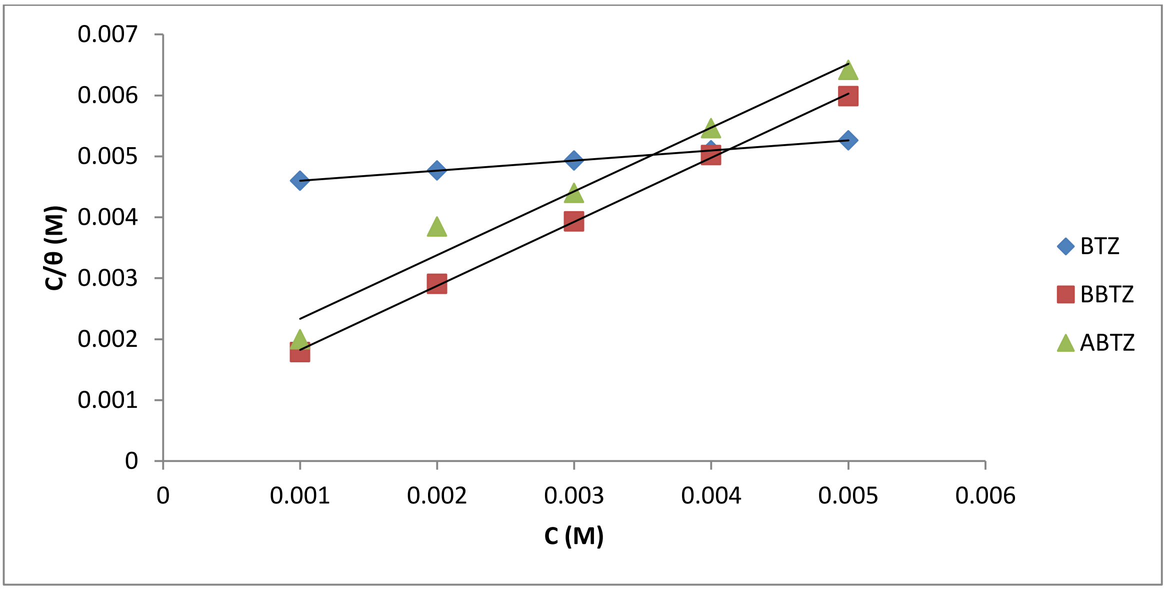


Figure 4.5: Langmuir adsorption isotherm plot for the adsorption of triazole derivatives on mild steel surface in 1.0M HCl solution

Inhibitors	**slope**	**K_{ads} (M^{-1})**	**Regression coefficient**	**$\Delta G^0{}_{ads}$ ($kJ.mol^{-1}$)**
Benzotriazole	0.165	250	0.999	-23.635
1-Benzoyl-1H-benzotriazole	1.00	3334	0.999	-30.05
1-Acetyl-1H-benzotriazole	1.00	1000	0.969	-27.07

Table 4.4: Slope, equilibrium constant, regression coefficient and free enthalpy of adsorption of in benzotriazole, 1-benzoyl-1H-benzotriazole and 1-acetyl-1H-benzotriazole in 1 M HCl.

Generally the magnitude of ΔG_{ads} around -20 kJ/mol less negative indicates physisorption and those around -40kJ/mol or more negative indicate chemisorption. In the present case calculated values for the benzotriazole, 1-benzoyl-1H-benzotriazole and 1-acetyl-1H- benzotriazole are -23.635, -30.05 and -27.07 respectively. This indicated that the adsorption of inhibitors on the mild steel surface involved both physical and chemical process [36-42].

4.4 Electrochemical Measurements

4.4.1 Open Circuit Potential (OCP) Curves

The variation of open circuit potential with time for mild steel in 1M HCl solutions without and with triazoles is shown in figure 4.6 to Figure 4.8 respectively. The plot shows a clear change in the OCP curve due to the presence of the inhibitors. It is clear that the curves shift in positive direction in the presence of benzotriazole and its derivatives. The inhibited solution exhibited higher positive open circuit potential value, when compared with those obtained in blank solution, indicating formation of the protective film due to the adsorption of inhibitors on the mild steel surface. The continuous shift to the positive direction can be attributed to the formation of protective and inhibitive film, which increase with increasing the inhibitor concentration and exposure period [43].

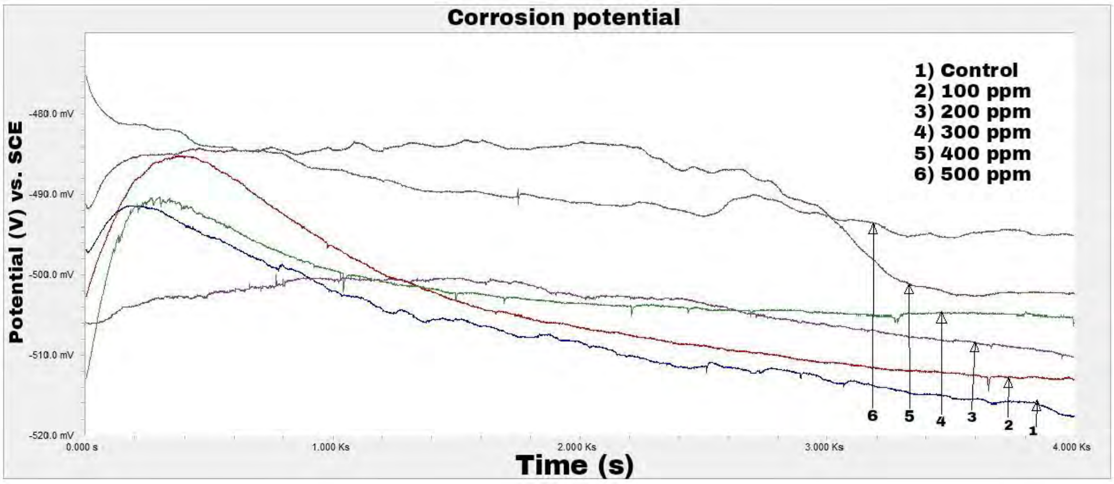


Figure 4.6: Open circuit potential of mild steel without and with different concentration of BTZ inhibitor in 1M HCl.

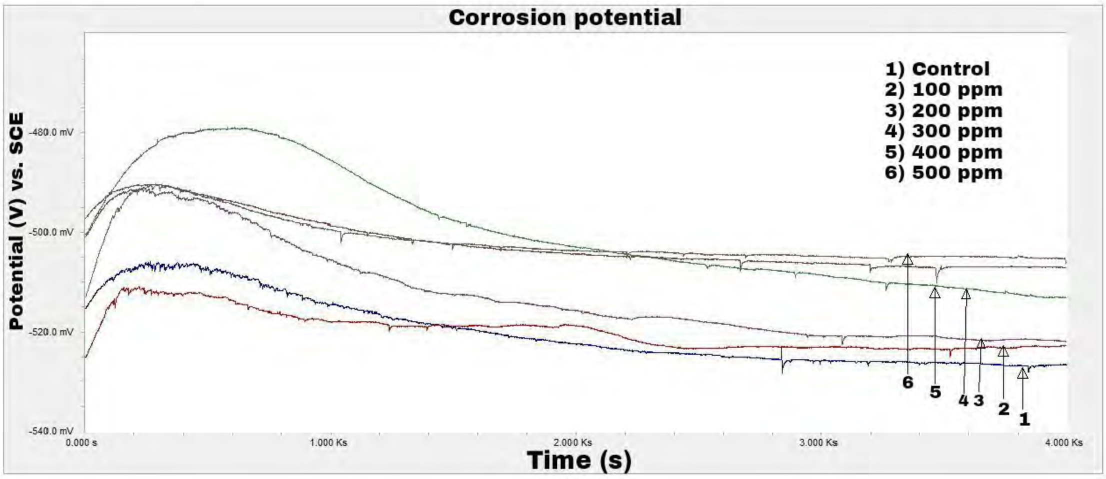


Figure 4.7: Open circuit potential of mild steel without and with diffirent concentration of BBTZ inhibitor in 1M HCl.

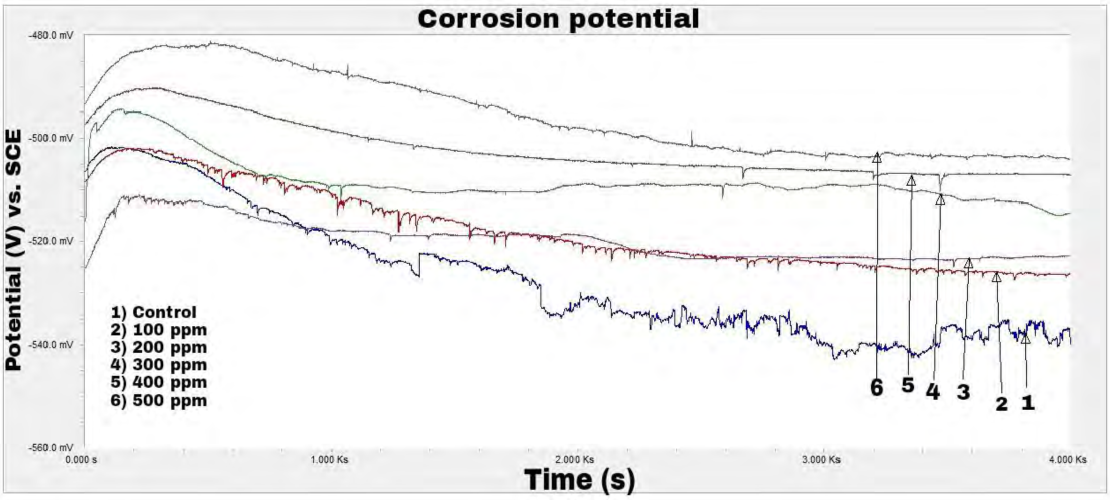


Figure 4.8: Open circuit potential of mild steel without and with diffirent concentration of ABTZ inhibitor in 1M HCl.

4.4.2 Potentiodynamic Polarisation Studies

Polarization measurements were carried out in order to get information regarding kinetics of anodic and cathodic reactions. The obtained polarization curves for mild steel in 1M HCl in absence and presence of different concentration of benzotriazole, 1-benzoyl-1H-benzotriazole and 1-acetyl-1H-benzotriazole are shown in figure 4.9 to 4.11 respectively. Corrosion kinetic parameter E_{corr}, I_{orr}, Tafel (β_a ,β_c) and inhibition efficiency are depicted in Table 4.5. It is clear from figures,4.9,4.10,4.11 that the presence of triazoles decreases both cathodic and anodic slopes with the increased inhibitor concentration. This could be attributed to the adsorption of inhibitor on to metal surface. Since both anodic dissolution of iron and hydrogen evolution is suppressed the studied inhibitors behave like mixed type inhibitors [44-47].

The results reported in Table 4.4 indicates that the I_{corr} values decreased significantly with increasing concentration of triazoles and maximum inhibition efficiency of 93.65%,85.73% and 78.52% were obtained at 500 ppm concentration of triazoles. This is due to adsorption of inhibitors molecules on to metal surface. Further the concentration of triazoles having less effect on corrosion potential (E_{corr}) suggest that compound were mixed type inhibitors and adsorbed on the surface thereby blocking the corrosion reaction. As previously reported in the presence of inhibitor if E_{corr} shift is greater than 85 mV with respect to E_{corr} in uninhibited solution, the inhibitor can be considered as cathodic or anodic type otherwise it is mixed. In present study maximum deviation range was less than 85 mV, suggesting that triazoles behave as mixed type inhibitors [48-52]

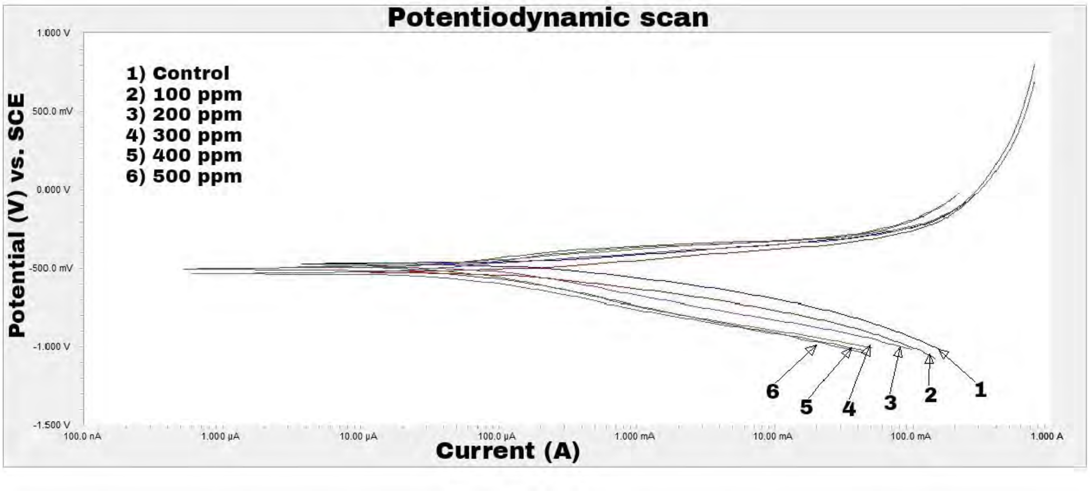


Figure 4.9: Potentiodynamic polarization of mild steel without and with different concentration of BTZ in 1M HCl.

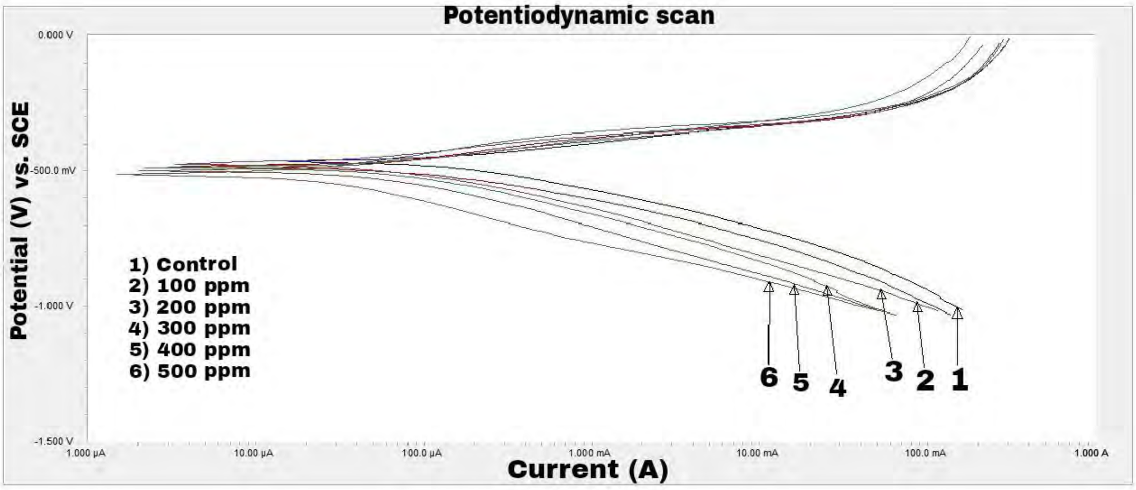


Figure 4.10: Potentiodynamic polarization of mild steel without and with different concentration of BBTZ in 1M HCl.

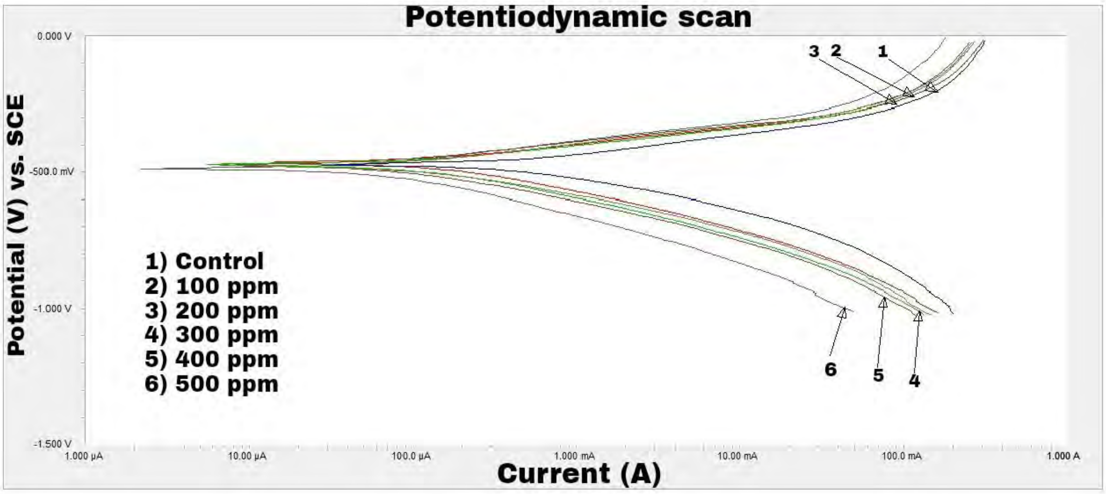


Figure 4.11: Potentiodynamic polarization of mild steel without and with different concentration of ABTZ in 1M HCl.

Concentration of Inhibitors (ppm)	$-E_{corr}$ (mv)	I_{corr} ($\mu A/cm^2$)	β_a (v/dec)	β_c (v/dec)	IE %
1.0M HCl	-471.0	197.0	91.30 e^{-3}	163.4 e^{-3}	-
BTZ					
100	-524.0	157.0	86.80 e^{-3}	142.8 e^{-3}	20.30
200	-488.0	108.0	70.40 e^{-3}	160.2 e^{-3}	45.18
300	-495.0	74.60	66.10 e^{-3}	155.8 e^{-3}	62.13
400	-483.0	46.70	85.60 e^{-3}	100.8 e^{-3}	76.29
500	-504.4	12.50	82.40 e^{-3}	109.3 e^{-3}	93.65
BBTZ					
100	-483.0	76.30	94.10 e^{-3}	129.6 e^{-3}	57.13
200	-487.0	58.60	83.30 e^{-3}	142.5 e^{-3}	67.07
300	-471.0	46.90	80.00 e^{-3}	139.4 e^{-3}	73.65
400	-499.0	38.00	84.00 e^{-3}	138.2 e^{-3}	78.65
500	-513.0	25.40	111.2 e^{-3}	151.6 e^{-3}	85.73
ABTZ					
100	-494.0	104.0	77.20 e^{-3}	150.3 e^{-3}	47.20
200	-491.0	92.19	90.13 e^{-3}	142.1 e^{-3}	53.20
300	-488.0	62.84	59.34 e^{-3}	144.7e^{-3}	68.10
400	-485.0	52.30	74.33 e^{-3}	132.5 e^{-3}	73.45
500	-485.0	42.30	53.67 e^{-3}	124.1 e^{-3}	78.52

Table 4.5: Polarization curves for corrosion of mild steel in 1M HCl in the absence and presence of different concentration of (a) BTZ, (b) ABTZ, (c) ABTZ.

4.5 Surface Studies

4.5.1 Scanning Electron Microscopic (SEM) Analysis

A micrograph of the polished mild steel surface before immersion in 1M HCl is shown in Figure 4.12 (A).The micrograph shows the presence of smooth surface without pits. The photograph of mild steel after immersion in 1M HCl is shown in

Figure 4.12 (B). The photograph indicates that surface was strongly damaged in absence of inhibitors. A photograph of mild steel after immersion in 1M HCl solution containing 500 ppm of Benzotriazole,1-Benzoyl1-H-benzotriazole and 1-Acetyl-1H-benzotriazole is shown in Figure (4.12.(C-E)) It is found that surface is free from pits and it was smooth. Thus we can conclude that in the presence of the inhibitors corrosion was inhibited strongly.

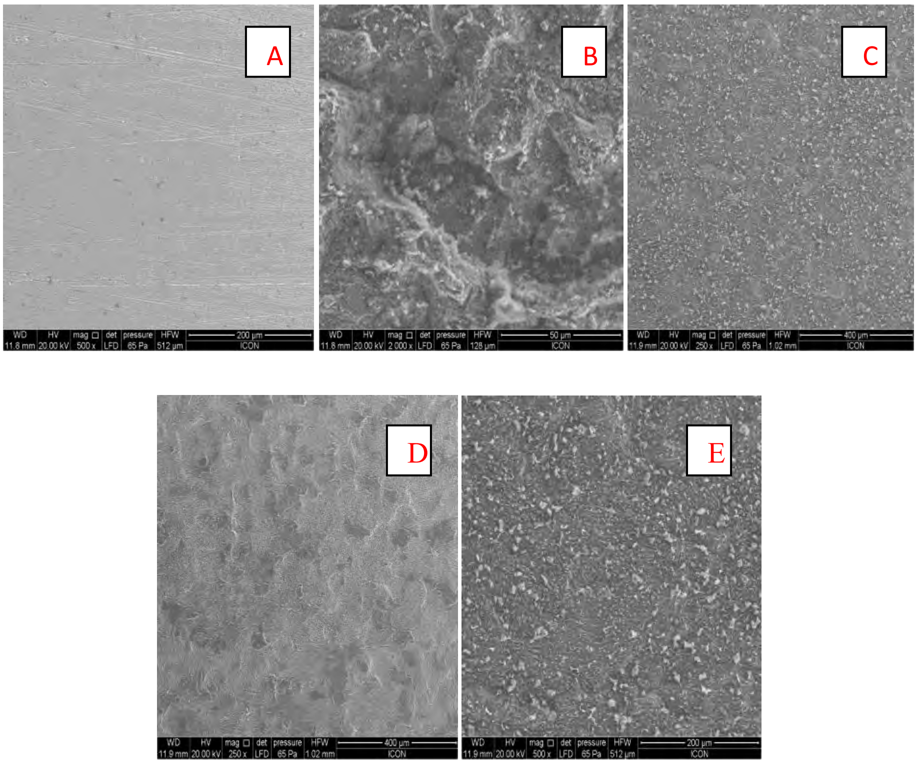
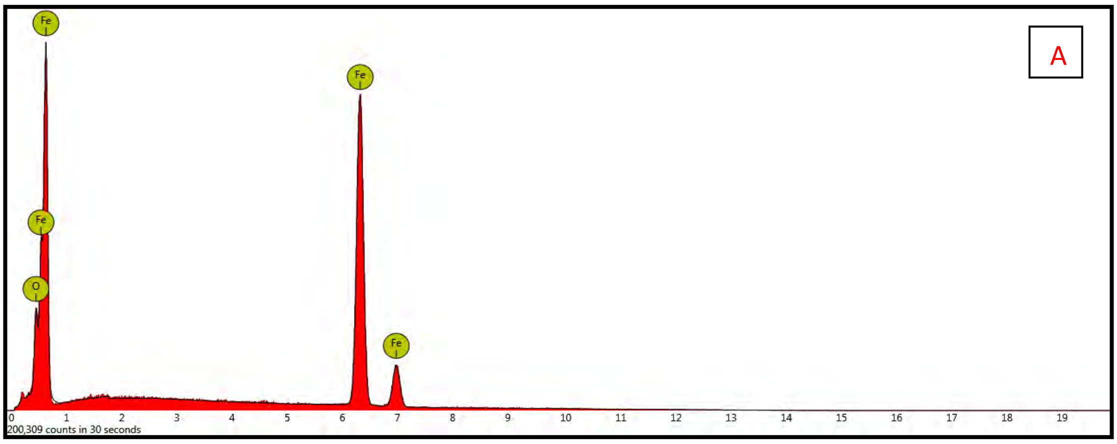


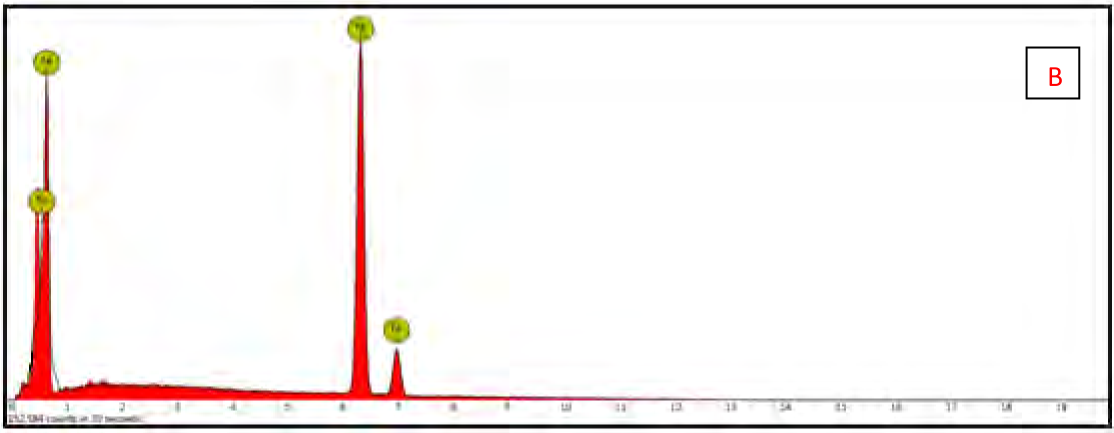
Figure 4.12: SEM of mild steel with (A) Polished, (B) 1M HCl, (C) 500 ppm of BTZ, (D) 500 ppm of BBTZ and (E) 500 ppm of ABTZ.

4.5.2 Energy-dispersive X-ray spectroscopy (EDX)

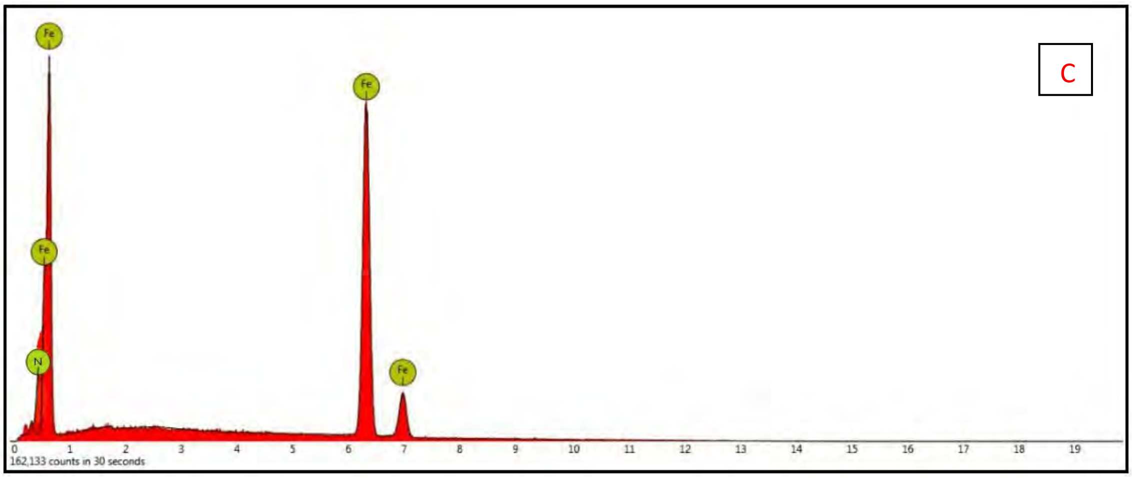
Figure 4.13 shows the spectral profile of mild steel specimens in the absence and presence of benzotriazole, 1-benzoyl1-H-benzotriazole and 1-acetyl-1H-benzotriazole.The spectral profile of the polished mild steel specimen before immersion in 1M HCl shows the signal for Fe and O. After immersion in 1 M HCl the spectral profile shows signal for Fe only. The spectral profile in the presence of benzotriazole shows an additional peak characteristic for existence of nitrogen (N) .The spectral profiles in presence of 1-benzoyl-1H-benzotriazole and 1-acetyl-1H-benzotriazole shows additional peaks characteristic of N and O, indicating the adsorption of inhibitors molecule on the metal surface. EDX investigation thus confirms the polarization data, that the presence of triazole derivatives inhibits the corrosion of mild steel in 1M HCI due to adsorption of its molecules on the mild steel surface preventing it from being corroded easily.



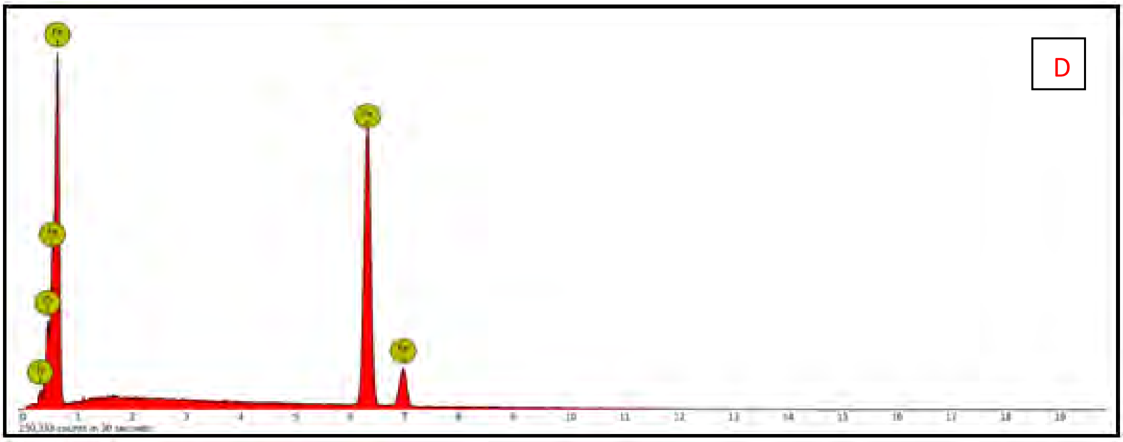
A) Polished sample



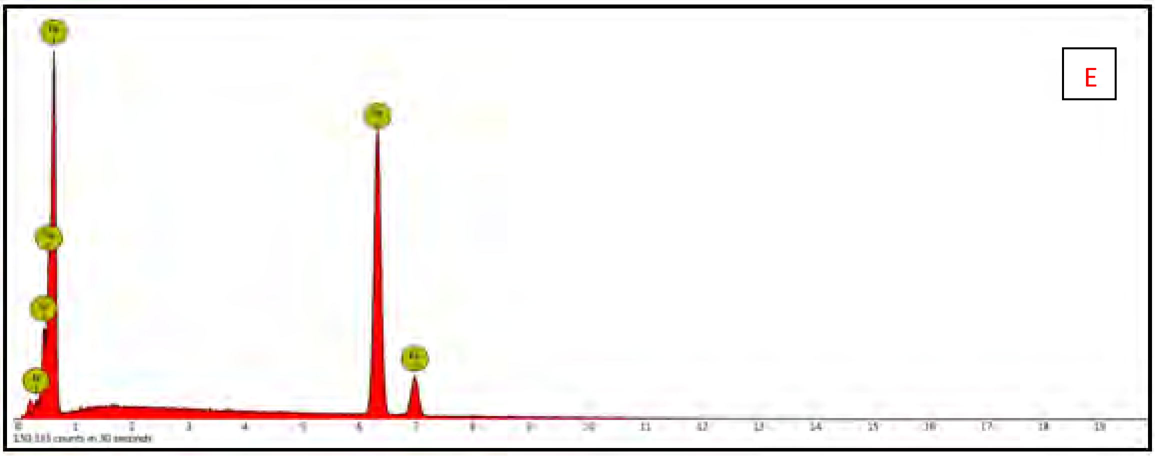
B) Control (1M HCl)



C) 1M HCl+500 ppm BTZ



D) 1M HCl+500 ppm BBTZ



E) 1M HCl+500 ppm ABTZ

Figure 4.13:EDX of mild steel with: (A)Polished, (B) 1M hydrochloric acid, (C) 500 ppm of BTZ, (D) 500 ppm of BBTZ and (E) 500 ppm ABTZ.

4.6 Mechanism of Inhibition

The inhibition effect of benzotriazole, benzoyl benzotriazole and acetyl benzotriazole derivatives towards the corrosion of mild steel in 1M HCl solution may be attributed to the adsorption of these compounds at the metal-solution interface. The inhibition process is a function of the metal, inhibitor concentration and temperature as well as inhibitor adsorption abilities which depends on adsorption sites [53-55] .The mode of adsorption (physisorption and chemisorption) observed could be attributed to the fact that inhibitors contain different donating atoms which can be adsorbed chemically and physically [56-58].Triazole ring can be considered to be a typical example of π excessive N heterocyclic compound[59]. In case of benzotriazole the inhibition effect is due to interaction of pi electrons of benzene and triazole rings as well as the presence of electron-donating atoms such as nitrogen through which benzotriazole form bond with mild steel .similarly the inhibitive effect of benzoyl benzotriazole and acetyl benzotriazole is because of pi electron of benzene and triazole ring, along with hetero atoms such as nitrogen and oxygen through which the inhibitor adsorbed on mild steel surface to form insoluble, stable and uniform film[60].Inhibition efficiency values obtained for the triazoles shows the follows the order BTZ>BBTZ>ABTZ.

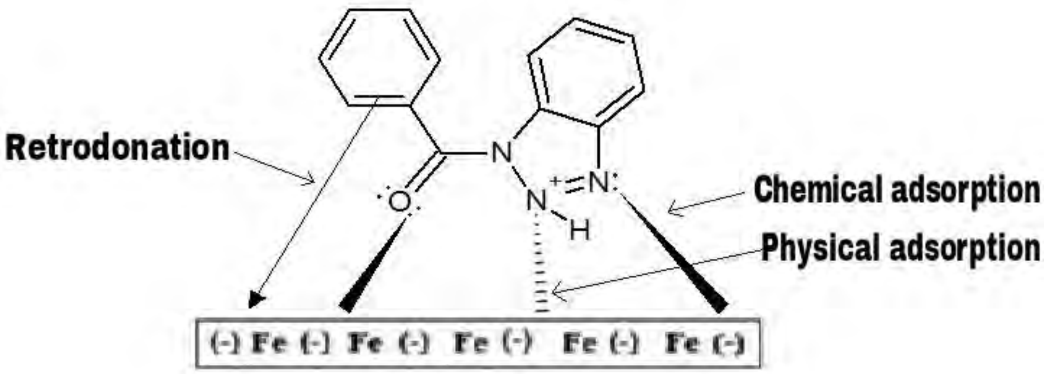


Figure 4.14: Pictorial representation of adsorption of one of the triazole derivative on MS surface in 1M HCl

BTZ exhibit the best inhibitory effect than BBTZ and ABTZ. In BBTZ and ABTZ, the benzoyl (PhCO-) and acetyl (CH_3CO-) group tends to withdraw electrons towards itself, their by decreases the electron density around triazole nitrogen, which results in lower inhibition efficiency. The higher inhibition efficiency of BBTZ as compared to ABTZ attributed to the presence of extra benzene ring of benzoyl group which contain π electrons though which it can form bond with metal.

4.7 Conclusion

1) Benzotriazole and its derivatives i.e 1-acetyl-1H-benzotriazole,1-benzoyl-1H-benzotriazole were found to be effective corrosion inhibitors and acts as mixed type inhibitors for mild steel corrosion in 1M HCl.
2) Inhibition efficiency increases with increasing inhibitor concentration but decreases with increase in temperature.
3) The values of apparent activation energy increases with the increase in the inhibitor concentration. Enthalpy of activation reflects the endothermic nature of mild steel dissolution process. Entropy of activation decreases with increasing inhibitor concentration; hence decrease in the disorder of the system.
4) The adsorption of triazoles on mild steel follows the Langmuir adsorption isotherm.
5) Gibb's free energy, enthalpy and entropy of adsorption indicate that the adsorption process is spontaneous and endothermic and the inhibitor molecules adsorbed on the metal surface through physical adsorption.
6) The results obtained from polarization measurements revealed that triazoles behave as a mixed type of inhibitor.
7) SEM-EDX analysis shows that there was improvement in surface morphology of inhibited mild steel as compared with uninhibited mild steel.

4.8 References

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Chapter 5

ADSORTION AND INHIBITIVE PROPERTIES OF QUINOXALINE DERIVATIVES ON CORROSION OF MILD STEEL IN HYDROCHLORIC ACID SOLUTION

Chapter 5

ADSORTION AND INHIBITIVE PROPERTIES OF QUINOXALINE DERIVATIVES ON CORROSION OF MILD STEEL IN HYDROCHLORIC ACID SOLUTION

5.1 Introduction

Corrosion is common problem encountered in the oil and gas industries. Oil and gas pipelines, refineries and petrochemical plants have serious corrosion problems. Internal corrosion in oil and gas industry is generally caused by temperature ,carbon dioxide (CO_2), hydrogen sulfide (H_2S), water, flow velocity, and surface chemistry of steel [1-2].Various factors have to be considered while dealing with corrosion problems of oil and gas industries. The type of reservoir rocks, the acid used for stimulation, the oil well equipments such as tubing and casings and the operating condition are some of the important factors that affect the corrosivity. Oxygen, which plays such an important role in corrosion, is not normally present in producing formation. It is only at drilling stage that oxygen contaminated fluids are first introduced. Drilling muds, left untreated will corrode not only well casing, but also drilling equipment, pipelines and mud handling equipment. Water and carbon dioxide, produced or injected for secondary recovery, can cause severe corrosion of oil and well steels. Acid used to remove scale, readily attack metals. Hydrogen sulphide (H_2S) poses other problems. Handling all these corrosion situations, with the added complications of high temperature, pressures and stresses involved in drilling or production requires the expertise of corrosion engineer, an increasing key figure in industries [3-7].Combating corrosion in oil and gas industry is paramount since the economic loss in these industries due to corrosion is extremely high. Among the various methods to combat corrosion in oil and gas industry, the use of corrosion inhibitor is one of the best and economic methods.

To avoid the high cost of managing/cleaning spills, down time of shutting down the plant for maintenance, or injury to employees and damage to company integrity, prevention of corrosion by use of corrosion inhibitors (CI) becomes essential. Therefore, very large sums are spent on CIs, as they are a simple, practical and cost effective means of reducing corrosion. CIs are substances that are added in small amounts to the corroding fluid to retard the speed of corrosive attack on the metal surface it contacts [8-11]. They offer surface protection by adsorption of their active functionalities on metal surfaces [12-18]. A thin protective film that acts as a blanket on the metal surface and protects it from the aggressive medium is formed. The inhibitor effectiveness varies with properties, such as its chemical composition, concentration and operating temperature [18-24]. Many compounds that contain functionalities, such as nitrogen, oxygen, multiple bonds, conjugated double bond systems, heteroatoms and aromatic rings, have been found to be efficient CIs for different metals in various media [25-28]. However, some of them are toxic or very expensive, hence the need to source CIs from cheap, sustainable and non-toxic materials.

Quinoxaline derivatives are a very important class of nitrogen-containing heterocycles (containing benzene and pyrazine rings in their structure), as they constitute useful intermediates in organic synthesis. This substructure plays an important role as a basic skeleton for the design of a number of heterocyclic compounds with different biological activities, making this type of compounds important in the fields of (a) medicine: antitumor, anticonvulsant, antimalarial, anti-inflammatory, antiamoebic, antioxidant, antidepressant, antiprotozoal, antibacterial, and anti-HIV agents [29-39] and (b) technology: fluorescent dying agents, electroluminescent materials, chemical switches, cavitands, and semiconductors [40-45]. Quinoxalines are important in the pharmaceutical industry, with antibiotics such as echinomycin, levomycin, and actinoleutin having quinoxaline as part of their structure [46].

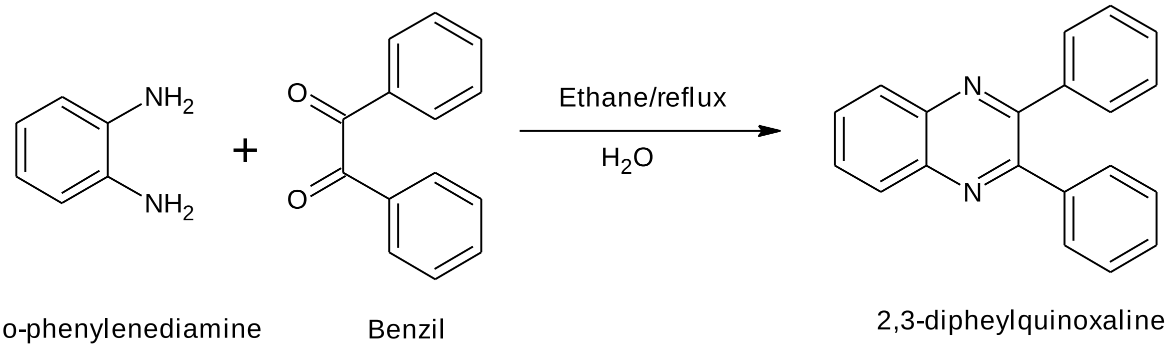
Aoufir et al. [47] have studied the inhibition effect of (E)-3-(4-methoxystyryl)-7-methylquinoxalin-2(1H)-one (SMQ) and 2-(4-methoxyphenyl)-7-methyl-thieno[3,2- b] quinoxaline (TMQ) on the corrosion of mild steel in 1.0 M HCl solution and found that both the inhibitors acted as mixed type. Gaz et al.[48] have studied the anti-corrosive properties of (E)-3-styrylquinoxalin-2(1H)-one (STQ), (E)-1-benzyl-3-(4-methoxystyryl) quinoxalin-2(1H)-one (BMQ) and (E)-3-(2-(furan-2-yl) vinyl) quinoxalin-2(1H)-one (FVQ) on corrosion of mild steel in 1 M HCl and found that the quinoxaline derivatives show good inhibitive property and inhibition efficiency, in the following order: BMQ > FVQ> STQ.

In this chapter we intend to find out inhibition performance of Quinoxaline (QX) and its derivatives namely 2-methyl quinoxaline (2-MQX), and 2, 3-diphenyl quinoxaline (2,3-DPQX) towards corrosion of mild steel in 1M HCl. Surface coverage by these compounds over mild steel substrates in corrosive environment was studied using SEM and EDX .The activation and thermodynamic parameters of dissolution and adsorption were calculated. Possible mechanism of inhibition based on surface analytical and electrochemical studies is explained. The choice of this compound was based on the consideration that it contains many π-electrons and two N atoms which induce greater adsorption of the inhibitor compared with compounds containing only one N atom.

5.2 Synthesis

5.2.1 2, 3-diphenyl quinoxaline.

To the warm solution of 2.1 g of benzil in 8 mL of rectified spirit, mix a solution of 1.1 g (0.01 mol) of o-phenylenediamine in 8 mL rectified spirit. Boil in a water bath for 30 min, add water until a slight cloudiness persists and allow tocool. Filter and recrystallized from aqueous ethanol to give 1.43g of 2, 3-diphenylquinoxaline, m.p.125-126 ^{0}C[49].



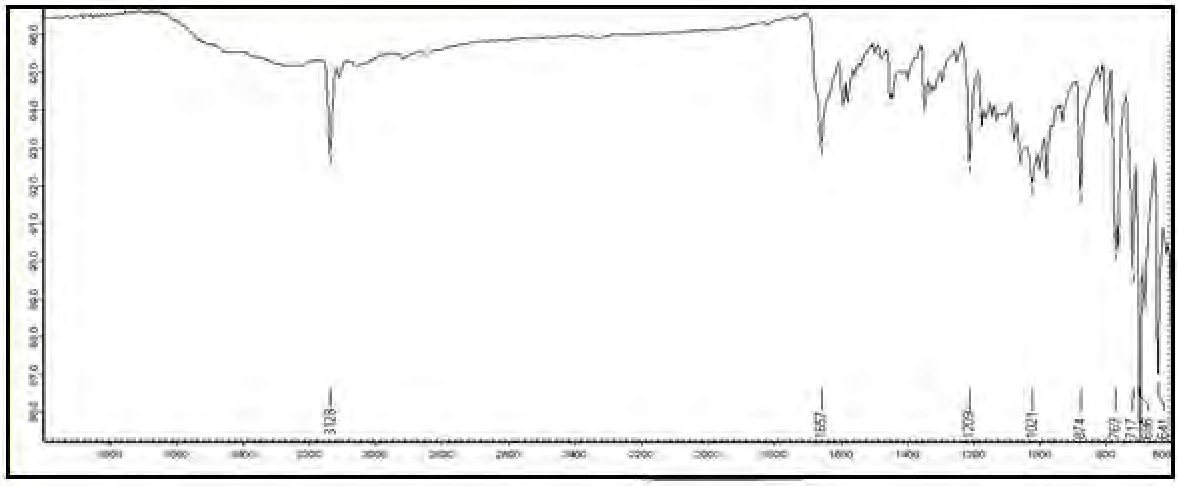
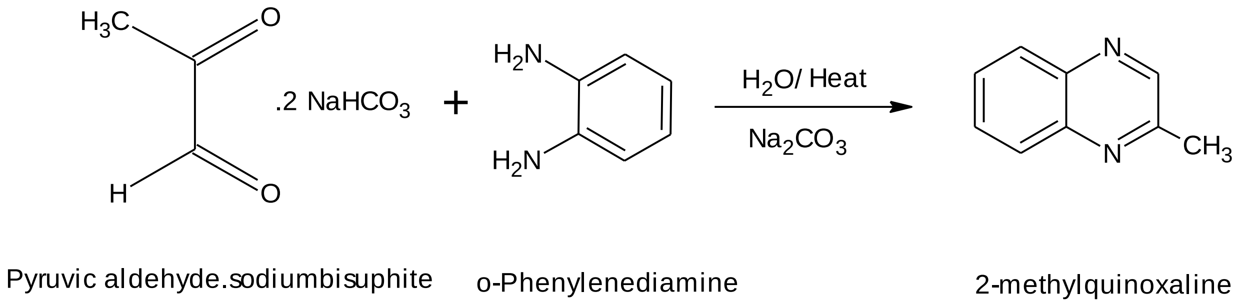


Figure 5.1: FTIR spectrum of synthesized 2, 3-diphenyl quinoxaline

The FTIR spectrum of 2,3-diphenyl quinoxaline shown in figure 5.1.In the spectrum the band appeared at around 1400 cm^{-1} to 1657 cm^{-1} are due to C=C stretching vibration of aromatic ring. The band appeared at around 1021 cm^{-1} to 1209 cm^{-1} corresponds to C-H bending vibration of aromatic phenyl ring. The peak at around 3128 cm^{-1} belongs to aromatic C-H stretching vibration. The peaks at around 717 cm^{1} and 769 cm^{-1}indicate mono substituted benzene ring. The absorption band at1496 cm^{-1}is due to –C=N stretching.

5.2.2 2-methyl quinoxaline

Seven grams of o-phenylenediamine is dissolved in 100mL. of water, and the solution is heated to 70°. With stirring, a solution of 17.2 g.of pyruvic aldehyde-sodium bisulfite in 75 mL of hot water (about 80°) is added to the o-phenylenediamine solution. The mixture is allowed to stand for 15 minutes and then is cooled to about room temperature and 25 g. of sodium carbonate monohydrate is added. The quinoxaline separates as an oil. The mixture is extracted with three 15mL portions of ether. The combined extracts are dried over anhydrous magnesium sulfate or sodium sulfate, filtered, and concentrated on the steam bath. The residual liquid, consisting of almost pure 2 methyl quinoxaline, which melts at 180-181°C [50].



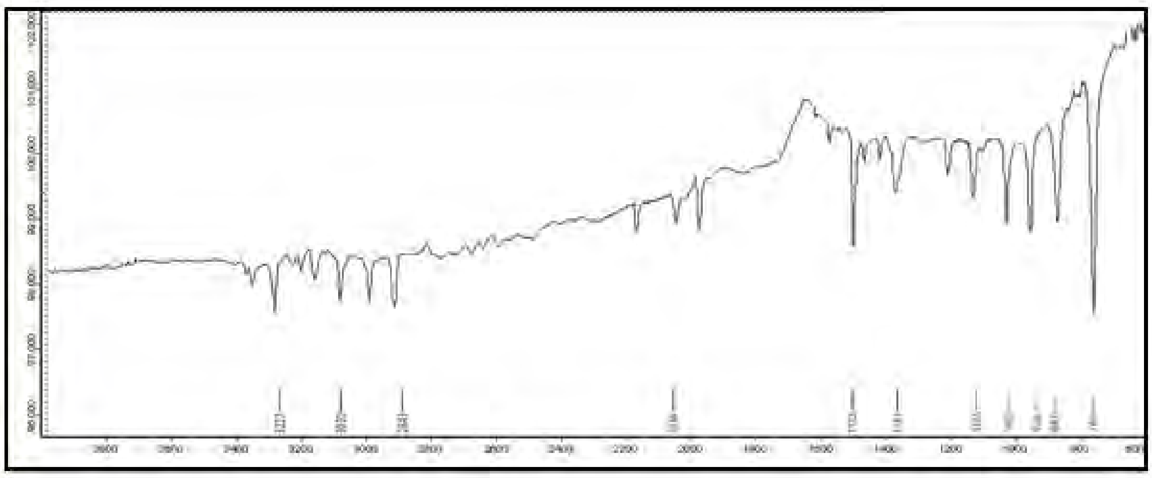
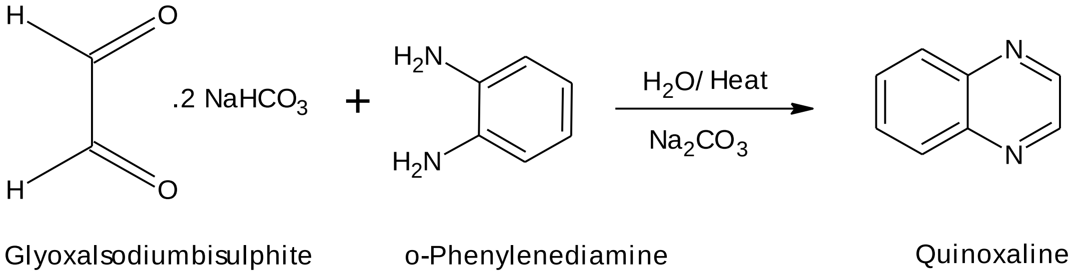


Figure 5.2: FTIR spectrum of synthesized 2-methyl quinoxaline

The FTIR spectrum of 2-methyl quinoxaline shown in figure 5.2 aromatic C-H stretching is observed at around 3030 cm^{-1} to 3227 cm^{-1} ,C=C Stretching occurs around 1512 cm^{-1}. The band appeared at around 1002 cm^{-1} to 1125 cm^{-1} corresponds to C-H bending vibration of aromatic phenyl ring. The peaks at around 780 cm^{1} and 887 cm^{-1}indicate mono substituted benzene ring. The absorption band in the range 1383 $cm^{-1}$is due to –C=N stretching.

5.2.3 Quinoxaline

Seven grams of o-phenylenediamine is dissolved in 100mL of water, and the solution is heated to 70°. With stirring, a solution of 17.2g.of glyoxal-sodium bisulfite in 75 mL of hot water (about 80°) is added to the o-phenylenediamine solution. The mixture is allowed to stand for 15 minutes and then is cooled to about room temperature and 25 g. of sodium carbonate monohydrate is added. The quinoxaline separates as anoil. The mixture is extracted with three 15mL portions of ether. The combined extracts are dried over anhydrous magnesium sulfate or sodium sulfate, filtered, and concentrated on the steam bath. The residual liquid, consisting of almost pure quinoxaline, which melts at m.p. 29–30° [50].



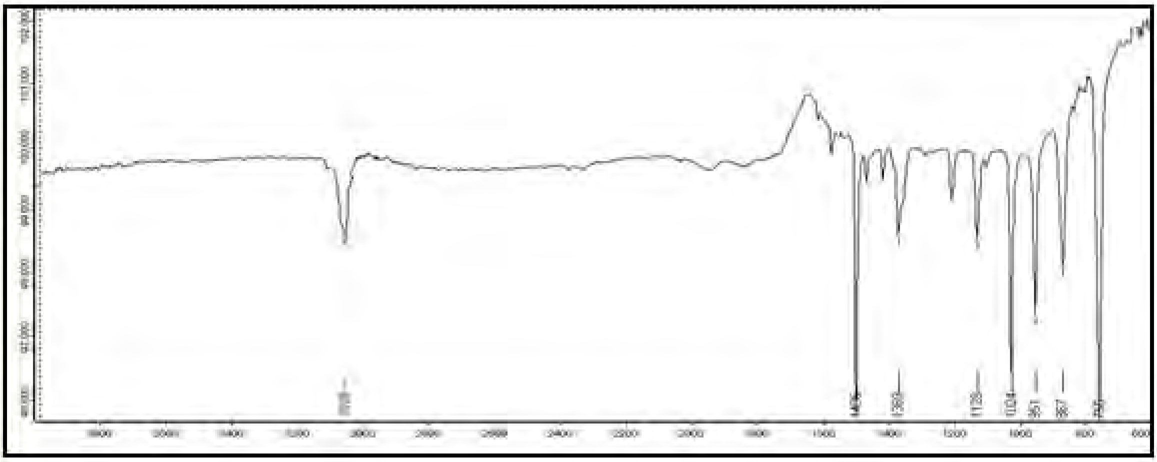


Figure 5.3: FTIR spectrum of synthesized quinoxaline

The FTIR spectrum of quinoxaline is shown in figure 5.3.In the spectrum the band appeared at around 1496 cm^{-1} is due to C=C stretching vibration of aromatic ring.The band appeared at around 1024 cm^{-1} to 1128 cm^{-1} corresponds to C-H bending vibration of aromatic phenyl ring. The peak at around 3028 cm^{-1} belongs to aromatic C-H stretching vibration. The peaks at around 756 cm^{1} and 867 cm^{-1}indicate mono substituted benzene ring. The absorption band in the range 1490 cm^{-1}is due to –C=N stretching.

5.3 Results and Discussion

5.3.1 Weight Loss Measurement

Table 5.1 shows weight loss parameters such as percentage inhibition efficiency and corrosion rate in 1 M HCl at 298 k in the absence and presence of quinoxaline and its derivatives. The observations shows that decrease in weight loss and increase in inhibition efficiency are concentration dependant. The maximum inhibition efficiency was attained at 500 ppm, beyond this concentration there is no any remarkable change in the inhibition efficiency for 24 h immersion period.

Inhibitor	**Concentration (ppm)**	**Weight loss (mg)**	**Corrosion rate ($mgcm^{-2}h^{-1}$)**	**Surface coverage (θ)**	**E (%)**
Blank	0.00	173	24.02	-	-
2,3-DPQX	100	26	3.611	0.8497	84.97
	200	20	2.778	0.8843	88.43
	300	15	2.083	0.9132	91.32
	400	13	1.805	0.9248	92.48
	500	09	1.250	0.9479	94.79
2-MQX	100	55	7.638	0.6820	68.20
	200	46	6.388	0.7341	73.41
	300	39	5.416	0.7745	77.45
	400	30	4.166	0.8265	82.65
	500	18	2.500	0.8959	89.56
QX	100	73	10.138	0.5780	57.80
	200	64	8.889	0.6300	63.00
	300	51	7.083	0.7052	70.52
	400	43	5.972	0.7514	75.14
	500	33	4.583	0.8092	80.92

Table 5.1: The weight loss data obtained for mild steel in 1M HCl containing different concentration of tetrazoles at 298K

5.3.2 Effect of Temperature

Generally speaking, the impact of temperature on the corrosion process of metal in aggressive solution is complex, because many changes occur on the metal/solution interface, such as rapid etching, desorption of inhibitors and the decomposition or rearrangement of inhibitor itself [51-52]. In order to study the effect of temperature on the inhibition performance of quinoxline and its derivatives, weight loss measurements were performed in 1.0 M HCl in the absence and presence of 500ppm of inhibitor from 298 to 328 K. Results obtained after 24 h exposure time are presented in Table 5.2

Inhibitors	**Tempearture K**	**Corrosion rate (mg cm^{-2} h^{-1})**	**E (%)**
1.0M HCl	298	24.028	-
	308	35.416	-
	318	48.333	-
	328	61.387	-
2,3-DPQX	298	1.250	94.79
	308	3.073	87.28
	318	5.138	78.61
	328	7.777	67.63
2-MQX	298	2.500	89.59
	308	5.228	78.03
	318	7.917	67.05
	328	9.166	61.84
QX	298	4.583	80.92
	308	6.950	71.09
	318	10.833	54.91
	328	12.500	47.97

Table 5.2: Effect of quinoxaline derivative concentration on corrosion rate and inhibition efficiency for mild steel in 1M HCl at different temperature.

The results obtained from Table 5.2, reveal that the corrosion rate increased with increase in temperature in both uninhibited and inhibited solution. Also the inhibition efficiency is observed to decrease with increase in temperature. The decrease in inhibition efficiency with temperature might be attributed to desorption of the inhibitor molecules from the metal surface at higher temperatures [53].

To calculate activation parameters of the corrosion process, Arrhenius Eq. (1) and transition state Eq. (2) were used,

$$logCR = \frac{-\mathrm{E_a}}{2.303\mathrm{RT}} + \log \mathrm{A} \tag{1}$$

$$CR = \frac{\mathrm{RT}}{\mathrm{Nh}} \exp\left(\frac{\Delta \mathrm{S}}{\mathrm{R}}\right) \exp\left(-\frac{\Delta \mathrm{H}}{\mathrm{RT}}\right) \tag{2}$$

where, E_a is the activation energy, ΔS is the entropy of activation, ΔH is the enthalpy of activation, A is the Arrhenius pre-exponential factor, h is Planck's constant, N is Avogadro's number, T is the absolute temperature and R is the universal gas constant. Fig. 5.4(A) shows Arrhenius plots of logarithm of (CR) vs 1/T for mild steel in 1M HCl without and with addition of 500 ppm of inhibitors. From the value of slope, the value of E_a were calculated for inhibitor and listed in Table 5.3. The value of E_a in the inhibited solution is higher than that for uninhibited solution, indicating that more energy barrier have been achieved in presence of quinoxaline and its derivatives [54].

Using Eq. (2), another linear plot of log of CR/T versus 1/T was drawn [Fig. 5.4 (B)] with slope (−ΔH/2.303R) and intercept [log (R/Nh+ΔS/2.303R)] which was used for the calculation of ΔH and ΔS. All the values are listed in Table 3.3. The positive values of ΔH reflect the endothermic nature of the mild steel dissolution process. The negative values of ΔS imply that the disorderness is increased on going from reactant to product. It is observed that the shift of ΔS to more positive values on increasing the concentration of the inhibitors is the driving force that can overcome the barriers for the adsorption of inhibitor onto the mild steel surface[55].

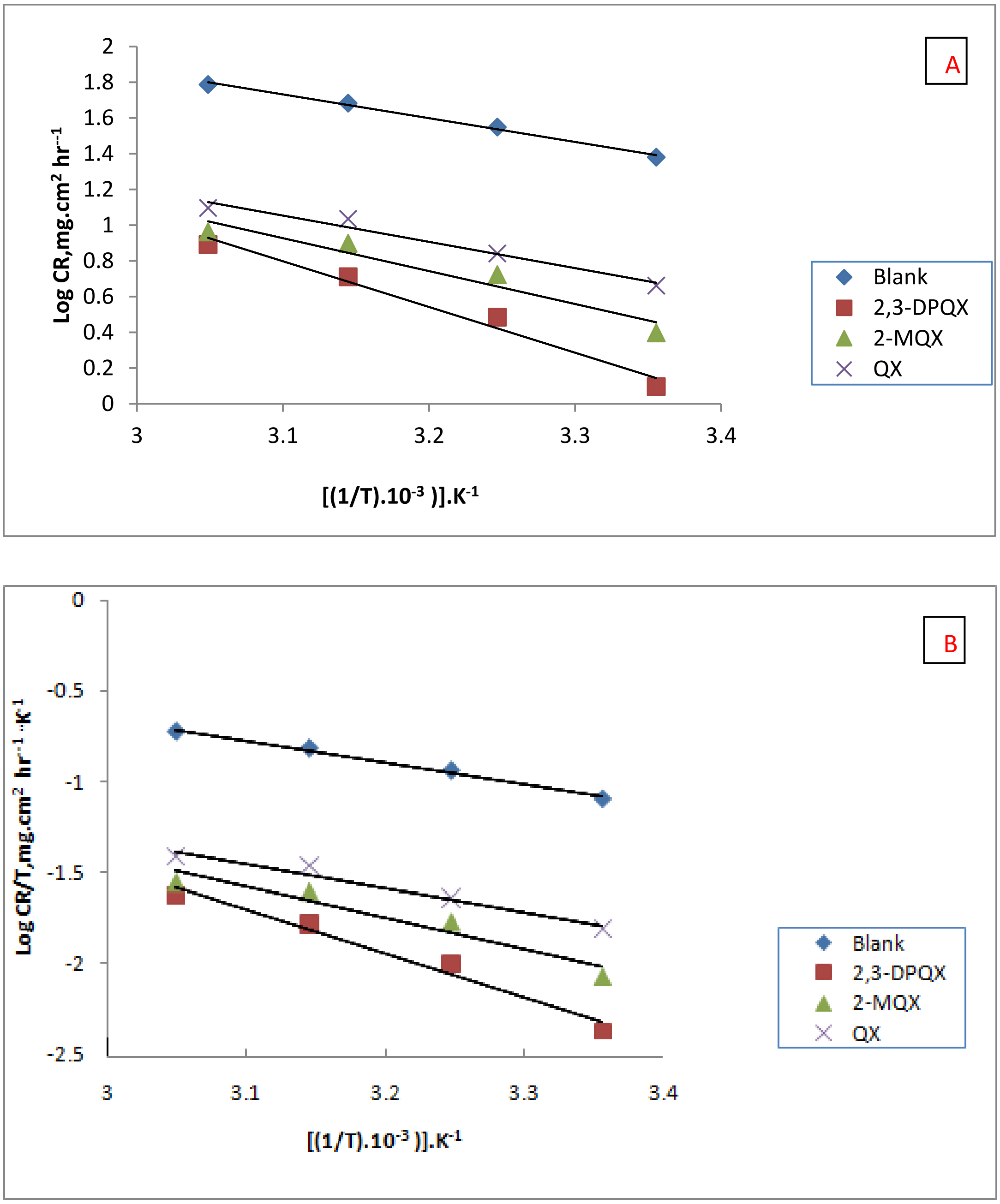


Figure 5.4: Arrhenius plots of (A) log CR vs. 1000/T and (B) Transition state plots of (b) log (CR/T) vs. 1000/T for mild steel in 1M HCl solution in the absence and presence 500ppm of 2,3-DPQX, 2-MQX and QX.

Inhibitors	E_a (kJ mol^{-1})	ΔH(kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
1.0M HCl	25.48	22.84	-141.62
2,3-DPQX	28.08	25.58	-146.08
2-MQX	35.25	37.78	-126.21
QX	49.01	46.57	-85.85

Table 5.3: Thermodynamic activation parameter for mild steel in 1M HCl in absence and presence of optimum concentration (500 ppm) of 2,3-DPQX, 2-MQX and QX

5.3.3 Adsorption isotherm

The organic corrosion inhibitor reacts in acidic media by adsorption at the metal/solution interface. The adsorption depends essentially on the structures and electronic properties of inhibitor compounds, such as, aromaticity, electronic density on donor atom and the π orbital character of donating electrons [56-57]. Furthermore, the solvent H_2O molecules can be adsorbed at the metal/solution interface. Therefore, the adsorption of organic inhibitor molecules from the aqueous solution can be considered as a quasi-substitution process between the organic molecules in the aqueous phase Org(sol) and water molecules at the electrode surface H_2O(ads) [58]: Org(sol)+ $xH_2O(ads) \leftrightarrow xH_2O(sol)$+Org(ads) Where x is the size ratio, that is, the number of water molecules changed by one organic inhibitor. The adsorption isotherm can be giving information about the properties of the tested inhibitors. The degree of surface coverage (θ) of the inhibitor is calculated, to determine the adsorption isotherm. In this study, degree of surface coverage values (θ) for the concentrations of inhibitors range between 100 ppm and 500 ppm in acidic media have been determined from the weight loss measurements. To define the mode of adsorption isotherm, different fit of the θ values to various isotherms, as well as Temkin, Langmuir, Frumkin and Flory-Huggins, were made. The excellent fit is obtained with the Langmuir isotherm. Langmuir adsorption isotherm is described by the following equations:

$$C/\theta = 1/K_{ads} + C \qquad (3)$$

Where K_{ads} is the adsorption equilibrium constant, C is the inhibitor concentration, and θ is the surface coverage. Fig. 5.5 shows the plots of C/θ versus C and the estimated linear correlation is obtained for quinoxaline and its derivatives.

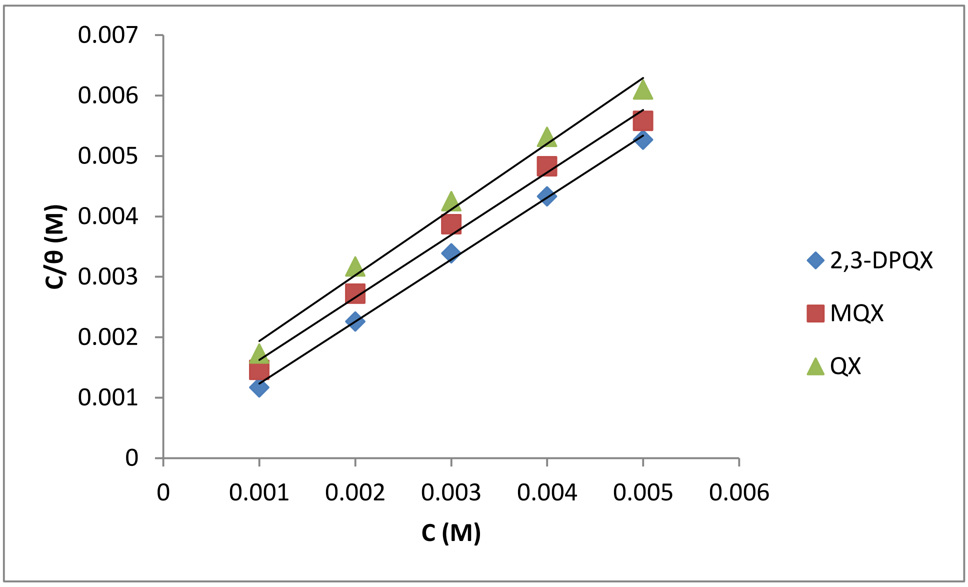


Figure 5.5: Langmuir adsorption isotherm plot for the adsorption of quinoxaline derivatives on the mild steel surface in 1M HCl solution.

The strong correlations (R^2=0.997, R^2= 0.990 and R^2= 0.998) confirm the validity of this approach. The adsorption equilibrium constant (K_{ads}) has been found to be 6767 M^{-1} for 2,3-DPQX and 2857 M^{-1} for 2-MQX and 1112 M^{-1} for QX.

It suggests that the adsorbed inhibitor molecules form monolayer on the mild steel surface and there is no interaction among the adsorbed inhibitor molecules [59]. On the other hand, the high value of adsorption equilibrium constant reflects the high adsorption capacity of inhibitors on mild steel surface [60-61]. The standard free energy of adsorption (ΔG^0_{ads}) can be determined by the following equation:

$$\Delta G^0_{ads} = -RT \ln(55.5\, k_{ads}) \qquad (4)$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K), the value 55.5 is the concentration of water in solution expressed in M[62].

The $\Delta G°$ ads value is calculated as-31.77 kJ mol^{-1} for 2,3-DPQX, -29.67 kJ mol^{-1} for 2-MQX and -27.33 kJ mol^{-1}. In the literature, if the absolute values of ΔG^0_{ads} are less than 20 kJ mol^{-1} adsorption consistent with the electrostatic interaction between the charged metal and charged molecules (physisorption),but if those more than 40 kJ mol-1 involve sharing or transfer of electrons from the inhibitor compound to the metal surface to form a co-ordinate type of bond (chemisorption) [63-65]. The values of ΔG^0_{ads} calculated in this study are between 20 kJ mol^{-1} and 40 kJ mol^{-1} suggest that the adsorption of inhibitors has the type of interactions: physisorption and chemisorption [66].

5.4 Electrochemical Measurements

5.4.1 Open Circuit Potential (OCP) Curves

The electrochemical behavior of mild steel in 1 M HCl was studied on the basis of change in corrosion potential (E_{corr}) with time. The change in open circuit potential of mild steel in absence and presence of various concentration of inhibitors i.e. 2,3-diphenyl quinoxaline,2- methyl quinoxaline and quinoxaline in 1M HCl is shown in fig.5.6 to fig.5.8 respectively. The change in OCP of mild steel in absence and presence of inhibitors were measured for a period of one hour with sample period of one data per second. The potential attains steady state after exposure of approximately 30 minutes. The steady state potential is an equilibrium state at which I_{ox} is equal to I_{red}. It has been observed that OCP of mild steel from moment of immersion in 1M HCl tends towards more negative value in the absence of inhibitor. This shows corrosiveness of medium which is due to breakdown of pre-immersion, air formed oxide film on the metal surface. In the presence of various concentrations of inhibitors the steady state potential of mild steel shifts more towards positive value. This is due to adsorption of inhibitors on metal surface resulting in passivation of metal [67].

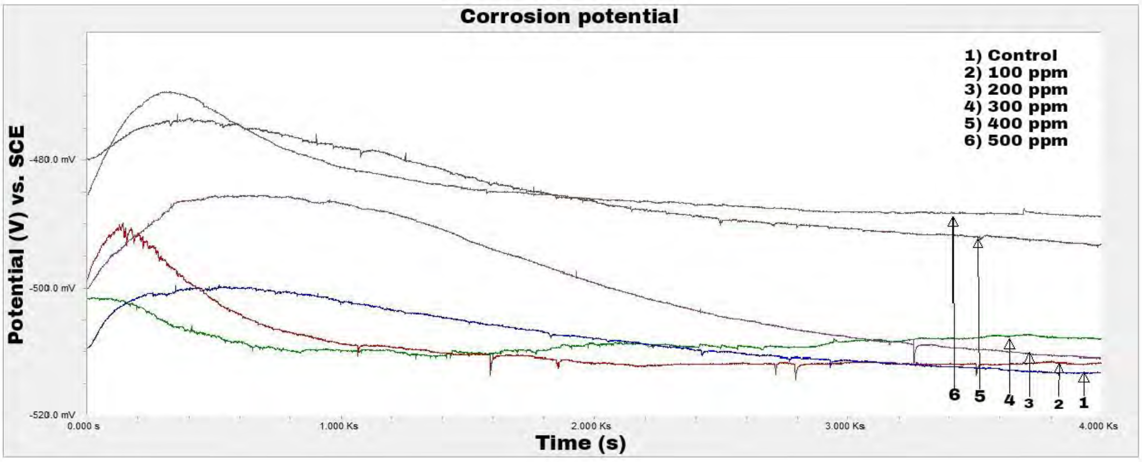


Figure 5.6: Open circuit potential of mild steel without and with different concentration of 2,3-DPQX inhibitor in 1M HCl.

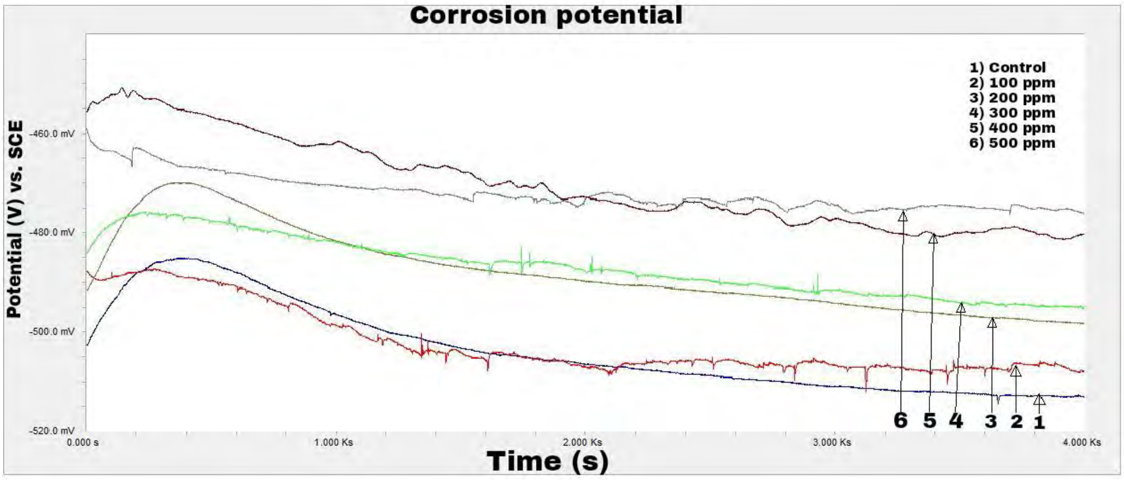


Figure 5.7: Open circuit potential of mild steel without and with different concentration of 2,3-MQX inhibitor in 1M HCl.

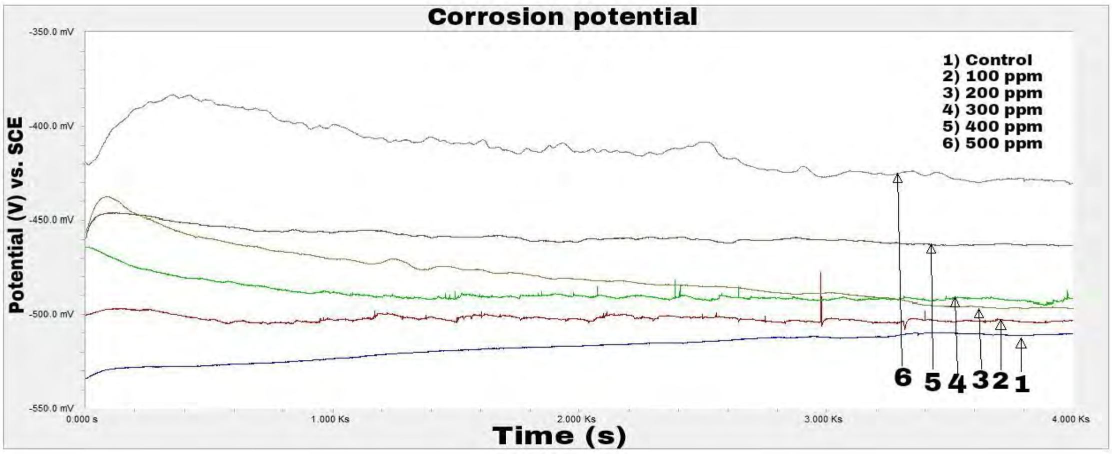


Figure 5.8: Open circuit potential of mild steel without and with different concentration of QX inhibitor in 1M HCl.

5.4.2 Potentiodynamic polarization measurements

The potentiodynamic curves for mild steel in 1 M HCl in the absence and presence of quinoxaline, diphenylquinoxaline and methyl quinoxaline are shown in Fig.5.9-5.11. It is clear that; the investigated inhibitors affect by retardation of anodic dissolution of mild steel and cathodic hydrogen discharge reactions. Electrochemical parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel constants (β_a and β_c), degree of surface coverage (θ) and inhibition efficiency (IE %) were calculated from Tafel plots and are given in Table 5.4. It is observed that the presence of inhibitor lowers i_{corr}. Maximum decrease in i_{corr} values was observed for diphenylquinoxaline indicating that this is the most effective corrosion inhibitor. It is also observed from Table 5.4 that E_{corr} values and Tafel slopes do not change significantly in inhibited solution as compared to uninhibited solution. The investigated compounds do not shift the E_{corr} values significantly, suggesting that they behave as mixed type inhibitors [68]. Both cathodic (β_c) and anodic Tafel lines (β_a) are parallel and are shifted to more negative and positive direction, respectively by adding inhibitors. This is indicating that the mechanism of the corrosion reaction does not change and the corrosion reaction is inhibited by simple adsorption mode [69]. The irregular trends of β_a and β_c values indicate the involvement of more than one type of species adsorbed on the metal surface. The order of inhibition efficiency was found to be (Table 4): Diphenylquinoxaline>Methyl quinoxaline>Quinoxaline.

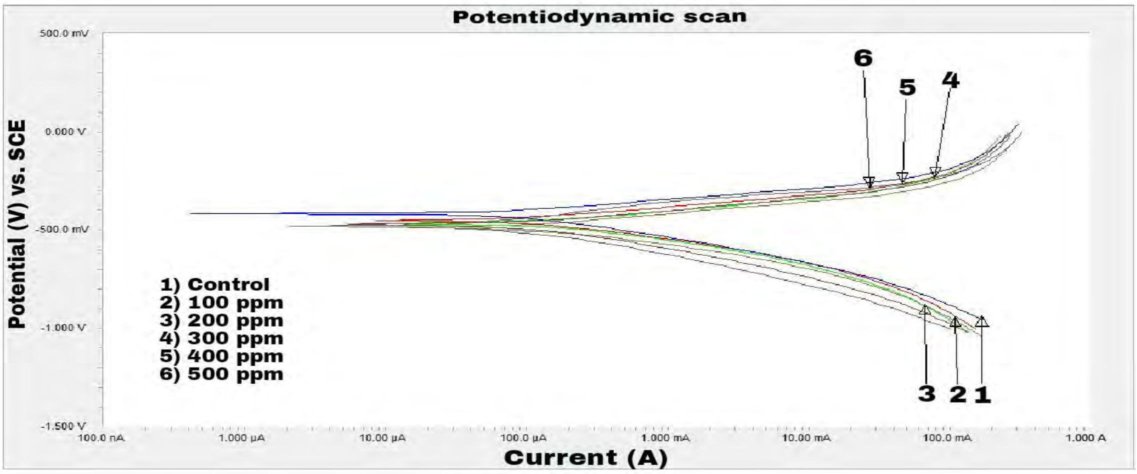


Figure 5.9: Potentiodynamic polarization of mild steel without and with different concentration of 2,3-DPQX in 1M HCl.

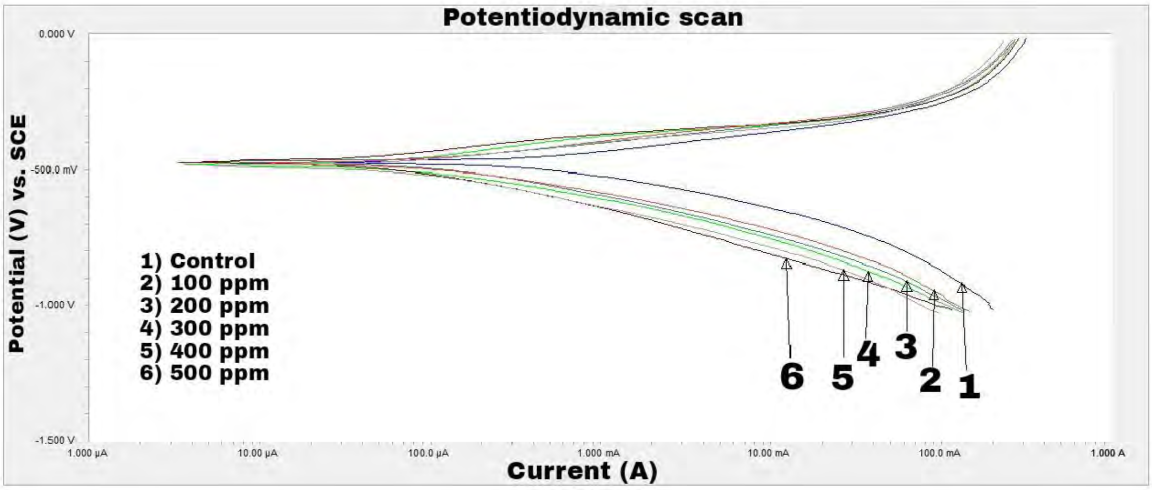


Figure 5.10: Potentiodynamic polarization of mild steel without and with different concentration of 2-MQX.

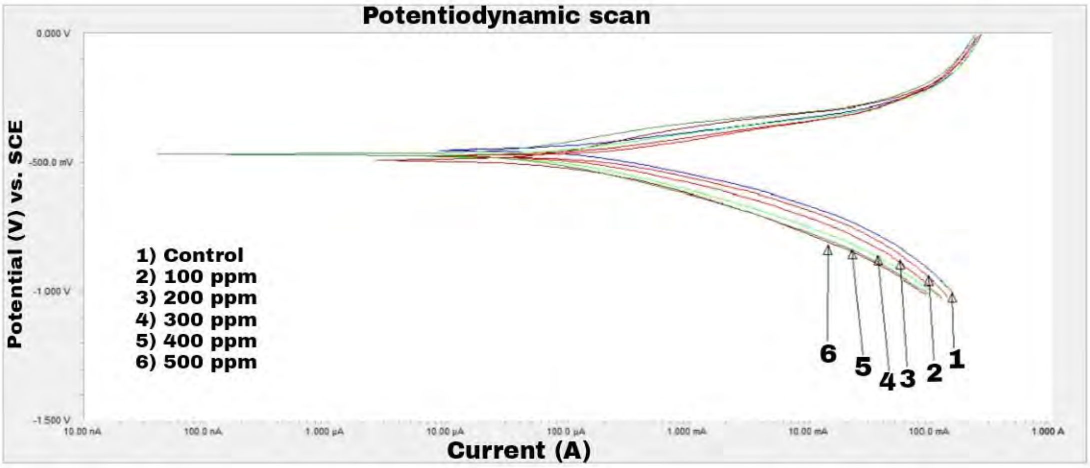


Figure 5.11: Potentiodynamic polarization of mild steel without and with different concentration of QX.

Concentration of Inhibitors (ppm)	-E_{corr} (mv)	I_{corr} (µA/cm^2)	β_a (v/dec)	β_c (v/dec)	IE %
1.0M HCl	-485	585	92.40 e^{-3}	169.7 e^{-3}	-
			2,3-DPQX		
100	-527	98.0	65.80 e^{-3}	136.9 e^{-3}	83.24
200	-532	79.50	80.20 e^{-3}	138.2 e^{-3}	86.41
300	-506	58.60	59.90 e^{-3}	159.1 e^{-3}	89.98
400	-523	39.55	68.94 e^{-3}	146.2 e^{-3}	93.23
500	-509	24.86	53.20 e^{-3}	134.4 e^{-3}	95.75
			2-MQX		
100	-529	177.0	67.70 e^{-3}	120.4 e^{-3}	69.74
200	-508	145.5	61.80 e^{-3}	166.5 e^{-3}	75.12
300	-522	122.9	80.12 e^{-3}	145.6 e^{-3}	78.99
400	-513	93.6	79.54 e^{-3}	143.8 e^{-3}	84.00
500	-510	57.8	58.20 e^{-3}	141.5 e^{-3}	90.11
			QX		
100	-458	262	68.56 e^{-3}	156.8 e^{-3}	55.21
200	-465	217	62.90 e^{-3}	141.4 e^{-3}	63.23
300	-462	163.2	65.55 e^{-3}	168.0 e^{-3}	72.10
400	-467	139.8	61.20 e^{-3}	141.8 e^{-3}	76.10
500	-492	51.3	54.48 e^{-3}	122.5 e^{-3}	91.24

Table 5.4: Polarization curves for corrosion of mild steel in 1.0 M HCl in the absence and presence of different concentration of (a) 2,3-DPQX, (b) 2-MQX, (c) QX.

5.5 Surface Studies

5.5.1 Scanning Electron Microscopic (SEM) Analysis

In order to evaluate the condition of metal surface in contact with acid solution in absence and presence of inhibitor, a surface analysis is carried out using scanning electron microscope and Energy dispersive X- ray spectrometer.

The surface morphology of the mild steel specimens immersed in1M HCl for 24 h without and with optimum concentration of the quinoxaline and its derivatives is shown in Figure 5.12. A micrograph of the polished mild steel surface before immersion in 1M HCl is shown in figure (5.12(A)).The micrograph shows the surface was smooth and without pits.Fig.(5.12(B)) represents SEM micrograph of mild steel surface immersed in 1M HCl without inhibitors which appears to be highly corroded and damaged due to free acid attack.

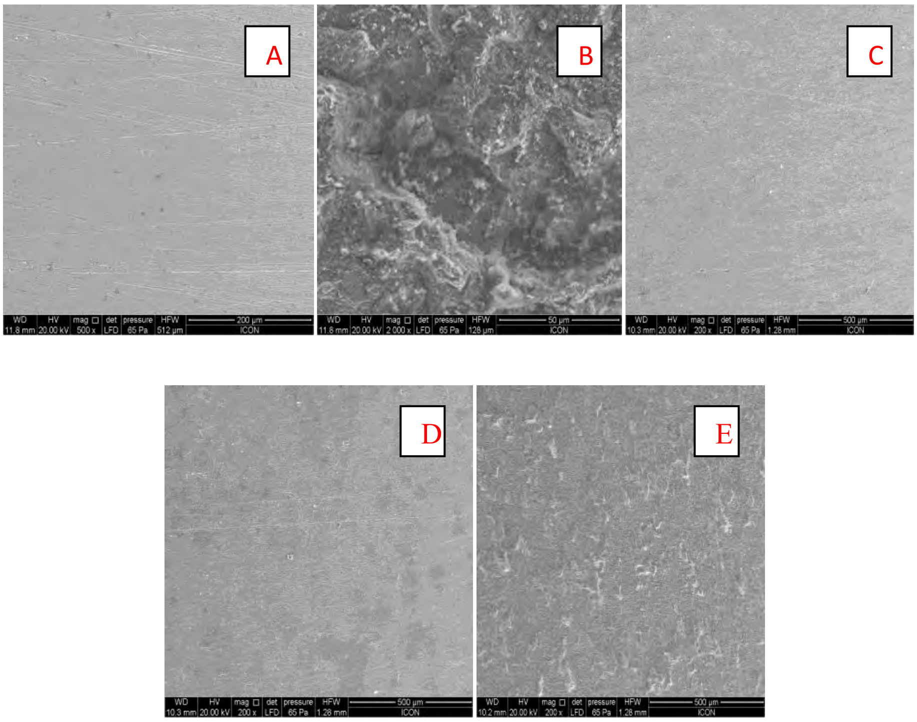


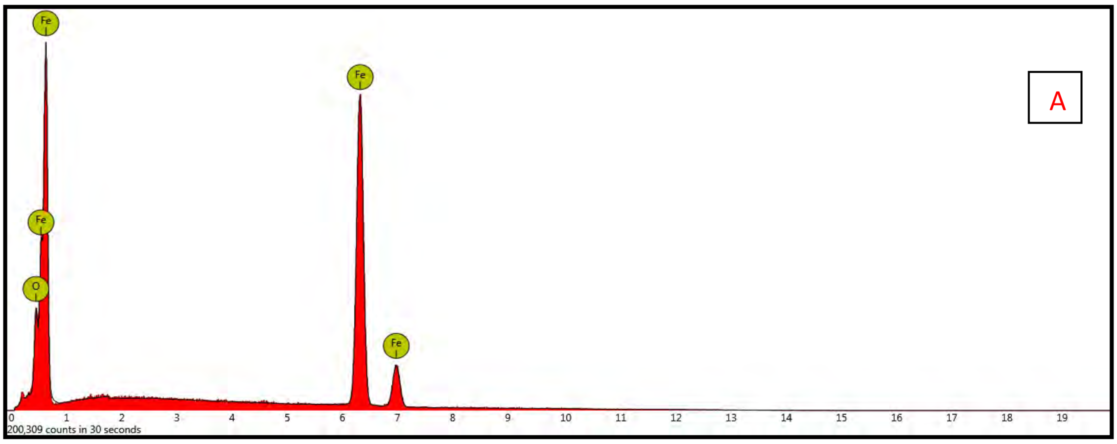
Figure 5.12: SEM of mild steel with (A) Polished, (B) 1M HCl, (C) 500 ppm of 2, 3-DPQX,(D) 500 ppm of 2-MQX and (E) 500 ppm of QX.

Fig.5.12(C-E) represents SEM micrograph of mild steel in the presence of optimum concentration of the inhibitors in acid solution causes significant improvement in the surface morphology. Thus it can be concluded that quinoxaline and its derivatives forms protective surface film on the metal surface through adsorption which protect the metal from acid solution

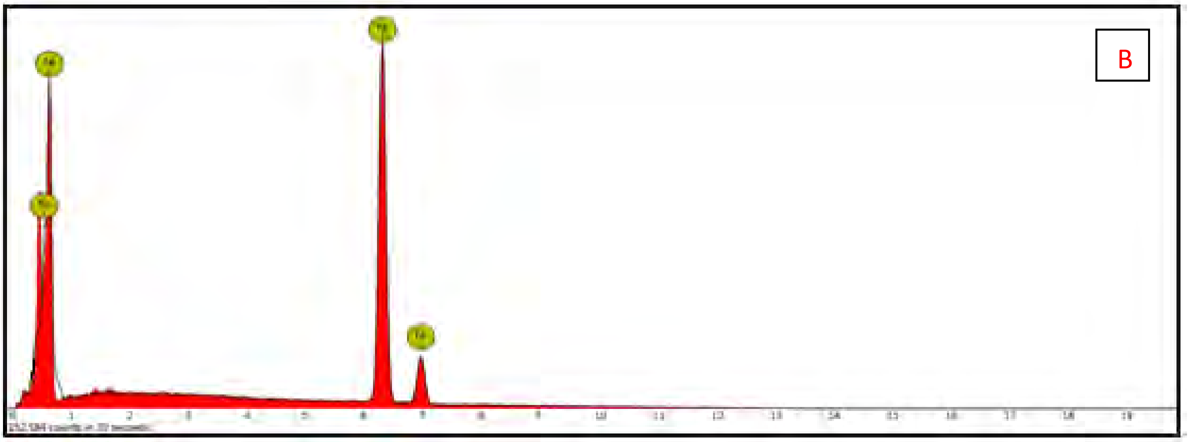
5.5.2 Energy-dispersive X-ray spectroscopy (EDX)

To further support our weight loss and electrochemical finding that quinoxaline and its derivatives inhibit mild steel corrosion by forming a protective film on surface, we recorded the EDX spectra in absence and presence of optimum concentration of inhibitors.

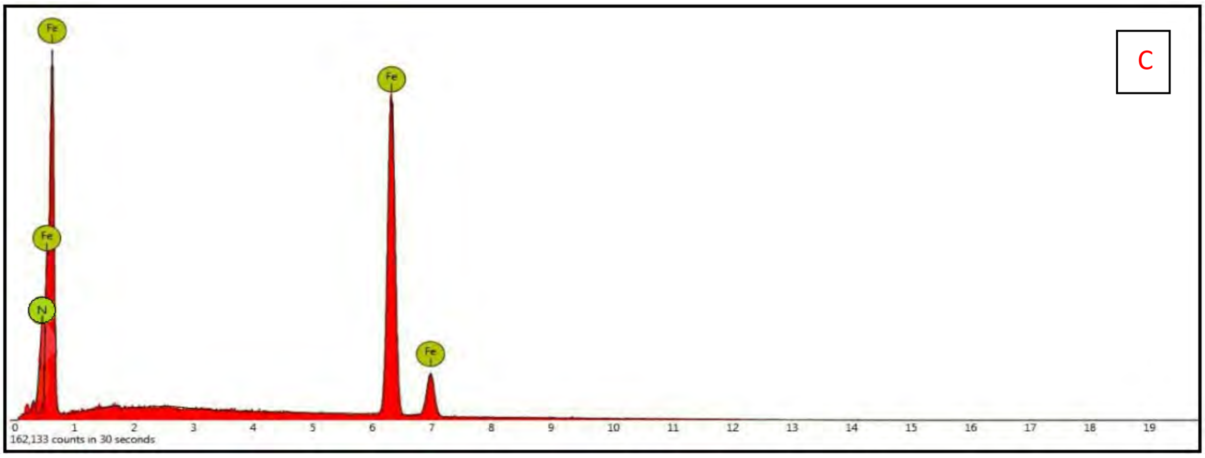
The spectral profile of the polished mild steel sample before immersion in 1M HCl shows (Fig.5.13(A)) the signal for Fe, and O . On immersion in 1M HCl (5.13(B)), the signal for O disappeared due to breaking of pre immersion air formed oxide film. Signal for Fe also slightly decreased. The profile in presence of quinoxaline and its derivatives show (5.13(C-E)) additional signal for nitrogen atoms. This is due to adsorption of inhibitor on the mild steel surface.



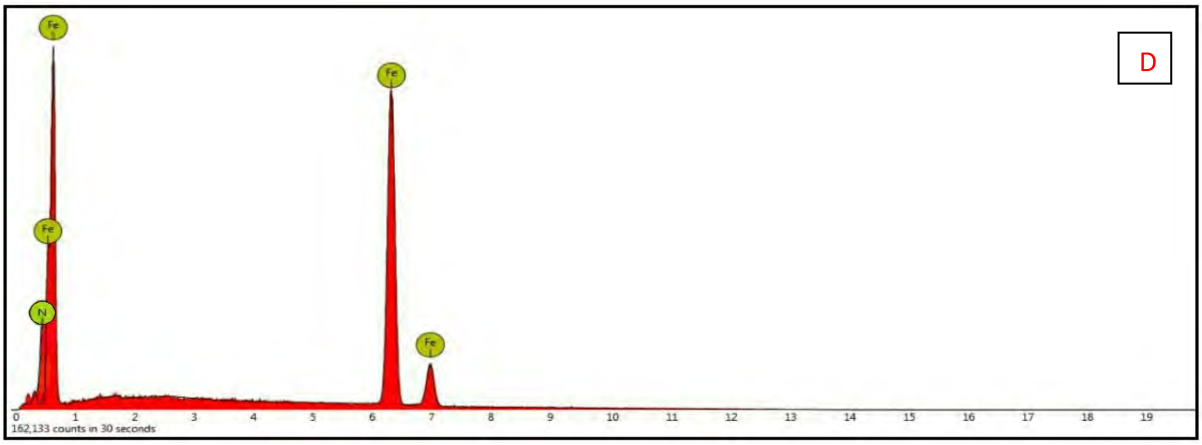
A) Polished sample



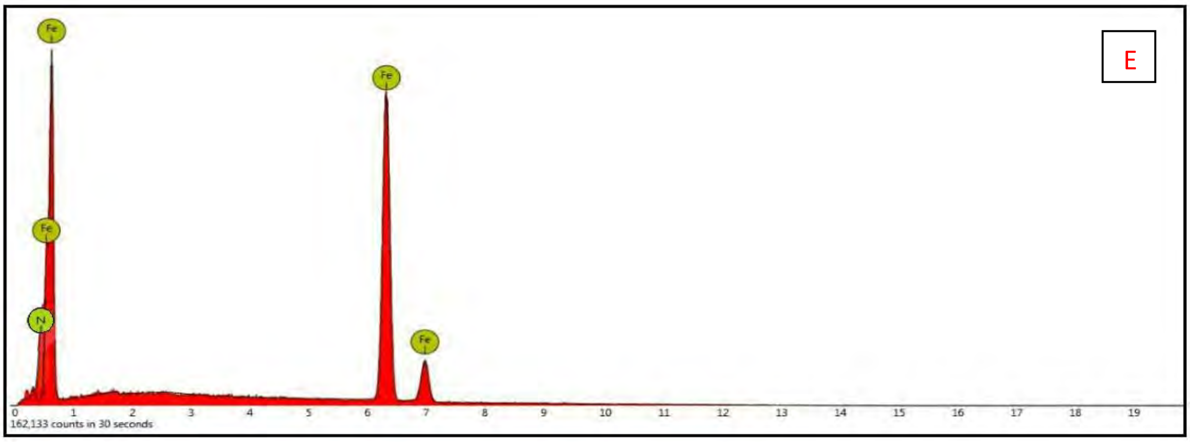
B) Control (1M HCl)



C) 1M HCl+500 ppm 2,3-DPQX



D) 1M HCl+500 ppm 2-MQX



E) 1M HCl+500 ppm QX

Figure 5.13:EDX of mild steel with: (A)Polished, (B) 1M hydrochloric acid, (C) 500 ppm of 2,3-DPQX, (D) 500 ppm of 2-MQX and (E) 500 ppm QX.

5.6 Mechanism of Inhibition

Corrosion inhibition of mild steel in 1M HCl by quinoxalines can be explained on the basis of molecular adsorption. It is generally considered that the first step in the corrosion inhibition of a metal is the adsorption of the inhibitor molecules at metal / solution interface [70-72]. The corrosion inhibition property of the quinoxalines can be attributed to the presence of two nitrogen atoms and π-electrons on benzene ring. The adsorption of the inhibitor on the steel surface can occur either directly by the electrostatic interaction between the charged molecules and charged metal. There may also be an interaction of π-electrons with the metal. The adsorption of the inhibitor on mild steel may also be due to the interaction of unshared pair of electrons in the molecule with the metal. All the above interactions cause the adsorption of quinoxalines on corroding the sites of the metal and prevent the anodic reaction.

The adsorption of quinoxalines cannot be considers as purely physical or purely chemical phenomenon. The charge on metal surface is due to electric field which emerges at the metal/electrolyte interface. It is well-known that mild steel specimens are positively charged with respect to the potential of zero charge (PZC) in acid solutions [73]. It is a well-known fact that the inhibitors not only offer electrons to metal atoms but also have unoccupied higher energy orbital to accept electrons from d-orbital of metal atom for strengthening of bonding interaction [74]. In aqueous solution of 1M HCl, quinoxaline molecule may adsorb through protonated heteroatoms and already adsorbed Cl ion mild steel surface. Initially, the protonated form of quinoxalines molecule in acid medium start competing with H^+ ions for electrons on mild steel surface. After release of H_2 gas, the cationic form of inhibitors returns to its neutral form and heteroatoms with free lone pair electrons promote chemical adsorption. Thus, there is a synergism between the adsorbed Cl^- ions and protonated quinoxalins. Hence, we can assume that the inhibition of mild steel corrosion in 1 M HCl is due to the adsorption of quinoxalines on the mild steel surface [75].

The order of inhibition efficiency of the synthesized quinoxalines is 2, 3-DPQX>2- MQX>QX. 2,3-DPQX exhibiting a maximum inhibition efficiency of about 95% which is slightly higher than 2-MQX and QX. This may be due to the presence of the 2-phenyl substituent which increase adsorption on mild steel surface.2-MQX has slightly high inhibition efficiency than QX due to the presence of electron donating $-CH_3$ group. All the three inhibitors exhibit a maximum inhibition efficiency of 80 to 95% at a concentration of 500 ppm. Their inhibition efficiency may be due to the presence of two nitrogen atom, phenyl group and methyl group.

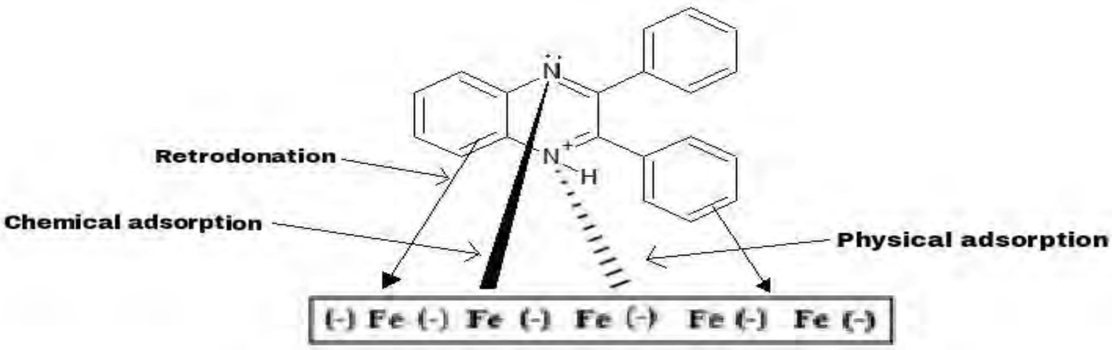


Figure 5.14: Pictrorial representation of adsorption of one of the quinoxaline derivative on MS surface in 1M HCl.

5.7 Conclusion

1. The quinoxaline and its derivatives act as efficient corrosion inhibitors in 1M hydrochloric and they exhibit a maximum inhibition efficiency of 80-95%. The quinoxaline and its derivatives inhibit corrosion of mild steel in the following order 2, 3-DQX>2-MQX>QX.
2. The inhibition efficiency increases with increase in inhibitor concentration.
3. The adsorption of quinoxaline and its derivatives on a mild steel surface obeys the Langmuir adsorption isotherm.
4. Inhibition efficiency of the quinoxaline and its derivatives decreases with increase in temperature and further it leads to an increase in activation energy.
5. The negative ΔG°_{ads} values suggest that both physisorption and chemisorptions are involved in the adsorption of the inhibitors on the metal surface.
6. Tafel slopes obtained from potentiodynamic polarization curves indicate that all the inhibitors behave as mixed type inhibitors.
7. SEM and EDAX study clearly reveals that there is a change in the surface characteristics of the metal surface due to the addition of the quinoxaline and its derivatives.

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Chapter 6

INVISTIGATION OF QUINOLINE DERIVATIVES AS CORROSION INHIBITORS FOR MILD STEEL IN 1M HCl

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6.1 Introduction

Corrosion is the deterioration of a metal as a result of chemical reaction between it and the surrounding. Corrosion causes heavy economic losses. India with GDP of amount 2 trillion loses as much as 100 billion dollar every year on account of corrosion. Mild steel is widely used as construction material in most of major industries due to its excellent mechanical properties and low cost. The major problem of mild steel is its dissolution in acidic medium [1–6].Acids are widely used for acid pickling, industrial acid cleaning, acid descaling, oil well acidizing and other applications. Acidization of oil well is one of the important stimulation techniques for enhancing oil production. It is commonly brought about by forcing 15% to 28% hydrochloric acid as a solution. Hydrochloric acid is useful in removing lime stone, carbonate and dolomite from reservoirs rocks. Pickling involves chemical removal of oxides and scale from surface of iron and steel by an aqueous solution of hydrochloric acid. Acid cleaning generally refers to the use of acid solutions for final preparation of metal surface before plating, painting or storage. Due to their high corrosive nature acid may cause damage to the system components. Thus it is necessary to develop some effective corrosion inhibitors .The use of organic inhibitor is the most effective and most economic method for protection of metal from corrosion. Generally, organic inhibitors inhibit metallic corrosion by adsorbing on the surface and thereby forming a protective barrier [7-14].The adsorption of an inhibitor is influenced by various factors such as electron density of donor site, presence of functional groups, electronic structure of inhibiting molecule, molecular area and molecular weight of inhibitor. Organic compounds containing heteroatoms including N, S, and/or O with polar functional groups and conjugated double bonds have been reported as effective corrosion inhibitor [14-21].

Perusal of literature reveals that many N-heterocyclic compounds such as tetrazole derivatives [22], triazole derivatives [23], benzimidazole derivatives [24], pyrazole derivative [25], bipyrazole derivatives [26], indole derivatives [27], pyridazine derivatives [28] and pyrimidine derivatives [29] have been used for the corrosion inhibition of iron or steel in acidic media.

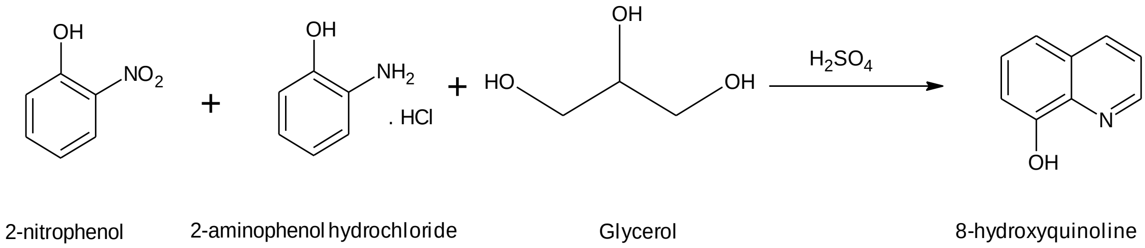
Quinoline nucleus occurs in several natural compounds (Cinchona Alkaloids) and pharmacologically active substances displaying a broad range of biological activity. Quinoline has been found to possess antimalarial, anti-bacterial, antifungal, anthelmintic, cardio tonic, anticonvulsant, anti-inflammatory, and analgesic activity[30].Recently, several reports have been documented in the literature on the use of quinoline derivatives as corrosion inhibitor in acidic media. Compounds such as 5-Nitro-8-hydroxy quinoline [31], 3-formyl-8-hydroxy quinoline [32], 8-hydroxy-7-quinolinecarboxaldehyde [33], 5,5′- (((2-hydroxypropane-1,3-diyl)-bis-(oxy))-bis-(methylene))-bis-(8-quinolinol) [34], 5-(((1H–benzimidazol-2-yl) thio) methyl) 8-quinolinol [35], have been reported as effective corrosion inhibitors for steel in 1 M HCl.

In view of the literature cited above, the present work describes the study of inhibitive behaviour and adsorption mechanism of five quinoline derivatives on the corrosion of MS in 1M HCl using mass loss and electrochemical techniques. The passive film formed on the metal surface was characterized by EDX and SEM. Further, the inhibition performance of the five derivatives have been compared and discussed.

6.2 Synthesis

6.2.1 8-Hydroxyquinoline (8-HQ)

8-Hydroxyquinoline was prepared by gently boiling, for 3-4 hours, a mixture of 7 g of 2-nitrophenol, 15 g of 2-aminophenol hydrochloride, 25 g of glycerol and 20 g of sulphuric acid. The reaction mixture is diluted with water, made alkaline, and the 8-hydroxyquinoline distilled over in steam. 8-hydroxyquinoline melts at 73-74°C [36].



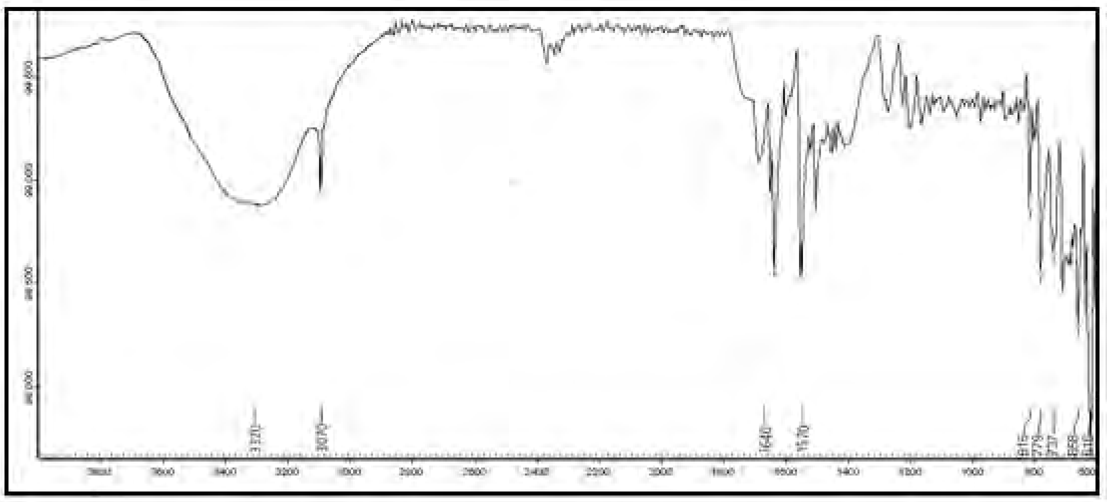


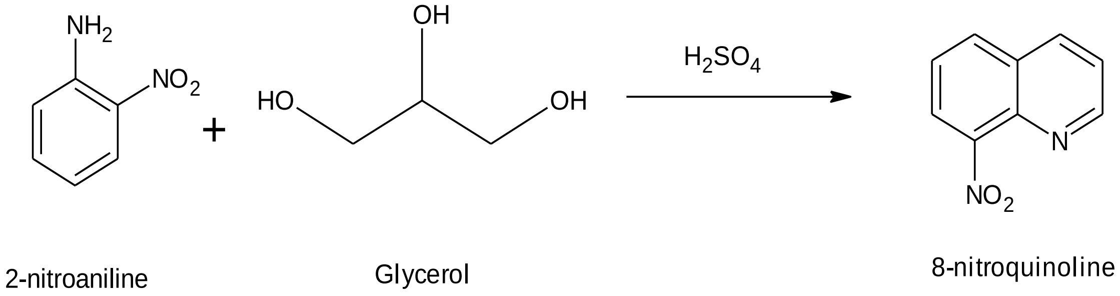
Figure 6.1: FTIR spectrum of synthesized 8-Hydroxyquinoline

The FTIR spectrum of 8-hydroxy quinoline is shown in figure 6.1.In the spectrum the band appeared at around 1400 cm^{-1} to 1640 cm^{-1} are due to C=C stretching vibration of aromatic ring. The band appeared at around 3200 cm^{-1} to 3500 cm^{-1} corresponds to O-H stretching vibration. The peak at around 3070 cm^{-1} belongs to aromatic C-H stretching vibration. The peaks at around 737 $cm^{-1}$and 779 cm^{-1} belong to C-H rocking and bending vibration.

6.2.2 8-nitroquinoline (8-NQ)

100 g of conc. sulphuric acid and 51.5 g of arsenic acid were well shaken in a flask with 110 g. glycerine and 50 g of o-nitroaniline and then carefully heated on a sand bath under a reflux condenser. As soon as the reaction begins, the flask is removed from the sand bath until it has moderated; it is then boiled for 3 hours. When cold, a large volume of water is added to the contents of the flask, and the whole content allowed to stand overnight, and then filtered. Sodium hydroxide is carefully added to the filtrate until a brown precipitate appears which is filtered off and

discarded. Sodium hydroxide is then added to the filtrate until it turns alkaline. The 8-nitroquinoline thus obtained is washed with water, boiled up with alcohol and animal charcoal, and after filtration is precipitated by the addition of water. Yield was 55%, in the form of colourless monoclinic needles; insoluble in water; soluble in alcohol; m.p. 88°C[37].



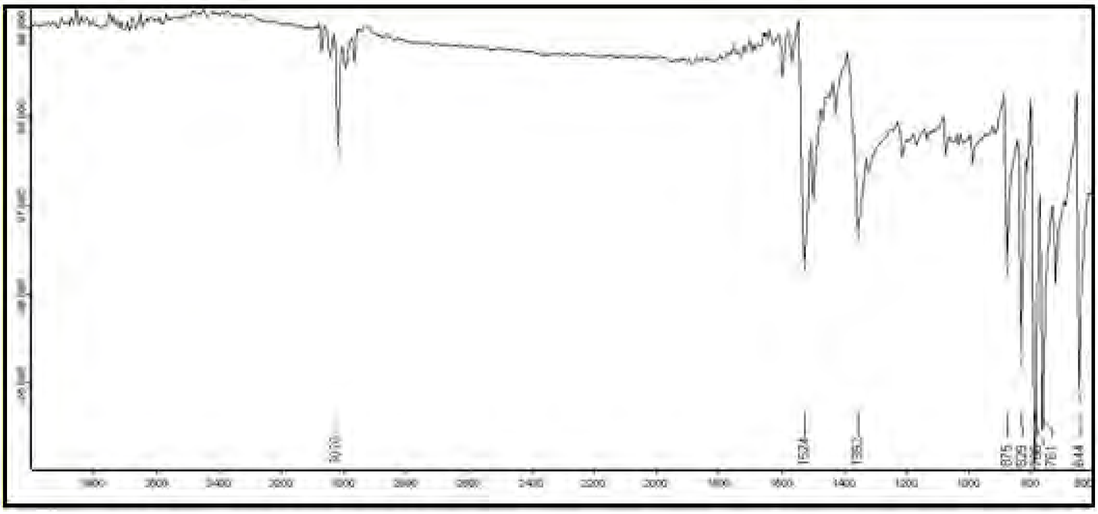
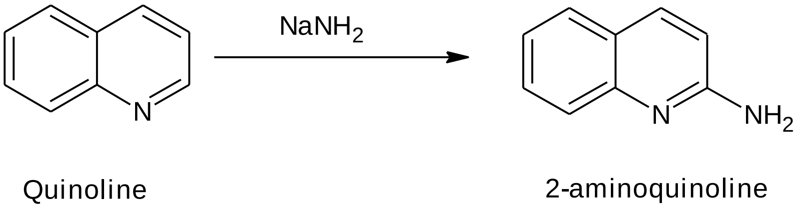


Figure 6.2: FTIR spectrum of synthesized 8-nitroquinoline

The FTIR spectrum of 8-nitro quinoline is shown in figure 6.2 The absorption peak at 3020 cm^{-1}corresponds to aromatic C-H stretching vibration .The peaks at around 1400 $cm^{-1}$to 1600 cm^{-1} belongs to C=C stretching vibration. The absorption peaks at 1352cm^{-1} to1524 cm^{-1} is due to N-O stretching vibration. The peaks at around 761 cm^{-}1and 789 cm^{-1} belong to C-H rocking and bending vibration.

6.2.3 2-aminoquinoline (2-AQ)

Two molar equivalents of sodium amide are suspended in boiling xylene and one molar equivalent of quinoline is added. The mixture is heated to reflux until the rate of hydrogen evolution is low (approximately 1 hour). The cold reaction mixture is hydrolyzed by the cautious addition of excess water, and the xylene layer is separated and extracted with concentrated hydrochloric acid. The acid extracts are treated with excess sodium hydroxide and extracted with ether. The combined ethereal extracts and xylene layer are distilled, and the fraction boiling around 200°/30 mm. is recrystallized from toluene. The yield is 32% of white needles, m.p. 130°[38].



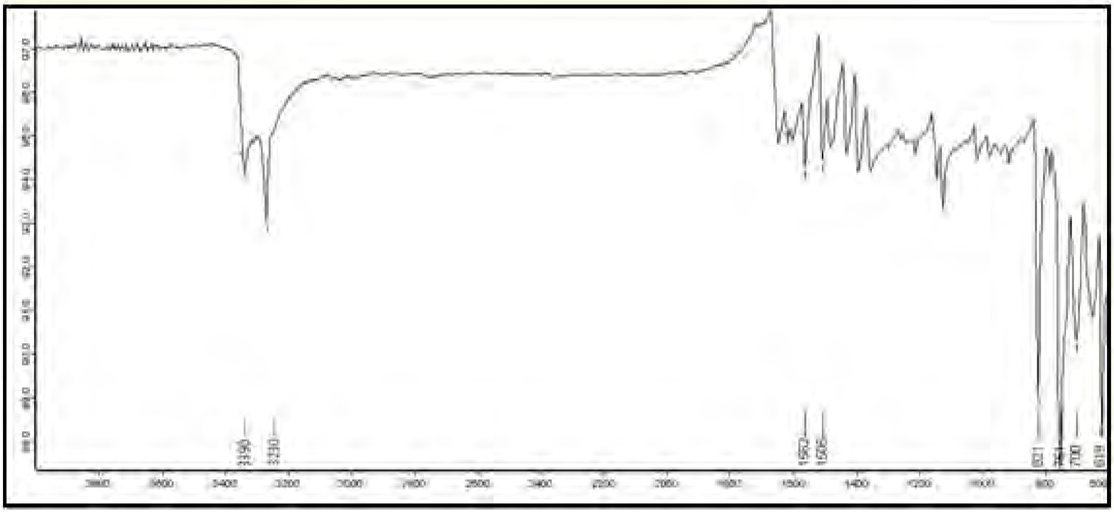
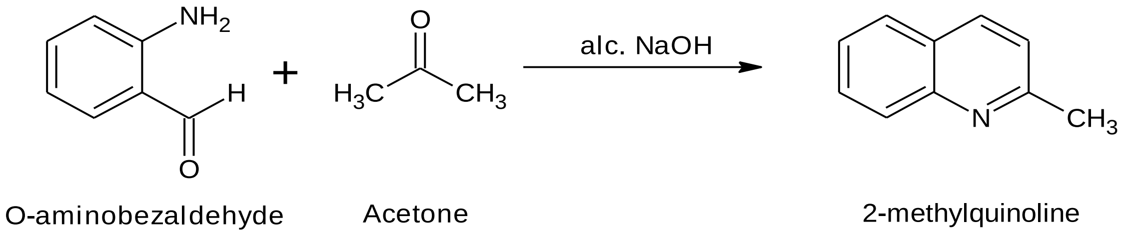


Figure 6.3: FTIR spectrum of synthesized 2-aminoquinoline

The FTIR spectrum of 2-aminoquinoline shown in figure 6.3.The peaks at around 3230 cm^{-1} to 3390 cm^{-1}contributes to aromatic N-H stretching vibration, and absorption bands at around 1400 cm^{-1} to 1600 cm^{-1}belongs to C=C Stretching vibration. C=N stretching occurs at around 1505 cm^{-1} to 1562 cm^{-1},and C-N stretching occurs at around 1080-1296 cm^{-1}.Peaks at around 619cm^{-1} to 821cm^{-1} corresponds to N-H wagging vibration.

6.2.4 2-methylquinoline (2-MQ)

20 g of o-aminobenzaldehyde and 9 g of dried and acetone is dissolved in absolute alcohol, and a few drops of alcoholic sodium hydroxide added. The condensation takes place at ordinary temperature. The quinaldine is distilled off in steam and washed with water until free from acetone. The product is colourless liquid immiscible in water, b.p. 247°C [39].



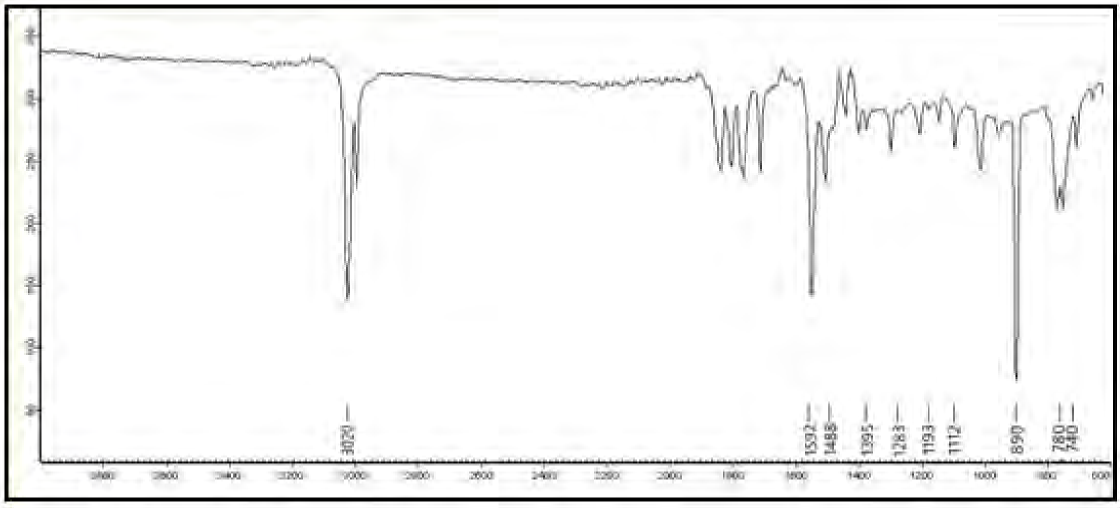


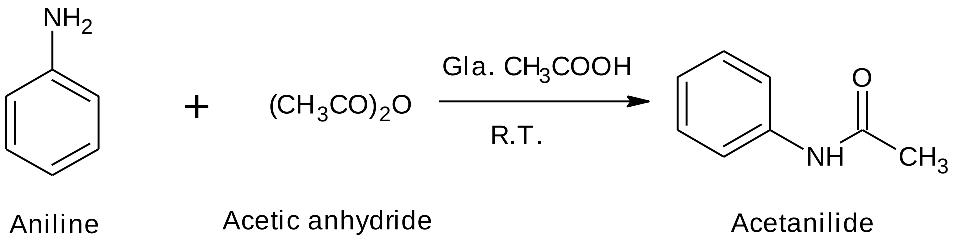
Figure 6.4: FTIR spectrum of synthesized 2-methyl quinolone

The FTIR spectrum of 2-methyl quinoline is shown in figure 6.4. Aromatic C-H stretching is observed at around 3020cm^{-1},C=C stretching occurs around 1488 cm^{-1} to 1592 cm^{-1}.The band appeared at around 1002 cm^{-1} to 1112 cm^{-1} corresponds to C-H bending vibration of aromatic phenyl ring. The absorption band in the range 1395cm^{-1}is due to –C=N stretching.

6.2.5 2-Chloroquinoline-3-Carboxaldehyde (2-Cl-3-FQ)

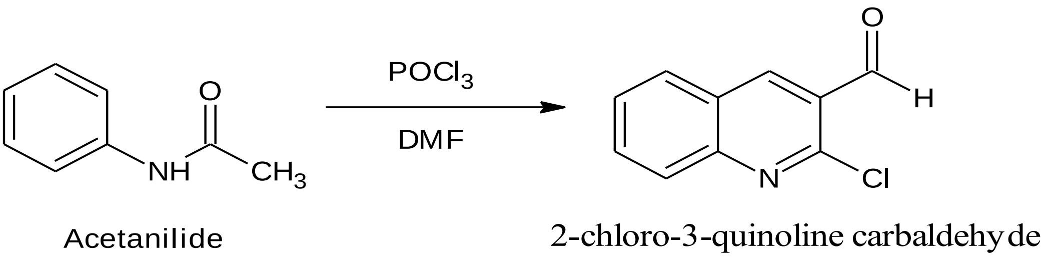
Step 1:-Preparation of acetanilide

Take 5 mL of acetic anhydride in a clean dry 100 mL conical flask and add 5 mL of glacial acetic acid and shake the contents thoroughly. To this mixture taken in the flask, add 5 ml of aniline and fit a water condenser. Place the flask on a wire-gauze placed on a tripod stand Boil the mixture for 10-15 minutes. Allow the mixture to cool. Detach the condenser and pour the liquid into about 150 mL ice-cold water contained in a beaker. During addition, stir vigorously the contents of the beaker with the help of glass-rod. Filter the white precipitates which separate out and wash with cold water.



Step 2:-Preparation of 2-Chloroquinoline-3-Carboxaldehyde

Take dimethyl formamide (DMF) 5 mL and cooled to 0^0C temperature in a flask equipped with a drying tube. Then 18 mL of $POCl_3$ (phosphorous oxy chloride) is added drop wise with stirring to it. Then to this solution add 4 g of acetanilide. After few minutes the solution of reaction mixture is refluxed for 6-8 hours using air condenser and the temperature of reaction mixture is maintained between 80-90^0C. After completion of requiring duration, the reaction mixture is cooled and poured in 100 mL beaker containing ice cold water and stirred about half an hour then filter precipitated quinoline and wash with water, dried and recrystallized from ethyl acetate [40].



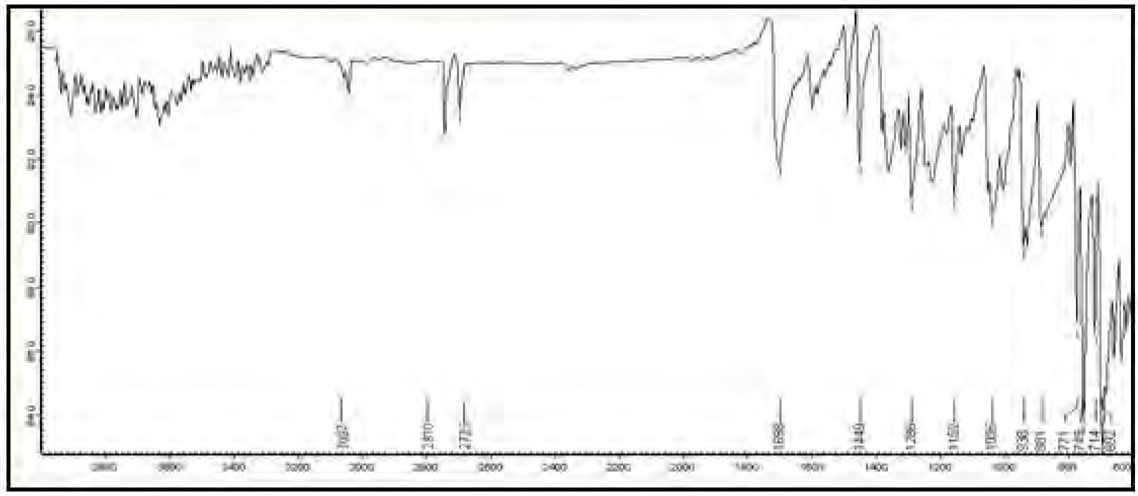


Figure 6.5: FTIR spectrum of synthesized 2-Chloroquinoline-3-Carboxaldehyde

The FTIR spectrum of 2-Chloroquinoline-3-carboxaldehyde is shown in figure 6.5 The peak at 3092 cm^{-1} contributes to aromatic C-H stretching vibration, and the peaks at around 1400 cm^{-1} to 1600 cm^{-1} prove the existence of C=C stretching. The peaks at around 2725 cm^{-1} to 2827 cm^{-1}corresponds to C-H stretching vibration of aldehyde. The peak at 1690 cm^{-1} belongs to C=O stretching vibration. The absorption peak at 1296 cm^{-1} to 1335 cm^{-1} corresponds to C-N stretching vibration. Peaks around 692$cm^{-1}$to 881 cm^{-1} belongs to C-Cl stretching vibration.

6.3 Results and Discussion

6.3.1 Weight loss Measurement

The corrosion of MS in 1N HCl in the absence and presence of various concentrations (100-500 ppm) of quinoline were studied by the weight loss experiments. The corrosion rate (W_{corr}) and the values of inhibition efficiency (%E) were calculated according to following equation:

$$E\,\% = \frac{W_0 - W}{W_0} \times 100 \qquad (1)$$

Where, W and W_0 are the weight loss of mild steel in the presence and absence inhibitors, respectively. The values of %E, W_0 and W were obtained from weight loss measurements with the addition of various concentrations of quinolines after 24 h of immersion in 1M HCl solutions. From table 6.1, it was found that the value of %E increases with an increase in the concentration of inhibitors which confirmed that the number of molecules adsorbed increased over the MS surface, blocking the active sites from acid attack and, thereby, protecting the metal from corrosion. At the highest concentration of 500 ppm of each additives studied, the %E attained was 92.57% for 2-AQ, 90-95% for 2-MQ, 83.52% for 8-NQ,82.13% 8-HQ and 81.90% for 2-Cl-3-FQ which confirmed that quinolines were very effective as inhibitors.

Inhibitor	**Concentration (ppm)**	**Weight loss (mg)**	**Corrosion rate (mg cm^{-2}h^{-1})**	**Surface coverage**	**E (%)**
Blank	0.00	431	59.86	-	-
	100	206	29.61	0.5220	52.20
	200	121	16.80	0.7192	71.92
2-AQ	300	98	13.61	0.7726	77.26
	400	68	9.44	0.8422	84.22
	500	32	4.44	0.9257	92.57
	100	137	19.03	0.6821	68.21
	200	78	10.83	0.8190	81.90
2-MQ	300	55	7.64	0.8723	87.23
	400	46	6.39	0.8932	89.32
	500	39	5.42	0.9095	90.95
	100	235	32.64	0.4547	45.47
	200	145	20.14	0.6635	66.35
8-NQ	300	106	14.72	0.7540	75.40
	400	85	11.80	0.8027	80.27
	500	71	9.86	0.8352	83.52
	100	280	38.89	0.350	35.03
	200	185	25.69	0.570	57.07
8-HQ	300	146	20.28	0.661	62.12
	400	99	13.75	0.770	77.03
	500	77	10.69	0.821	82.13
	100	285	39.58	0.3387	33.87
	200	197	27.36	0.5429	5429
2-Cl-3-FQ	300	163	22.64	0.6218	62.18
	400	110	15.28	0.7447	74.47
	500	78	10.83	0.8190	81.90

Table 6.1: The weight loss data obtained for mild steel in 1M HCl containing different concentration of quinolines at 298K

6.3.2 Adsorption isotherm

Fundamental information on the adsorption of inhibitor on metal surface can be obtained by adsorption isotherm. The weight loss temperature results were used to calculate the adsorption isotherm parameters. The most frequently used isotherms are Langmuir, Frumpkin, Temkin, Florry-Huggins and thermodynamic /kinetic model of El-Awady isotherm.

It was found that the adsorption of studied inhibitor on mild surface obeys Langmuir adsorption isotherm. Langmuir adsorption isotherm is given by following equation:

$$C/\theta=1/K_{ads}+C \qquad (2)$$

Where θ is the degree of surface coverage, C is the molar inhibitor concentration in the bulk solution and K_{ads} is the equilibrium constant of the process of adsorption. Plot of C/θ versus C of quinolines presented in fig.6.6.The obtained plots are almost linear with correlation coefficient (R^2=0.99) for Langmuir adsorption isotherm .K_{ads} can be calculated from intercepts of the straight lines in fig.6.6.

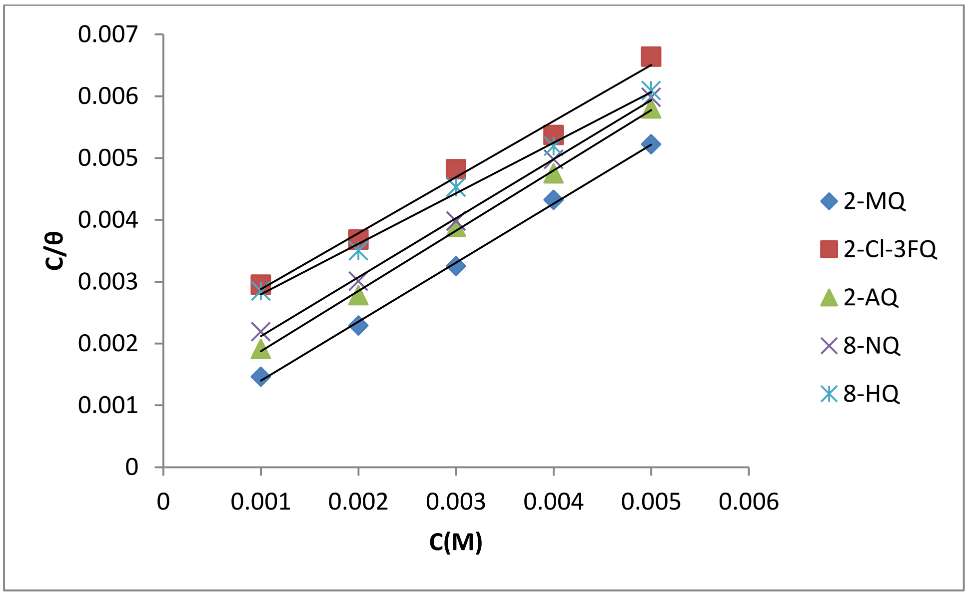


Figure 6.6: Langmuir adsorption isotherm plot for the adsorption of quinoline derivatives on the mild steel surface in 1.0M HCl solution

The standard free energy of adsorption (ΔG_{ads}) is calculated from equation [41].

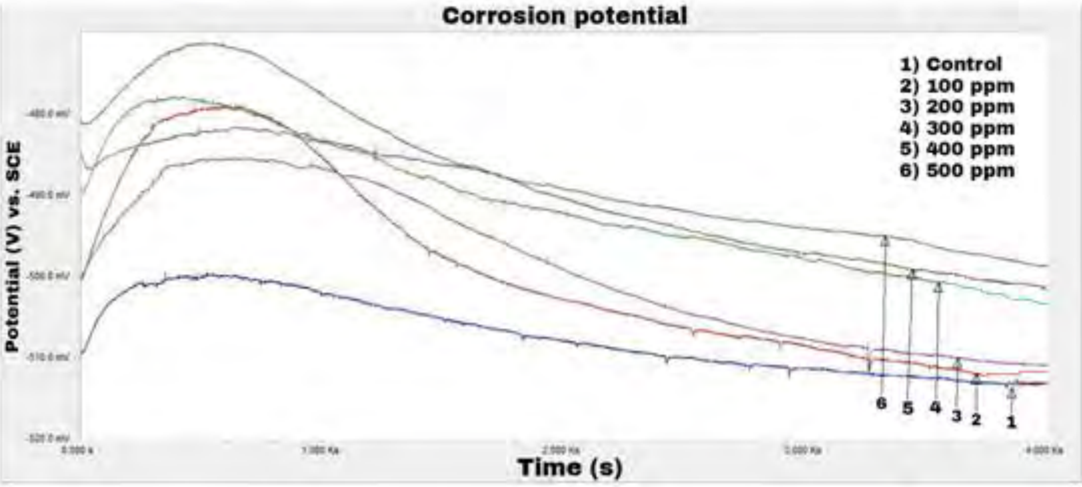
$$K_{ads}=(1/55.5)\exp(-\Delta G_{ads}/RT) \qquad (3)$$

Where the constant 55.5 is the molar concentration of water in solution in mol L^{-1}, R is universal gas constant and T is absolute temperature in kelvin. The negative values of ΔG_{ads} ensured the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface [42].Generally ,values of ΔG_{ads}, around -20 kJ mol^{-1}or lower are consistent with the electrostatic interaction between the charged molecules and charged metal, such as physisorption. When it is around -40 kJ mol^{-1} or higher, it involves charge sharing or charge transfer from organic molecules to the metal surface to form coordinate type of bond that is chemisorptions [43].In the present work the calculated value of ΔG_{ads} is -27.623 kJ mol^{-1} for 2-AQ, -29.34 kJ mol^{-1} for 2-MQ, -26.07 kJ mol^{-1} for 8-NQ, -25.352 kJ mol^{-1} for 8-HQ and -25.231 kJ mol^{-1} for 2-Cl-3-FQ, which indicate that adsorption of inhibitor on mild steel surface involves both physical and chemical adsorption.

6.4 Electrochemical Measurements

6.4.1 Open Circuit Potential (OCP) Curves

Inherent reactivity of the metallic materials in a particular environment is determined from its open circuit potential (corrosion potential). The influence of the corrosive and inhibitive species present in the electrolyte may be predicted by analysing the nature of the OCP curve. The variation of open circuit potential of mild steel exposed to 1M HCl solution containing quinoline derivatives in the concentration range 100-500ppm is shown in Fig.6.7-6.11.The steady state potential is obtained after 3600 seconds of the exposure period. In the presence of different concentration of inhibitors, OCP is shifted towards the positive potential direction in comparison to without inhibitor and get stabilized thus indicating the adsorption of the inhibitors on the metal surface. The magnitude of shift of polarization curve towards positive direction was found proportional to the concentration of the inhibitor [44].



6.7 .Open circuit potential of mild steel without and with different concentration of 2-AQ inhibitor in 1M HCl

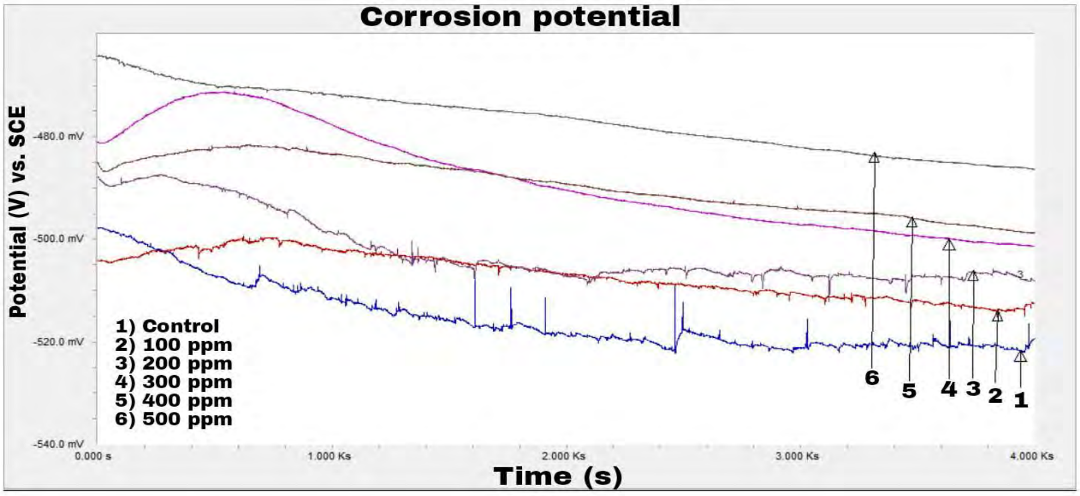


Figure 6.8: Open circuit potential of mild steel without and with different concentration of 2-MQ inhibitor in 1M HCl.

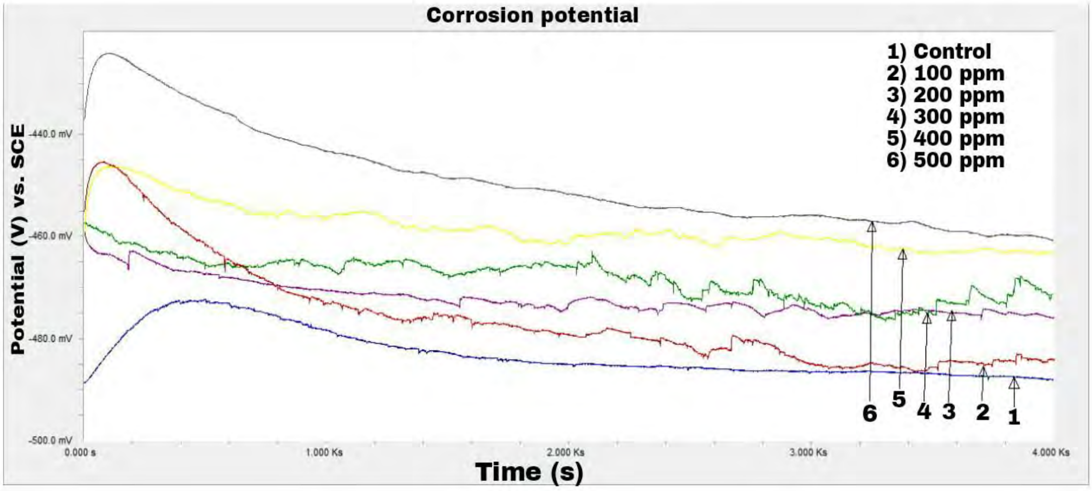


Figure 6.9: Open circuit potential of mild steel without and with different concentration of 8-MQ inhibitor in 1M HCl.

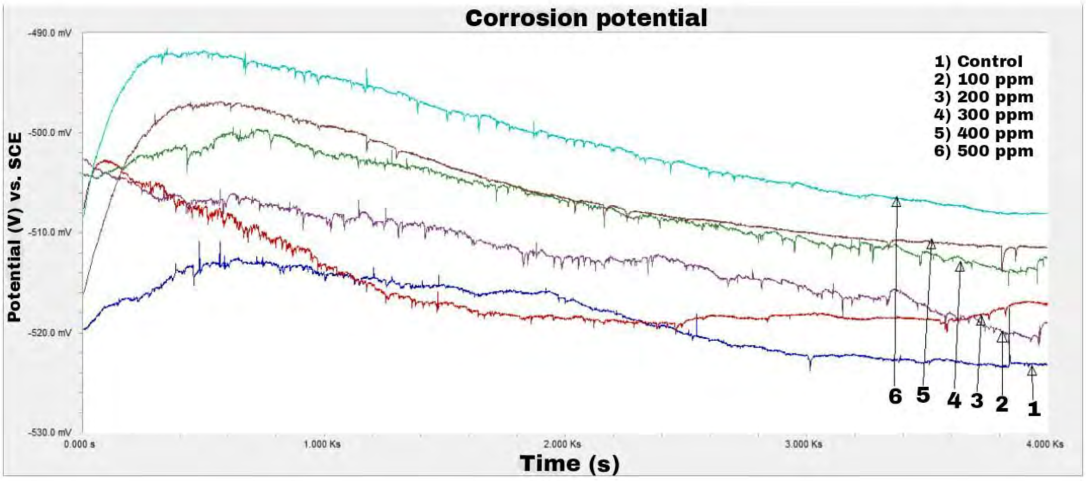


Figure 6.10: Open circuit potential of mild steel without and with different concentration of 8-HQinhibitor in 1M HCl.

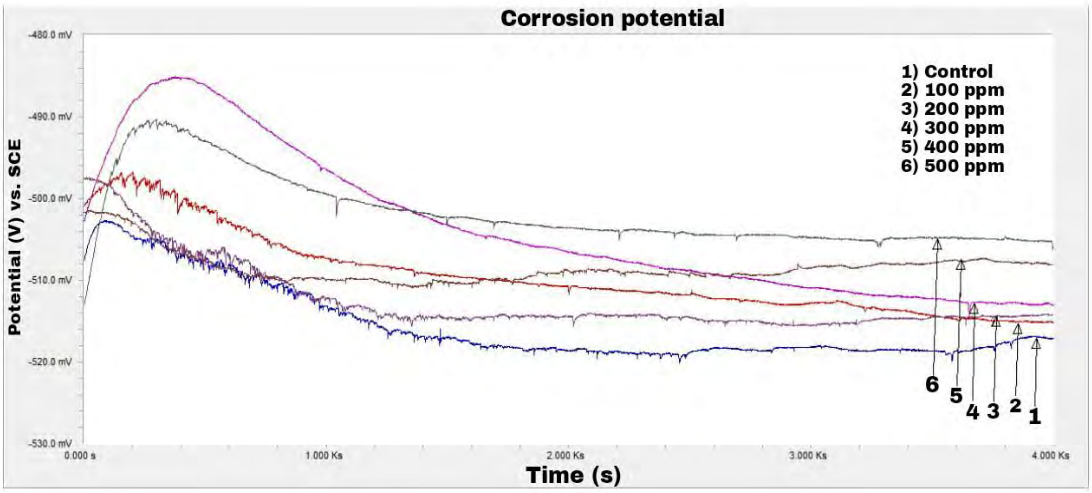


Figure 6.11: Open circuit potential of mild steel without and with different concentration of 2-Cl-3-FQinhibitor in 1M HCl.

6.4.2 Potentiodynamic Polarisation Studies

Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of quinoline derivatives is illustrated in fig.6.12-6.16.The presence of quinoline derivatives caused a clear decrease in both anodic and cathodic current densities with increase in inhibitor concentration, probably due to the adsorption of inhibitor at the active sites of the electrode surface, retarding both metallic dissolution and hydrogen evolution reaction [45-48]. The electrochemical kinetic parameters, i.e., corrosion current densities (i_{corr}), corrosion potential (E_{corr}), cathodic Tafel slop (β_c) anodic Tafel slope (β_a) are presented in table 6.2. The corrosion current density decreased with increasing the concentration of the inhibitor, which indicates that the presence of quinoline derivatives retard the dissolution of mild steel in 1 M HCl solution and degree of inhibition depends on the concentration of inhibitor.

It can also be observed that the corrosion potential values remained almost constant in presence of inhibitor, suggesting that quinoline derivatives acted as mixed-type inhibitor .Furthermore, it is observable that the shape of polarization curves are similar in the absence and presence of quinoline derivatives, suggesting that the inhibitor inhibits mild steel corrosion by simply adsorbing on mild steel surface without changing the mechanism of mild steel dissolution [49-52].

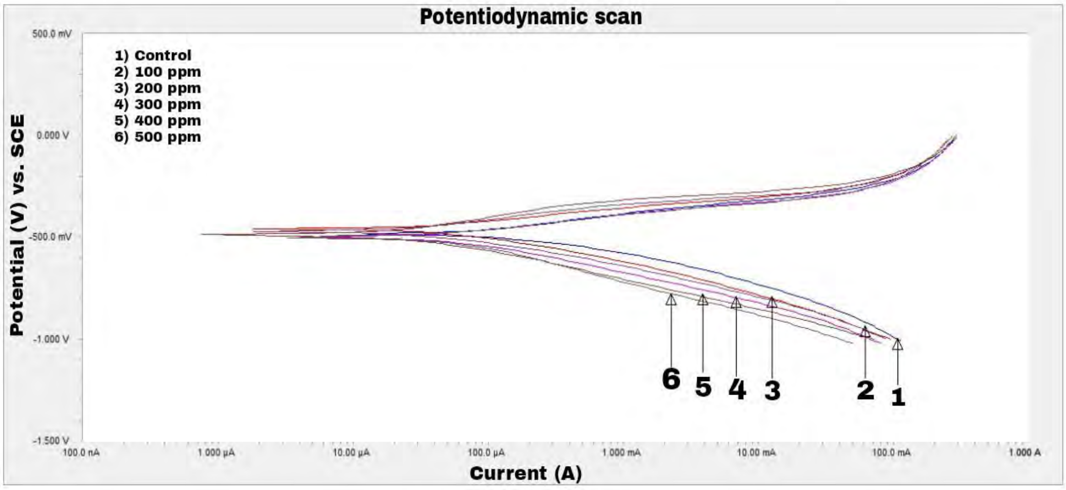


Figure 6.12: Potentiodynamic polarization of mild steel without and with different concentration of 2-AQ in 1M HCl.

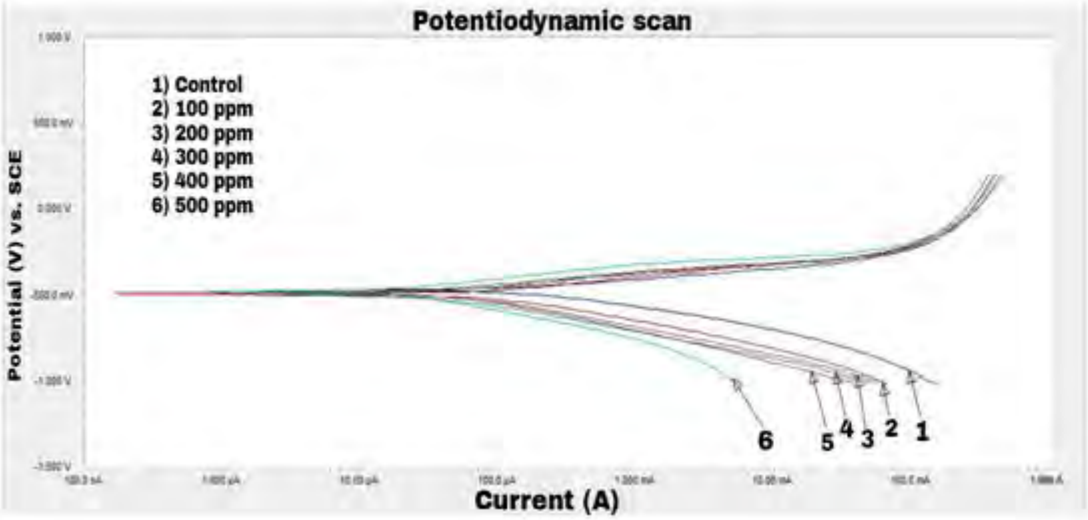


Figure 6.13: Potentiodynamic polarization of mild steel without and with different concentration of 2-MQ in 1M HCl.

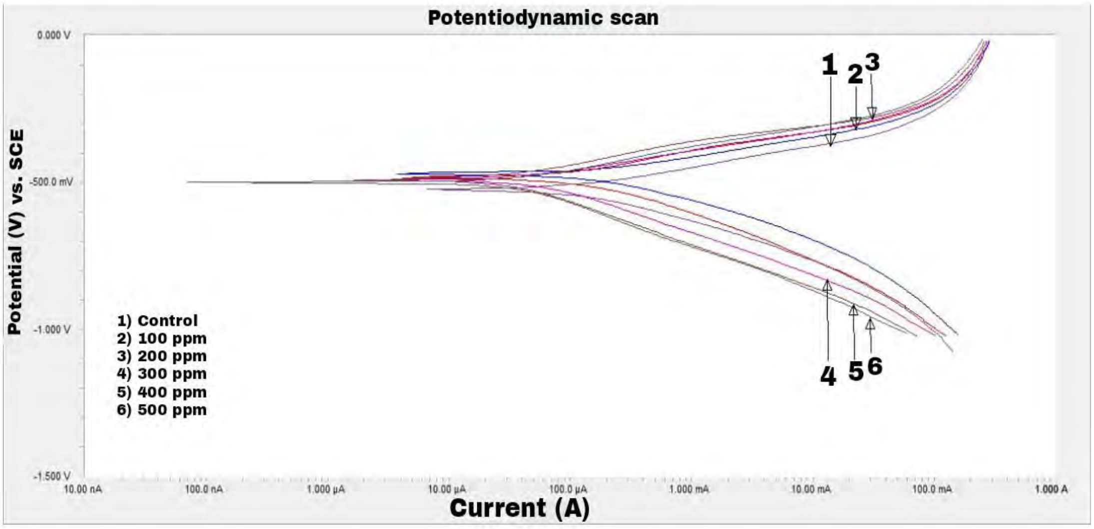


Figure 6.14: Potentiodynamic polarization of mild steel without and with different concentration of in 8-NQ 1M HCl.

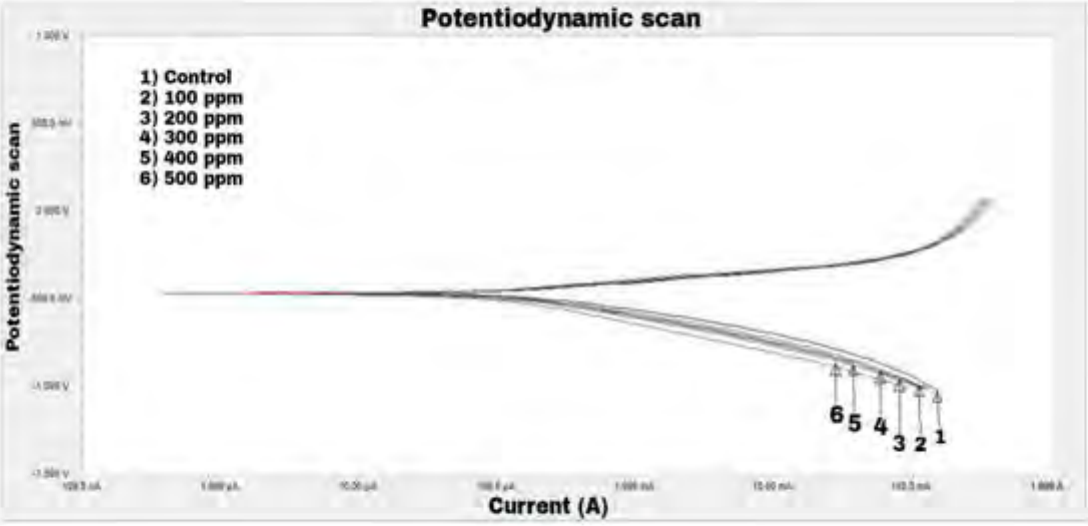


Figure 6.15: Potentiodynamic polarization of mild steel without and with different concentration of 8-HQ in 1M HCl.

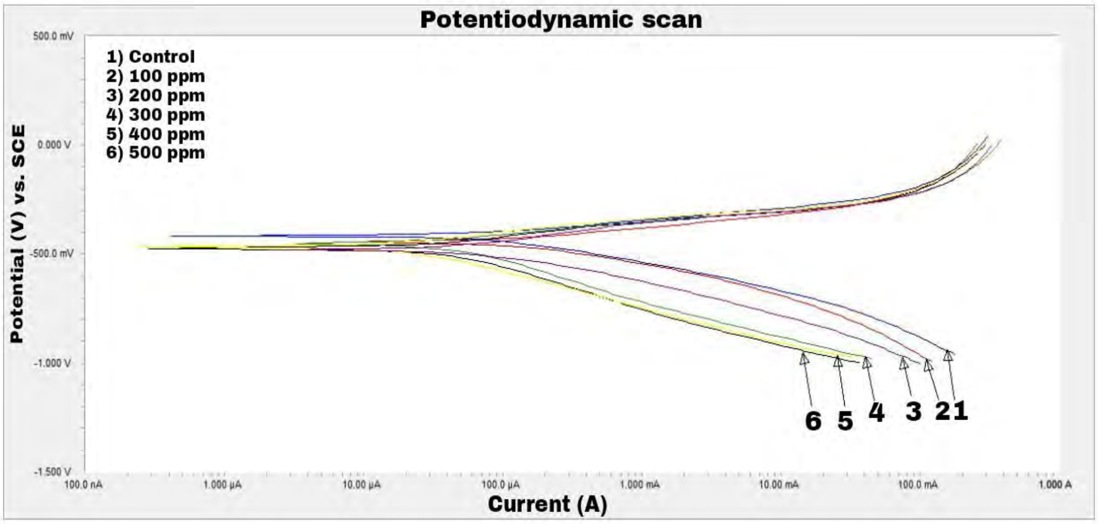


Figure 6.16: Potentiodynamic polarization of mild steel without and with different concentration of 2-Cl-3-FQ in 1M HCl.

Concentration of Inhibitors (ppm)	$-E_{corr}$ (mv)	I_{corr} ($\mu A/cm^2$)	β_a (v/dec)	β_c (v/dec)	IE %
1M HCl	475.0	133.0	76.90 e^{-3}	134.4 e^{-3}	-
2-AQ					
100	490	65.03	62.22 e^{-3}	132.5 e^{-3}	51.10
200	500	39.59	64.32 e^{-3}	122.3 e^{-3}	70.23
300	495	32.94	72.10 e^{-3}	121.1 e^{-3}	75.23
400	497	19.64	80.22 e^{-3}	123.0 e^{-3}	85.23
500	505	11.66	82.43 e^{-3}	103.3 e^{-3}	91.23
2-MQ					
100	485	43.58	64.29 e^{-3}	129.9 e^{-3}	67.23
200	498	23.51	82.34 e^{-3}	103.2 e^{-3}	82.32
300	497	15.10	80.20 e^{-3}	123.4 e^{-3}	88.64
400	488	12.99	68.26 e^{-3}	158.1 e^{-3}	90.23
500	495	11.67	57.56 e^{-3}	125.5 e^{-3}	91.22
8-NQ					
100	445	72.45	65.90 e^{-3}	128.9 e^{-3}	45.52
200	425	43.29	78.65 e^{-3}	125.6 e^{-3}	67.45
300	476	31.44	81.36 e^{-3}	122.1 e^{-3}	76.36
400	452	23.95	64.28 e^{-3}	118.5 e^{-3}	81.99
500	495	19.64	80.98 e^{-3}	112.2 e^{-3}	85.23
8-HQ					
100	472	85.10	65.70 e^{-3}	127.0 e^{-3}	53.84
200	481	54.10	90.40 e^{-3}	126.0 e^{-3}	68.15
300	503	40.20	85.30 e^{-3}	140.1 e^{-3}	72.77
400	508	35.20	86.90 e^{-3}	146.2 e^{-3}	79.65
500	463	26.64	85.30 e^{-3}	125.2 e^{-3}	85.42
2-Cl-3-FQ					
100	492	90.28	75.45 e^{-3}	140.1 e^{-3}	32.12
200	490	59.54	63.46 e^{-3}	132.0 e^{-3}	55.23
300	478	48.42	79.89 e^{-3}	110.9 e^{-3}	63.59
400	498	32.62	82.23 e^{-3}	122.1 e^{-3}	75.47
500	495	22.75	80.58 e^{-3}	126.8 e^{-3}	82.89

Table 6.2: Electrochemical data obtained from polarization of mild steel in 1M HCl in the absence and presence of different concentration of (a) 2-AQ, (b) 2-MQ, (c) 8-NQ, (d) 8-HQ, (e) 2-Cl-3-FQ.

6.5 Surface Studies

6.5.1 Scanning Electron Microscopic (SEM) Analysis

The SEM images were recorded to establish the interaction of inhibitor molecules with metal surface.

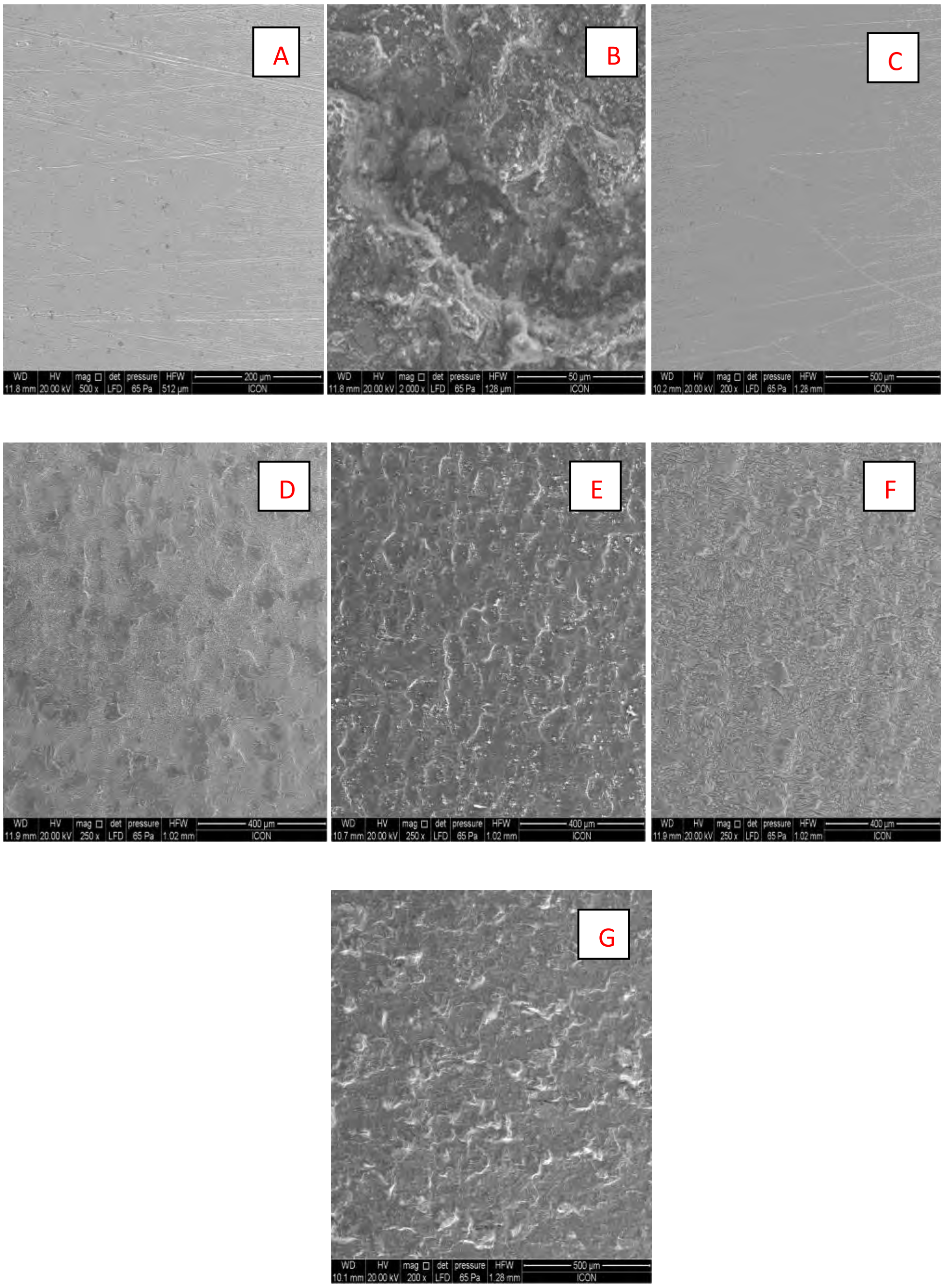
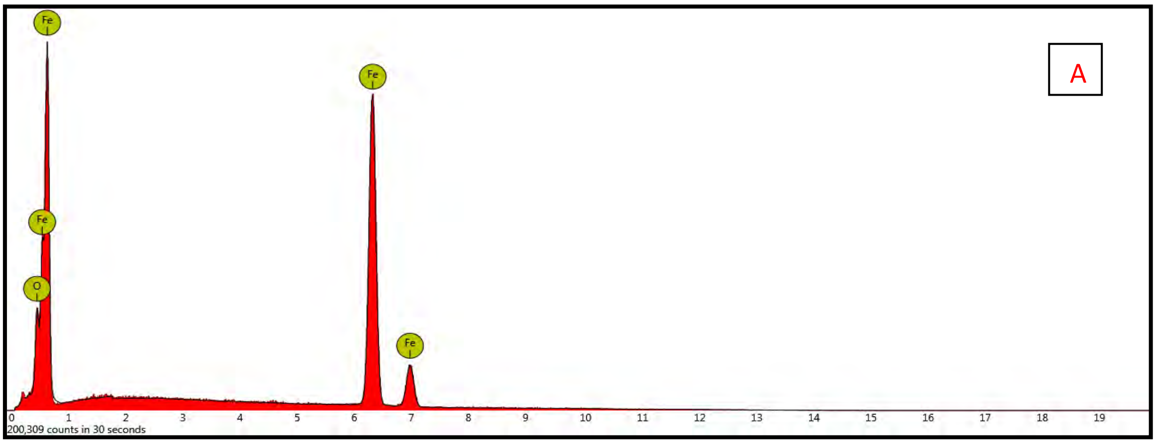


Figure 6.17: SEM of mild steel with (A) Polished, (B) 1M HCl, (C) 500 ppm of 2-AQ (D) 500 ppm of 2-MQ (E) 500 ppm of 8-NQ (F) 500 ppm of 8-HQ and (G) 500 ppm of 2-Cl-3-FQ

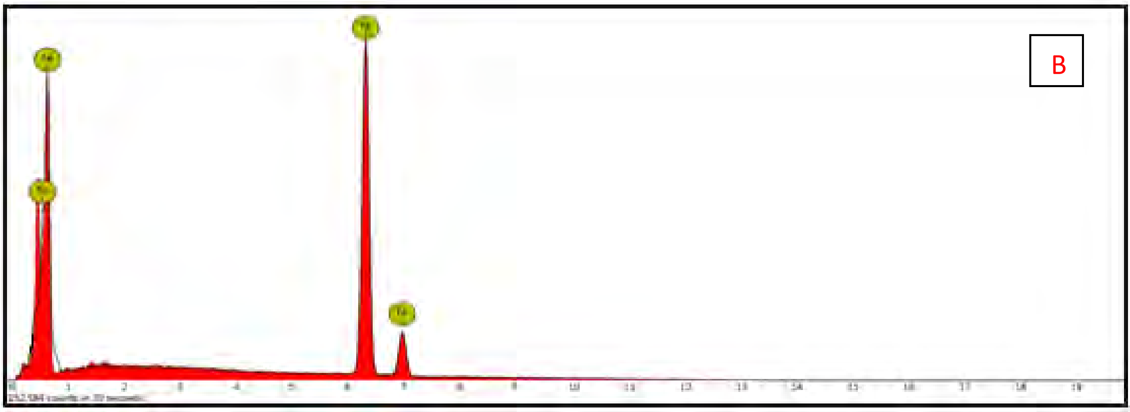
Fig. 6.17(A) represents the SEM image of polished mild steel specimen. Fig.6.17 (B) shows SEM image of surface of mild steel after immersion in acid without inhibitors. This image shows the effect of acid on surface damage due to corrosive attack leading to pitting and undulation. Fig.6.17(C-G) shows the appearance of smooth mild steel surface after addition of inhibitors to acid solution. This demonstrates that the addition of inhibitors reduces corrosive pitting which occurs in acid solution. The extent of protection can be considered to be high since pitting decreases significantly. Thus it can be concluded that corrosion is much less in presence of inhibitors and more polished surface was obtained in case of 2-AQ as compared to other quinolone derivatives, which in turn proves its higher inhibition efficiency.

6.5.2 Energy-dispersive X-ray spectroscopy (EDX)

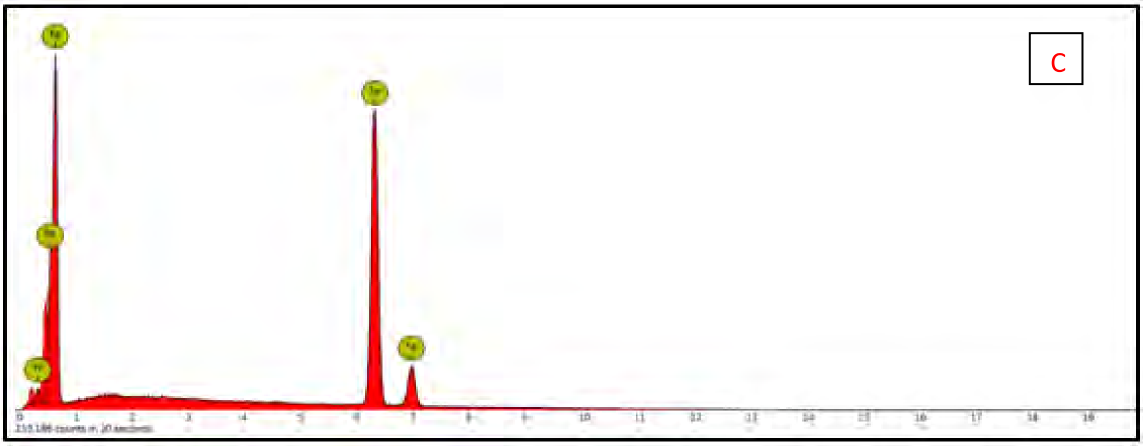
The energy dispersive X-ray analysis (EDX) technique was employed in order to get information about the composition of surface of mild steel sample in absence and presence of inhibitor in a 1M HCl. EDX spectrum of polished mild steel surface shown in Fig.6.18(A) indicates some characteristic peaks of the elements constituting surface. The spectrum of polished mild steel surface after immersion in 1M HCl solution for 24 h in absence of inhibitors is shown in fig.6.18(B).However, EDX spectrum in the presence of quinoline derivative (Fig.6.18 (C-G)) shows additional signal for nitrogen (N),oxygen (O) and chlorine (Cl) which may be attributed due to adsorption of quinoline derivatives on mild steel surface. Therefore, EDX and SEM examination of the mild steel surface support the results obtained from weight loss and electrochemical methods that investigated quinoline derivatives are efficient inhibitor for mild steel in 1M HCl.



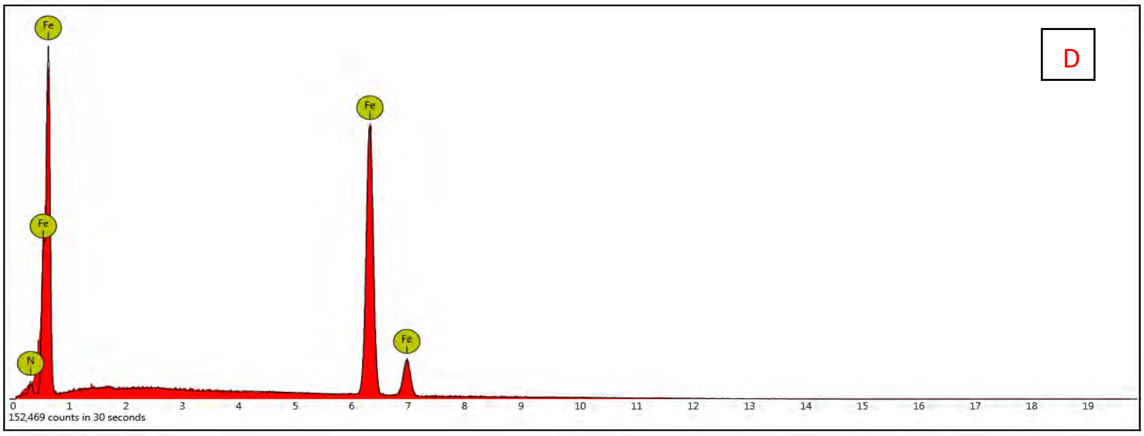
A) Polished sample



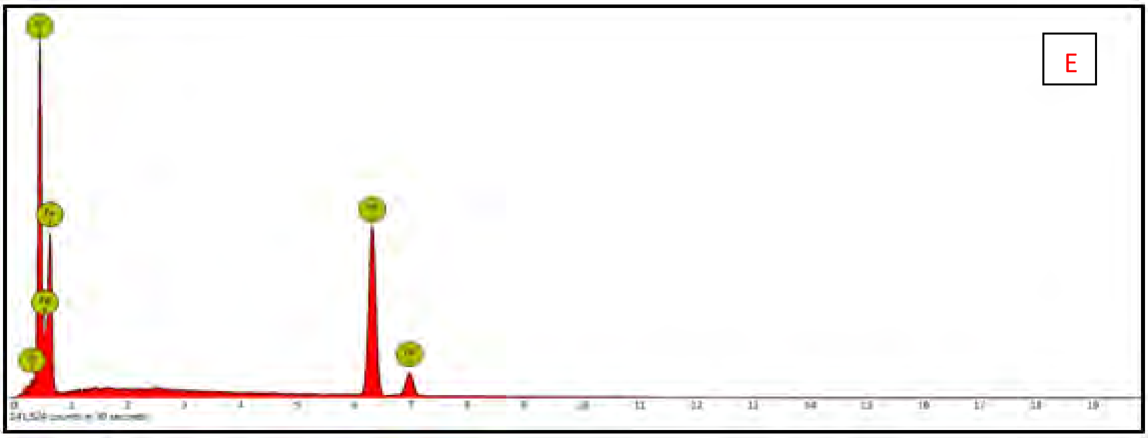
B) Control (1M HCl)



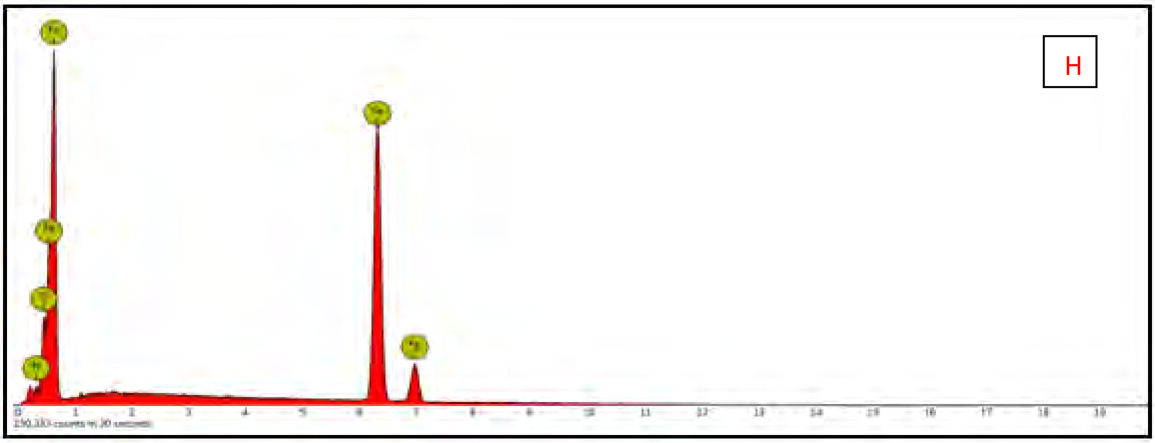
C) 1M HCl+500 ppm 2-AQ



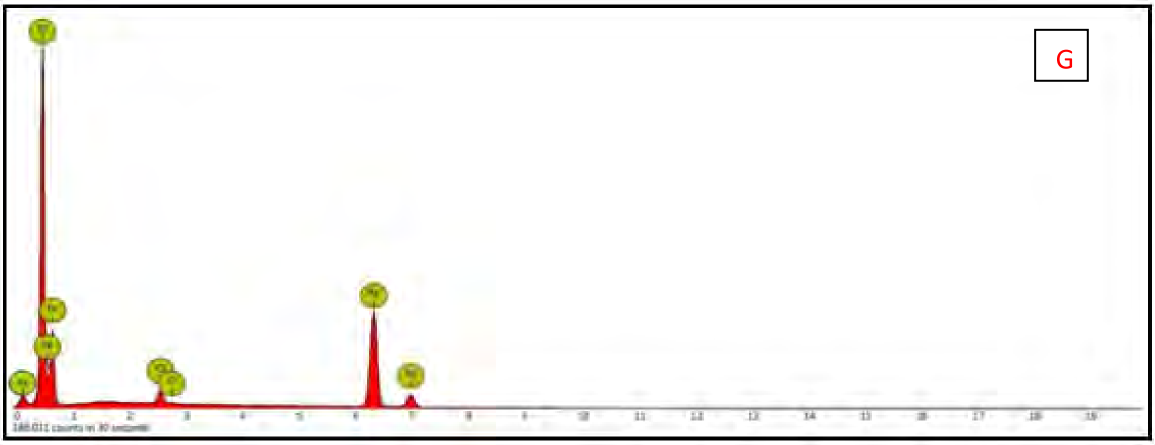
D) 1M HCl+500 ppm 2-MQ



E) 1M HCl+500 ppm 8-NQ



H) 1M HCl+500 ppm 8-HQ



G) 1M HCl+500 ppm 2-Cl-3-FQ

Figure 6.18 :EDAX of mild steel : (A)Polished, (B) 1M hydrochloric acid, (C) 500 ppm of 2-AQ (D) 500 ppm of 2-MQ (E) 500 ppm of 8-NQ (F) 500 ppm of 8-HQ and (G) 500 ppm of 2-Cl-3-FQ.

6.6 Mechanism of Inhibition

Inhibition of corrosion of mild steel in 1 M HCl by the investigated compounds as measured by chemical and electrochemical techniques were found to depend on both the concentration and the nature of the inhibitor. The observed corrosion data in presence of the inhibitors indicate that the corrosion inhibition is due to adsorption of the inhibitors at the metal-solution interface. However, inhibition efficiency of the additive compounds depends on many factors [53-55], which include the number of adsorption active centres in the molecule, and their charge density, complex formation molecular size, and mode of interaction with metal surface. It has been established that the inhibitor molecule containing heteroatoms particularly nitrogen, sulphur, oxygen and phosphorus inhibits metallic corrosion in acid solution by adsorbing at the metal/electrolyte interfaces. Previously, it has been investigated by several authors [56-58] that heteroatoms of the inhibitor molecule in acid solution easily undergo protonation due to the presence of unshared electron pair on these atoms, and therefore in acid solution organic compounds exist in cationic form. On the other hand the metallic surface becomes negatively charged due to the presence of uniform layer of counter ions (chloride ions of hydrochloric acid) present over the metallic surface. These appositively charged species attracted each other through electrostatic force of attraction, and therefore it can be concluded that first step involves physisorption during the inhibitor adsorption processes. However, as soon as inhibitor comes in its neutral form by release of hydrogen gas at cathode, the chemisorption takes place by transfer of free unshared electron pairs of heteroatoms into empty d-orbitals of surface iron atoms [59]. Moreover, this type of electron transfer causes excessive accumulation of negative charge on electron rich metallic surface which renders it to transfer its electrons to the empty anti-bonding molecular orbitals of the inhibitors through retro-donation. The combination of the all ways of adsorption strengthens adsorption of inhibitor molecules on mild steel surface [60].

The order of decreasing inhibition efficiency of the tested additives is: 2-AQ>2-MQ>8-NQ>8-HQ>2-Cl-3FQ. This order is due to the presence of electron donating groups in compounds 2-AQ, 2-MQ and 8-HQ but compounds 8-NQ and 2-Cl-3FQ have electron withdrawing groups compounds containing electron donating groups are more efficient than compounds containing electron withdrawing groups. The electron donating groups enhance adsorption and increase the surface coverage. Compound having electron donating groups with lone pairs on the atoms adjacent to the π system activate the aromatic ring by increasing the electron density on the ring through a resonance donating effect [61-63].

2-AQ shows highest inhibition efficiency of 92.57% due to the presence of strong electrons donating –NH_2 group. 2-MQ shows inhibition efficiency of 90.95% due to presence of electron donating –CH_3 group. 8-NQ possess –NO_2 group which is strongly deactivating but still it shows higher inhibition efficiency as compared to compound 8-HQ which contains electron donating –OH group. This is because the charge accumulation regions have a bias towards O atoms (Fig. 11b). O atom provides lone pair electrons to enable the formation of coordination bonds with Fe atoms. The lower inhibition efficiency of 2-Cl-3FQ is attributed to the presence of two electron withdrawing groups namely,-Cl and –CHO which decrease the electron density around nitrogen atom of quinoline ring. Therefore, the order of inhibition efficiency is 2-AQ>2-MQ>8-NQ>8-HQ>2-Cl-3FQ.

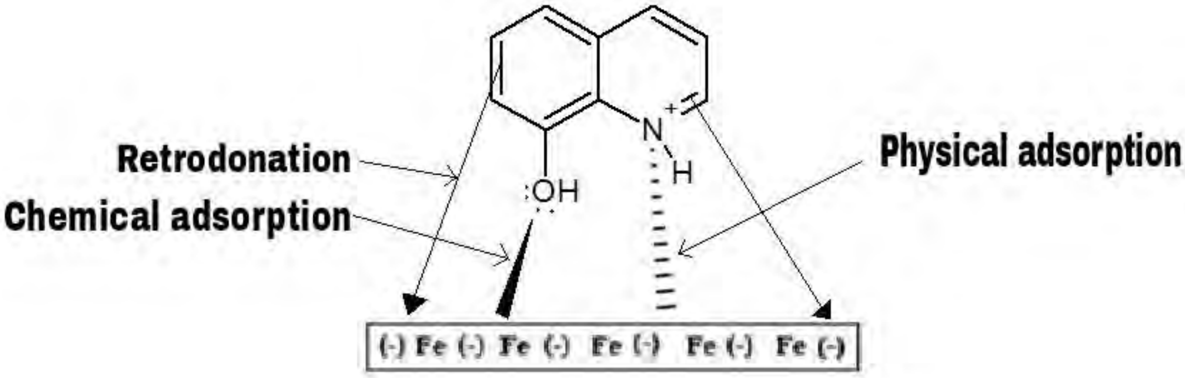


Figure 6.19: Pictrorial representation of adsorption of one of the tetrazole derivative on MS surface in 1M HCl

6.7 Conclusions

The tested quinoline derivatives namely,2-amino quinoline,2-methyl quinoline, 8-nitroquinoline, 8-hydroxy quinoline and 2-chloro-3-quinoline carboxylehyde inhibit the corrosion of mild steel in 1M HCl. It is obvious from nature of polarization curves that the addition of quinoline derivatives does not change the mechanism of either mild steel dissolution or hydrogen evolution reaction. These quinoline derivatives act as mixed type of inhibitor. The inhibition efficiency value increases with the inhibitor concentration and reaches a maximum at 500 ppm. The corrosion inhibition by 2-amino quinoline,2-methyl quinoline,8-nitroquinoline,8-hydroxy quinoline and 2-chloro-3-quinolinecarboxylehyde can be interpreted by a simple blocked fraction of the electrode surface related to the adsorption of the inhibitor species according to a Langmuir isotherm on the mild steel surface. The results obtained from polarisation curves and the weight loss are in reasonably good agreement. The inhibition efficiency of these derivatives are in the following order of : 2-aminoquinoline>2-methylquinoline>8-nitroquinoline>8-hydroxyquinoline>2-chloro-3-quinolinecarboxylehyde.

The inhibitive effect of quinoline dervative is due to the formation of adsorbed film on the metallic surface occured by electrostatic attraction between the heteroatoms in quinoline derivatives and iron mettalic surface,as it was demostrated by the SEM and EDX analysis.

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LIST OF PUBLICATIONS

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A. Papers Published in Journal and Proceedings

Sr. no.	Paper Title	Name of Journal /Proceedings
1.	Study of 1,2,4-Triazole As Effective Corrosion Inhibitor For Mild Steel Used In Oil And Gas Industries In 1M HCl	International journal of scientific research in science, engineering and technology Vol.5, issue 4,(2018),pp.95-102.
2.	Inhibitive effect of 8-hydroxy Quinoline on the corrosion of mild steel in 1M HCl	International journal of scientific research in science, engineering and technology Vol.5, issue 4, (2018), pp.103-107.
3.	Corrosion Control of Mild Steel used in Oil and Natural Gas Industries by Triazole derivatives in 1M HCl	CORCON- 2017, organized by NACE International, Gateway India Section (NIGIS).
4.	Corrosion Inhibition of Mild Steel used in Oil and Natural Gas Industries by Using 5-Phenyl tetrazole	CORCON- 2017, organized by NACE International, Gateway India Section (NIGIS).

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Study of 1,2,4-Triazole As Effective Corrosion Inhibitor For Mild Steel Used In Oil And Gas Industries In 1M HCl

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ABSTRACT

The corrosion inhibition effect of 1,2,4-triazole on mild steel in 1 M HCl solution has been investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization methods. The experimental results revealed that the compound having significant inhibiting effect on the corrosion of mild steel in 1M HCl solution. The inhibition efficiency was found to increase with increasing concentration of inhibitor and attain maximum value of 93% at 500 ppm concentration. Potentiodynamic polarization studies have shown that the compound acted as mixed-type inhibitor retarding the corrosion of mild steel by blocking the active sites of metal surface. The values of inhibition efficiency obtained from weight loss and polarization measurements are in good agreement. The adsorption of the inhibitor on mild steel surface followed Langmuir adsorption isotherm with negative value of the free energy of adsorption $\Gamma G^0_{ads.}$The surface morphology of the mild steel specimen was evaluated by using scanning electron microscopy(SEM)and energy dispersive x-ray analysis(EDAX) techniques.

Keywords: Triazole, Mild Steel, Inhibitor, Surface Morphology.

I. INTRODUCTION

Mild steel is an important category of material due to wide range of industrial applications[1-4]. Hydrochloric acid solutions are widely used for pickling, descaling, acid cleaning and oil well acidizing industry which leads to electrochemical corrosion. Among the various methods available, use of corrosion inhibitor is one of the most practical and economical method for corrosion protection of steel especially in acid media[4-8].An organic corrosion inhibitor is a chemical material applied to a liquid or gas within industrial processes to decrease the corrosion rate of metal or its alloy[9].Organic inhibitors containing heteroatom such as O,N,S and P are frequently used in order to minimize the corrosion attack on metal in acid media [10-15]. Organic inhibitors are generally adsorbed on metal surface and forms protective film which acts as barrier between the metal and aggressive solutions. The efficiency of organic compounds as an inhibitor depends on its ability to get adsorbed on the metal surface by replacing water molecule from metal surface. Nitrogen containing heterocyclic compounds are found very effective and efficient corrosion inhibitor of mild steel in acidic media. Persual of literature reveals that many N-heterocyclic compounds such as pyrazole, bipyrazole, benzimidazole, triazole, tetrazole, quinoline, isoquinoline,indole and quinoxaline have been used for corrosion inhibition of mild steel in acidic media [16-20]. Triazole and its derivatives are important constituents of pharmacologically active compounds. They possess wide spectrum of activities ranging from antibacterial, anti-inflammatory, anticonvulsant and anti-neoplastic[21].A few triazole have been reported as corrosion inhibitor in different corrosive environment.

The present study was undertaken to investigate the inhibition of corrosion of mild steel in 1M hydrochloric acid by 1,2,4-triazole.The study was conducted by using weight loss, electrochemical technique, Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques.

II. METHODS AND MATERIAL

2.1. Material and sample preparation

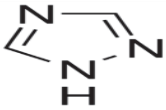
The weight loss and electrochemical experiments were performed on mild steel specimen having chemical composition, C-0.16%, Si-0.10%, Mn-0.40%, P-0.013%, S-0.02% and remaining iron. The exposed dimensions were 1cm x 3cm x 0.025cm and 1cm^2 for the weight loss and electrochemical experiment respectively. Before exposure to test solution exposed areas were polished successively with different grades of metallographic emery paper,1/0,2/0,3/0 and 4/0, washed with doubled distilled water, degreased with acetone and finally dried and stored in desiccators.

2.2. Test solution

1 M HCl was prepared by dilution of 36% HCI (analytical grades) in bi-distilled water.

The characterization data, IUPAC name, structure and abbreviation used for the studied compound are given below in Table 1.

Table 1. IUPAC name, molecular structure, melting point and analytical data of studied inhibitor.

Inhibitor	Molecular Structure	Analytical data
1,2,4-Triazole		**MP-** 120-122 °C

2.3. Weight loss measurement:

The weight loss experiment was performed by immersing mild steel specimen in 50 ml of test solution with and without different concentration of inhibitors. After 24 h immersion time, the mild steel specimens were taken out, cleaned with distilled water, dried and accurately weighed. Each experiment was performed in triplicate to obtain good result and the mean value is reported. The inhibition efficiency was calculated by using the following relation:

$$\eta\% = \frac{W_0 - W_{corr}}{W_0}$$

Where W_0 and W_{corr} are the weight loss in absence and presence of inhibitors .The surface coverage is given by following relation

$\theta = \eta\%/100$.

2.4 Electrochemical measurement:

Polarization studies were carried out using electrochemical measurement system, DC 105, containing software of DC corrosion technique from M/S Gamry instrument, 734, Louis Drive, Warminster, PA, USA. For polarization studies, mild steel specimens having surface area of 1cm^2 were exposed to acid solution .Mild steel as working electrode, saturated calomel (SCE) as reference electrode and graphite as auxiliary electrode were used for all electrochemical measurement. Before each measurement the specimen were allowed to corrode freely, and their OCPs were measured as a function of time to obtain a steady-state potential. The anodic and cathodic Tafel curves were obtained by changing the electrode potential automatically from - 0.5 to 0.5 V at the scan rate of 5mv/s. Polarization study was done with and without inhibitors in 1M HCI.

2.5 Surface measurement:

The surface film formed on the metal specimen was evaluated by SEM-EDX analysis. This was carried out by using SEM/EDX model PHENOM PROX from the

Netherlands. The spectra were recorded for a sample exposed for 24 hours in 1M HCl in the absence and presence of 500 ppm inhibitor. The energy of acceleration beam employed was 20 kV.

III. RESULTS AND DISCUSSION

3.1 Weight loss measurement:

Weight loss data of mild steel in 1 M HCl in the absence and presence of various concentrations of inhibitor were obtained and given in table 2. Inhibition efficiencies were calculated according to following equation:

$$\%IE = \frac{W_0 - W_{corr}}{W_{corr}} \quad --- (1)$$

W_{corr} and W_0 are weight loss of mild steel in presence and absence of inhibitors respectively. The results showed that the inhibition efficiency increases with increasing the concentration of inhibitors. The results obtained from the weight loss measurement were in good agreement with those obtained from electrochemical measurements.

Table 2. The weight loss parameter obtained for mild steel in 1 M HCl containing different concentrations of 1, 2, 4-triazole.

Inhibitor	Concentration (ppm)	Weight loss (mg)	Surface coverage	Inhibition efficiency (%E)
Blank	-	235	-	-
1,2,4-triazole.	100	42	0.8212	82.12
	200	30	0.8723	87.23
	300	28	0.8808	88.08
	400	21	0.9106	91.06
	500	16	0.9319	93.19

3.2 Adsorption isotherm

The surface coverage values θ, (defined as θ = %IE/100), increased with increasing inhibitor concentration as a result of adsorption of more inhibitor molecules on the steel surface (Table-2). If molecular adsorption at the metal/solution interface is the mechanism through which the corrosion inhibition occurs, several adsorption isotherms can be tested. The simplest, being the Langmuir isotherm, is based on the assumption that all adsorption sites are equivalent and that molecular binding occurs independently from nearby sites being occupied or not. Under these circumstances, the proportionality between surface coverage θ and bulk concentration C of the adsorbing compound is as follows [22]:

$$KC = \theta / (1-\theta) \quad ----- (2)$$

Here K is the equilibrium constant. It is convenient to rearrange the equation, yielding:

$$C / \theta = C + 1/K \quad ----- (3)$$

The graph of C/θ vs C obtained straight line with R^2 value obtained varied close to unity confirming the validity of this approach .The slope of the straight line was almost close to unity, suggesting that adsorbed molecule formed monolayer on mild steel surface.

Free energy of the adsorption (ΔG^0_{ads}) can be calculated by using the following equation:

$$\Delta G^0_{ads} = -RT \ln (55.5\ k_{ads}) \quad ----- (4)$$

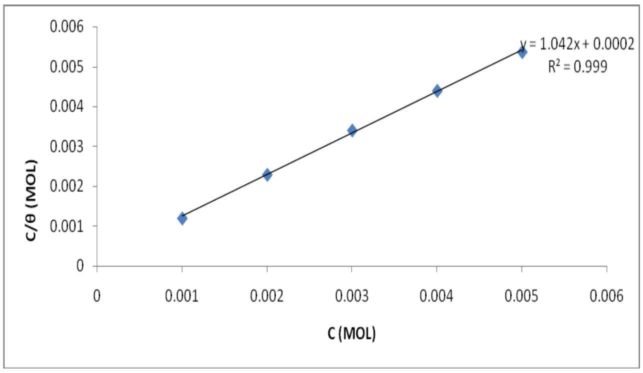


Figure 1. Langmuir isotherm plot for adsorption of 1,2,4-triazole on mild steel surface in 1 M HCl.

Generally, value of ΔG^0_{ads} up to -20 kjmol^{-1} are associated with physisorption while those around -40 kjmol^{-1} or higher are associated with chemisorptions. In present case the value was -31.05. This was lower than -40 kJ mol^{-1} but higher than -20 KJmol-1 indicating that the adsorption was neither typical physisorption nor chemisorption but it is mixed type. Thus in the present case adsorption of inhibitor molecule on the mild steel involved both physisorption and chemisorptions but physisorption was the predominant mode of adsorption. The negative value of ΔG^0_{ads} indicated the spontaneous adsorption of inhibitors on the surface of the metal [23,24]

3.3 Open circuit potential (OCP) measurement

The electrochemical behaviour of mild steel in 1M HCl was studied by monitoring change in corrosion potential (Ecorr.) with time. The change in open circuit potential of mild steel in absence and presence of various concentrations of inhibitors is shown in Figure 2.

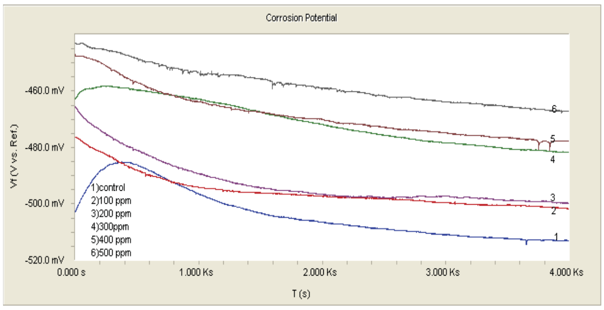


Figure 2. Open circuit potential diagram for mild steel in 1 M HCl without and with different concentrations of 1,2 , 4-Triazole.

The change in OCP of mild steel in absence and presence of inhibitors were measured for period of one hour with sample period of one data per second. The potential attains steady state after exposure of approximately 30 minutes. The steady state potential is an equilibrium state at which Iox. equal to Ired. It has been observed that OCP of mild steel from moment of immersion in 1M HCl tends towards more negative value in absence of inhibitor. This shows corrosiveness of medium which is due to breakdown of pre-immersion, air formed oxide film on the metal surface. In the presence of various concentrations of inhibitors the steady state potential of mild steel shifts more towards positive value. This is due to adsorption of inhibitors on metal surface resulting in passivation of metal.

3.4 Potentiodynamic polarisation studies

The polarization behaviour of mild steel in 1 M HCl in the absence and presence of different concentration of inhibitors are shown in Figure 3.

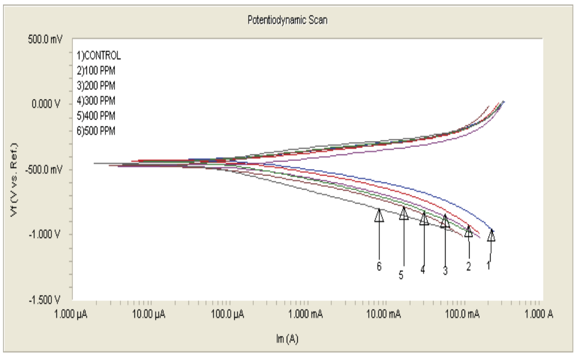


Figure 3. Polarization curve of mild steel in the absence and presence of 1,2,4-Triazole.

Electrochemical parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}), and Tafel slopes constant β_a and β_c calculated from Tafel plots are given in table 3. From the evaluated I_{corr} value, η% can be calculated using the relation $\eta\% = \frac{i_0 - i_{corr}}{i_0}$ .where i_0 and i_{corr} are the corrosion current densities in the absence and presence of inhibitors. From the data of table3 and figure 2, it is clear that in the presence of tetrazole there was remarkable decrease in i_{corr} value by shifting both anodic and cathodic Tafel slopes towards low current densities [25]. It was further confirmed that the shape of polarization curves were similar in absence and presence of inhibitors, suggesting that 1,2,4-triazole inhibited mild steel corrosion by simply adsorbing on the mild steel surface without changing the mechanism of mild steel dissolution[26]. An inhibitor can be classified as anodic, cathodic or mix type depending upon the displacement in E_{corr} value. If the displacement in E_{corr} for the inhibited and uninhibited solution is more than 85mV it can be classified as cathodic or anodic type. But the displacement in E_{corr} is less than 85 mV then it can be classified as mixed-type. Since the maximum displacement for studied compound was 23 mV indicating that tetrazole is mixed type of inhibitor [27].

Table 3. Tafel polarization parameters for mild steel in 1 M HCl in absence and presence of 1,2,4-triazole.

Acid Medium	**Concentration (ppm)**	**$-E_{corr}$ (mv)**	**I_{corr} (πA/cm^2)**	**β_a (v/dec)**	**β_c (v/dec)**	**IE %**
1 M HCl	-	-470.0	704.0	103.3 e^{-3}	196.4 e^{-3}	-
	100	-475.0	128.0	71.50 e^{-3}	144.3 e^{-3}	81.81
	200	-473.0	90.90	68.30 e^{-3}	133.6 e^{-3}	87.08
	300	-475.0	84.00	69.70 e^{-3}	164.5 e^{-3}	88.06
	400	-483.0	63.40	83.00 e^{-3}	169.3 e^{-3}	90.99
	500	-	36.90	93.1 e^{-3}	154.6	93.

IV. SURFACE STUDIES

4.1 SEM studies

To support our conclusion that the 1, 2, 4-triazole form protective surface film, SEM micrograph of the mild steel surface were recorded in the absence and presence of 500 ppm concentration of triazole. The result shows that the surface of polished mild steel coupon (Figure 4a) was considerably smoother with minimum undulation or pitting. (Fig-4b) shows the surface of coupon immersed in 1 M HCl solution which is strongly damaged due to acid corrosion. However the coupon immersed in the solution containing 500 ppm of 1,2,4-triazole was relatively smooth compared to free acid solution(Figure 4c).

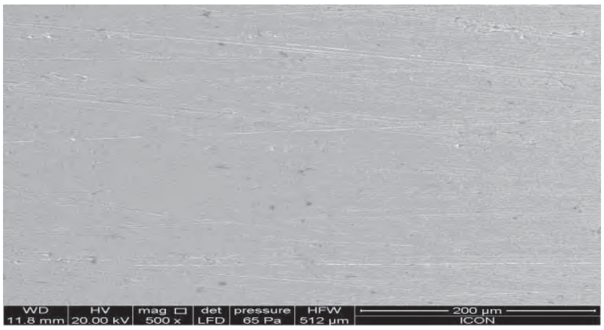


Figure 4(a). SEM micro graphs of mild steel surface before immersionin 1 M HCl

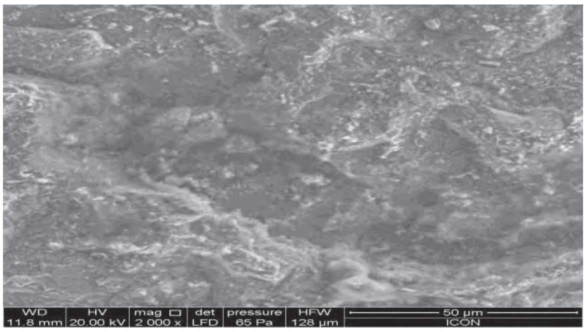


Figure 4(b). SEM micro graphs of mild steel surface after one day immersion in 1 M HCl

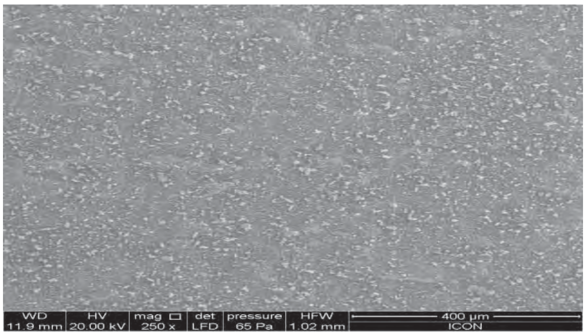


Figure 4(c). SEM micro graphs of mild steel surface after one day of immersion in 1 M HCl+500 ppm of 1,2,4-Triazole.

4.2 EDX studies

To further support our weight loss and electrochemical finding that 1, 2, 4-triazole inhibit mild steel corrosion by forming a protective film on surface, we recorded a the EDX spectra in absence and presence of 500 ppm of 1, 2,4-triazole.

The spectral profile of the polished mild steel sample before immersion in 1M HCl shows the signal for Fe, C and O. On immersion in 1M HCl, the signal for O is disappeared due to breaking of preimmersion air formed oxide film. Signal for Fe and carbon also slightly decreased. The profile in presence of 1, 2, 4-triazole shows additional signal for nitrogen atoms. This is due to adsorption of inhibitor on the mild steel surface.

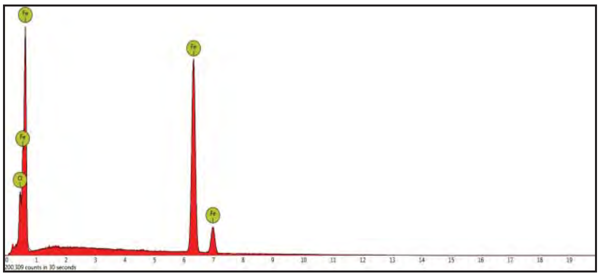


Figure 5. EDX of (a) polished mild steel surface

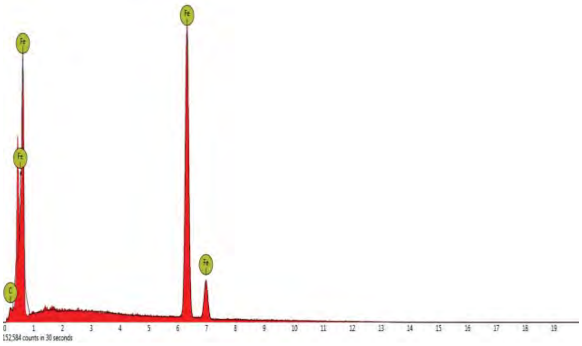


Figure 5. EDX of (b) after one day immersion in 1 M HCl

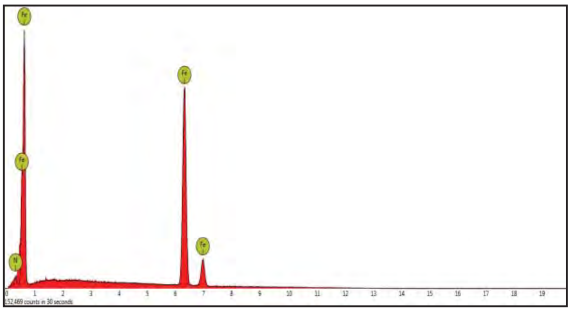


Figure 5. EDX of (c) after one day of immersion in 1 M HCl +500 ppm of 1,2,4-Triazole.

V. MECHANISM OF INHIBITION

Corrosion inhibitors are believed to act by adsorption on metal surface by either physical or chemical means. The physical adsorption occurs via electrostatic interaction between the oppositely charged inhibitor molecule and metal surface, whereas chemical adsorption take place via donor acceptor interaction between lone pair electrons of heteroatom (N,S,O),π electrons of aromatic rings and polar functional groups with vacant d orbital of metal. The compound inhibits corrosion by controlling both anodic as well as cathodic reactions. In acid solution, inhibitor can exist as protonated species. The nitrogen atom present in the molecule can be easily protonated in acidic solution which can get adsorbed onto the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on the anodic sites occurs through pi electrons of triazole ring and lone pairs of electrons of nitrogen atoms which decrease the anodic dissolution of mild steel.

VI. CONCLUSION

The corrosion behaviour of mild steel in 1 M HCl in absence and presence of tetrazole compound was investigated using the weight loss, open circuit potential and potentiodynamic polarization technique and surface analytical techniques. From the result obtained the following conclusion can be drawn:

1. 1, 2, 4-Triazole acted as a good and efficient corrosion inhibitor for the corrosion of mild steel in 1M HCl solution.
2. The inhibition efficiency increased with an increase in the concentration of inhibitor.
3. The adsorption of the inhibitor on mild steel surface obeyed Langmuir adsorption isotherm. The negative Gibbs free energy value indicated that the adsorption of inhibitor on surface is spontaneous process.
4. Polarization studies showed that 1,2,4-triazole acts as mixed inhibitor
5. The surface morphology techniques revealed the formation of smooth uniform surface on mild steel in presence of inhibitor.

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Inhibitive effect of 8-hydroxy Quinoline on the corrosion of mild steel in 1M HCl

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ABSTRACT

The inhibitive action 8-Hydroxy quinoline on corrosion of mild steel in 1 M HCl was investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization technique. The results showed that the 8-hydroxy Quinoline inhibited mild steel corrosion and inhibition efficiency increased with increase in concentration of inhibitor. The adsorption is spontaneous and followed Langmuir's adsorption isotherm. Polarization study indicated that the inhibitor acted as mixed-type. The protective film formed on surface is confirmed by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDX).Result obtained from weight loss technique are in good agreement with electrochemical and surface analytical results.

Key words: Mild Steel, Corrosion, HCl, SEM, EDX.

I. INTRODUCTION

Corrosion is the deterioration of a metal as a result of chemical reaction between it and the surrounding. Corrosion causes heavy economic losses. In India with GDP of amount 2 trillion, loses as much as 100 billion dollar every year on account of corrosion. Mild steel is widely used as construction material in most of major industries due to its excellent mechanical properties and low cost. The major problem of mild steel is its dissolution in acidic medium [1–6].Acids is widely used for acid pickling, descaling, oil well acidizing and other applications. Due to their high corrosive nature acid may cause damage to the system components. Thus it is necessary to develop some effective corrosion inhibitors .The use of organic inhibitor is the most effective and most economic method for protection of metal from corrosion. Generally, organic inhibitors inhibit metallic corrosion by adsorbing on the surface and thereby forming a protective barrier [7-14].The adsorption of an inhibitor is influenced by various factors such as electron density of donor site, presence of functional groups, electronic structure of inhibiting molecule, molecular area and molecular weight of inhibitor. Organic compounds containing heteroatoms including nitrogen, sulphur, and/or oxygen with polar functional groups and conjugated double bonds have been reported as effective corrosion inhibitor [14-20].

The aim of present work is to study the inhibition effect of 8-hydroxy Quinoline on mild steel in presence of 1 M HCl by using various techniques such as weight loss measurement, open circuit potential (OCP), and potentiodynamic polarization. Surface analytical techniques such as SEM AND EDX were also used to characterize corrosion product formed.

II. EXPERIMENTAL PROCEDURE

2.1. Material and sample preparation

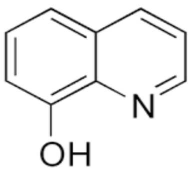
Mild steel of commercial grade in sheet form having composition as follows: C-0.16%, Si-0.10%, Mn –

0.40%, P - 0.012%, S - 0.02%, and Iron- balance, were used in the present investigation. For electrochemical polarization, samples of 1cm x 3cm were sheared from the commercial grade sheets. The surface of these samples was successively polished by using the Emery papers of grades 1 / 0, 2 / 0, 3 / 0, and 4 / 0 obtained from Signor, Switzerland to obtain a scratch free mirror finish surface. The polished samples were washed with detergent solution, rinsed with distilled water and finally degreased with acetone. The specimens were dried and stored in a desiccators containing silica gel as a dehydrating agent. The test solution of 1M HCl was prepared by diluting analytical grade HCl (MERCK, 37%) in double distilled water.

2.2. Synthesis of inhibitor

The 8-hydroxy quinoline used in present study was synthesized according to a previously described procedure [21].The completion of the reaction was verified by the disappearance of starting material on TLC plate. The IUPAC name, chemical structure and analytical data for synthesized compound given below.

Table 1. IUPAC name, molecular structure, melting point and analytical data of studied inhibitor.

Inhibitor	Molecular Structure	Analytical data
8-Hydroxy quinoline		**MP** – 74^{0}C - 76^{0}C. **FT-IR-ξmax/cm^{3}.** 3500,1680,1400,1550, 1360,1150 1080.

2.3weight loss measurements

Weight loss measurements were carried out in a glass vessel with 100 ml of 1M HCl solution with and without concentration of inhibitor ranges from 100-500 ppm. The immersion time for weight loss was 24 h at 27 ^{0}C.After dilution the mild steel specimens were withdrawn, rinsed with double distilled water, washed with acetone, dried and weight. The experiments were carried out in duplicate and the average value of weight loss was noted.

2.4 electrochemical measurements

The variation of corrosion potential of mild steel in 1 M HCl was measured against saturated calomel electrode in absence and presence of various concentrations of inhibitors. The time dependence of OCP for different experiments was recorded for 1 hours exposure period .Then the sample was used for potentiodynamic polarization experiments .The potential was swept between -0.5V to 0.5 V at the scan rate 5mV/second. Electrochemical Measurement System, DC 105,containing software of DC corrosion techniques from M/S Gamry Instruments Inc., 734, Louis Drive, Warminster, PA-18974, USA has been used for performing corrosion potential and polarization experiments. For electrochemical polarization studies (corrosion potential, and potentiodynamic polarization) flag shaped specimens with sufficiently long tail were cut from the stainless steel sheet. These samples were polished as described earlier leaving a working area of 1cm^{2} on both sides of the flag and a small portion at the tip for providing electrical contact. Rest of the surface was isolated from the corroding solution by coating with enamel lacquer including side edges. The test specimen was connected to the working electrode holder with the help of a screw. About 50ml of the corrosive medium was taken in a mini corrosion testing electrochemical cell. This volume was appropriate to permit desired immersion of electrodes. The electrochemical investigation was carried out using microprocessor based corrosion measurement system (CMS-105, Gamry Instruments Inc., USA.). The three-electrode system cell i.e.

working electrode, reference electrode (Saturated Calomel Electrode), and counter electrode (Graphite rod), was used throughout the electrochemical measurements. Open circuit potential measurements and potentiodynamic polarization experiments were carried out at the concentration of 100, 200,300,400 and 500 ppm of the inhibitor.

2.5 SEM AND EDX STUDIES

The composition and surface morphology of corrosion product on mild steel sample after immersion for 24 hours in 1 M HCl in the absence and presence of 500 ppm of 8-hydroxy Quinoline was studied using a scanning electron microscope and EDX examination using energy dispersive spectrometer. The accelerating voltage for SEM picture was 20.0 kv.

III. RESULTS AND DISCUSSION

3.1. Weight loss measurement

Weight loss data of mild steel in 1M HCl in the absence and presence of various concentrations of inhibitor were obtained and are given in Table 1. Inhibition efficiencies (%IE) were calculated according to [46]:

$$(\% \text{ IE}) = \frac{(W_0 - W\text{corr})}{W_0} \times 100 \quad \text{-----} (1)$$

Where, Wcorr and W_0 are the weight loss of mild steel in the presence and absence inhibitors, respectively.

The results show that the inhibition efficiencies increase with increasing inhibitor concentration. The results obtained from the weight loss measurements are in good agreement with those obtained from the electrochemical methods.

Table 2. The weight loss parameter obtained for mild steel in 1 M HCl containing different concentrations of 8-hydroxy quinoline.

Inhibitor	**Concentration (ppm)**	**Weight loss (mg)**	**Surface coverage**	**Inhibition efficiency (%E)**
Blank	-	**431**	-	-
8-Hydroxy quinoline	100	280	0.350	35.03
	200	185	0.570	57.07
	300	146	0.661	66.12
	400	99	0.770	77.03
	500	77	0.821	82.13

3.2 Adsorption isotherm

Fundamental information on the adsorption of inhibitor on metal surface can be provided by adsorption isotherm. The weight loss temperature results were used to calculate the adsorption isotherm parameters. The most frequently used isotherms are Langmuir, Frumkin, Temkin, Florry-Huggins and thermodynamic /kinetic model of El-Awady isotherm. It is found that the adsorption of studied inhibitor on mild surface obeys Langmuir adsorption isotherm. Langmuir adsorption isotherm is given by following equation:

$$C/\theta=1/K_{ads} \quad \text{---------} (2)$$

Where θ is the degree of surface coverage, C is the molar inhibitor concentration in the bulk solution and K_{ads} is the equilibrium constant of the process of adsorption. Plot of C/θ versus C of 8- hydroxyl quinoline presented in fig.(4).The obtained plots are almost linear with correlation coefficient (R^2=0.999) for Langmuir adsorption isotherm .K_{ads} can be calculated from intercepts of the straight lines in figure 1

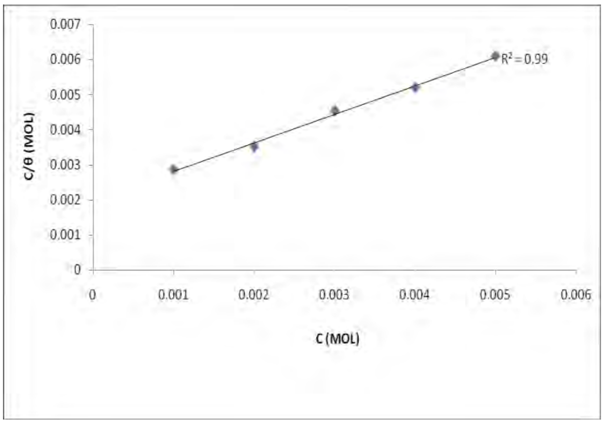


Figure 1. Langmuir adsorption isotherm for mild steel in 1 M HCl at various temperatures.

The standard free energy of adsorption (ΔG_{ads}) is calculated from equation [22].

$K_{ads}= (1/55.5) \exp(-\Delta G_{ads}/RT)$ ------- (3)

Where the constant 55.5 is the molar concentration of water in solution in mol L^{-1} .R is universal gas constant and T is absolute temperature. The negative values of ΔG_{ads} ensured the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface [23].Generally ,values of ΔG_{ads}, around -20 KJ mol^{-1}or lower are consistent with the electrostatic interaction between the charged molecules and charge metal, such as physisorption. When it is around -40 KJ mol^{-1} or higher values it involves charge sharing or charge transfer from organic molecules to the metal surface to form coordinate type of bond that is chemisorptions [24].In the present work the calculated value of ΔG_{ads} is 25.53kJ/mol, which indicate adsorption of inhibitor on mild steel surface involves both physical and chemical adsorption.

3.3. Open Circuit Potential Measurement (OCP)

Inherent reactivity of the metallic materials in a particular environment is determined from its open circuit potential (corrosion potential). The influence of the corrosive and inhibitive species present in the electrolyte may be predicted by analysing the nature of the OCP curve. The variation of open circuit potential of Mild Steel exposed to 1M HCl solution containing inhibitor i.e.8-hydroxy quinoline in the concentration range 100-500ppm is shown in Figure 2 .The steady state potential is obtained after 3600 seconds of the exposure period. In the presence of different concentration of inhibitors, OCP is shifted towards the positive potential direction in comparison to without inhibitor and get stabilized thus indicating the adsorption of the inhibitors on the metal surface. The magnitude of shift of polarization curve towards positive direction was found proportional to the concentration of the inhibitor.

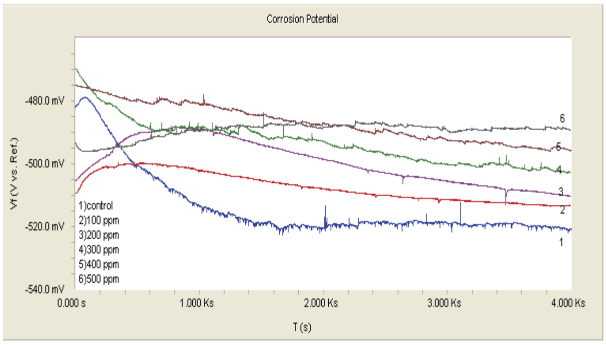


Figure 2. Open circuit potential diagram for mild steel in 1 M HCl without and with different concentrations of 8-hydroxy quinoline.

3.4. Potentiodynamic polarization curves

Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of 8-hydroxy Quinoline are illustrated in fig.3.The presence of 8-hydroxy quinoline caused a clear decrease in both anodic and cathodic current densities with increase in inhibitor concentration, probably due to the adsorption of at the active sites of the electrode surface, retarding both metallic dissolution and hydrogen evolution reaction [25].The

electrochemical kinetic parameters,i.e.,corrosion current densities(i_{corr}),
corrosion potential (E_{corr}), cathodic Tafel slop ($b_{c)}$ anodic Tafel slope (b_a) are presented in table (6).

Here, the IE% is defined by following equation:

$$IE\%== \frac{i_0 - i_{corr}}{i_0} \qquad \text{---------- (4)}$$

Where i_{corr} and i_{corr} are the corrosion current density values without and with inhibitor respectively. The corrosion current density decreased with increasing the concentration of the inhibitor, which indicates that the presence of 8-hydroxy quinoline retard the dissolution of mild steel in 1 M HCl solution and degree of inhibition depends on the concentration of inhibitor. It can also be observed that the corrosion Potential values remained almost constant in presence of inhibitor, suggesting that 8-hydroxy quinoline acted as mixed-type inhibitor. Furthermore ,it is observable that the shape of polarization curves are similar in the absence and presence of 8-hydroxy quinoline, suggesting that the inhibitor inhibits mild steel corrosion by simply adsorbing on mild steel surface without changing the mechanism of mild steel dissolution[26].

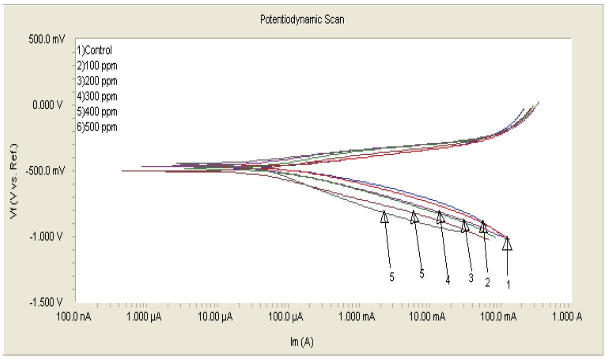


Figure 3. Potentiodynamic Polarization curves of mild steel in 1 m HCl in the absence and presence of different concentration of 8-hydroxy quinoline

Table 3. Polarization data of mild steel in 1M HCl solution in absence and presence of different concentration of 8-hydroxy quinoline.

Acid Medium	**Concentration (ppm)**	**-E_{corr} (mv)**	**I_{corr} (πA/cm^2)**	**β_a (v/dec)**	**β_c (v/dec)**	**IE %**
1 M HCl	-	475.0	133.0	76.90 e^{-3}	134.4 e^{-3}	
	100	472.0	85.10	65.70 e^{-3}	127.0 e^{-3}	53.84
	200	481.0	54.10	90.40 e^{-3}	126.0 e^{-3}	68.15
	300	503.0	40.20	85.30 e^{-3}	140.1 e^{-3}	72.77
	400	508.0	35.20	86.90 e^{-3}	146.2 e^{-3}	79.65
	500	463.0	26.64	85.30 e^{-3}	125.20 e^{-3}	85.42

IV. SURFACE STUDIES

4.1.SEM studies

In order to evaluate the condition of metal surface in contact with acid solution in absence and presence of inhibitor, a surface analysis is carried out using scanning electron microscope and Energy dispersive X- ray spectrometer.

The surface morphology of the mild steel specimens immersed in1M HCl for 24 h without and with optimum concentration of the 8-hydroxy Quinoline is shown in following figure. A micrograph of the polished mild steel surface before immersion in 1M HCI is shown in figure 4(a).The micrograph shows the surface was smooth and without pits.Fig.4(b) represents SEM micrograph of mild steel surface immersed in 1M HCl without 8-hydroy Quinoline which appears to be highly corroded and damaged due to free acid attack.Fig.4(c) represents SEM micrograph of mild steel in the presence of optimum concentration of the 8-hydroxy Quinoline in acid solution causes significant improvement in the surface morphology. Thus it can be concluded that8- hydroxyl Quinoline forms protective surface film on the metal surface through adsorption which protect the metal from acid solution.

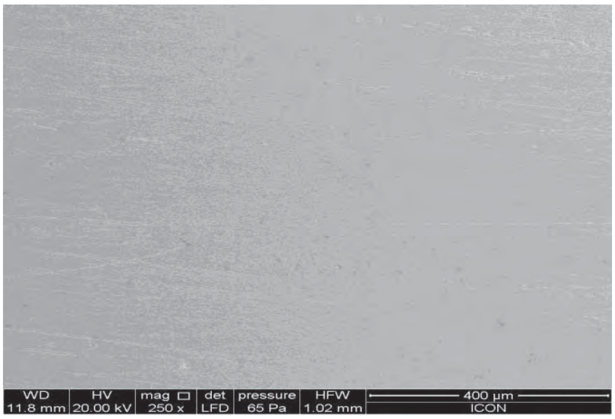


Figure 4.(a). SEM micro graphs of mild surface before immersion in 1 M HCl

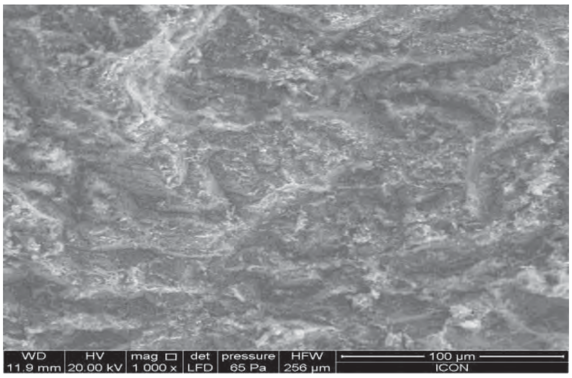


Figure 4.(b). SEM micro graphs of mild surface after one day immersion in 1 M HCl and

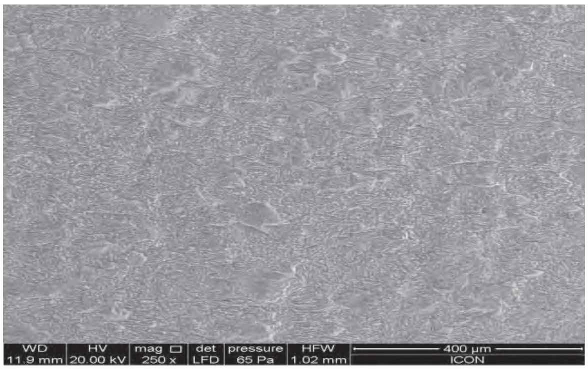


Figure 4(c). SEM micro graphs of mild surface after one day of immersion in 1 M HCl+500 ppm of 8-nitro quinoline.

4.2 EDX studies

Figure 5 (a) shows spectra of mild steel specimen before immersion in 1 M HCl which shows a signal for Fe and oxygen. Figure 5(b) shows EDX spectra of mild steel specimen immersed in 1 M HCl in the absence of 8-hydroxy Quinoline which is characterized by signal corresponding only for Fe. However, Figure 5(c) shows EDX spectrum in the presence of 8-hydroxy Quinoline with additional signal for nitrogen (N) which attributed due to adsorption of 8-hydroxy Quinoline on mild steel surface.

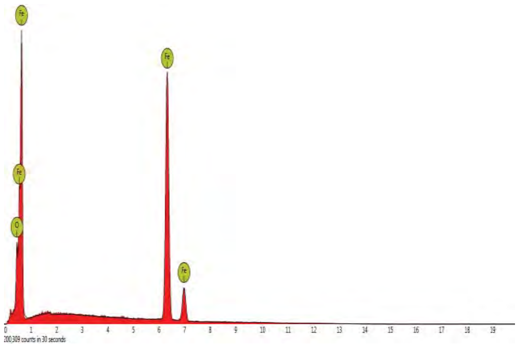


Figure 5(a). EDX spectra of polished mild steel surface

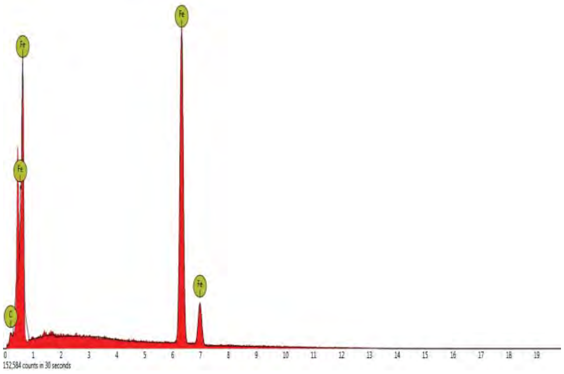


Figure 5 (b). EDX spectra of mild steel after one day immersion in 1 M HCl

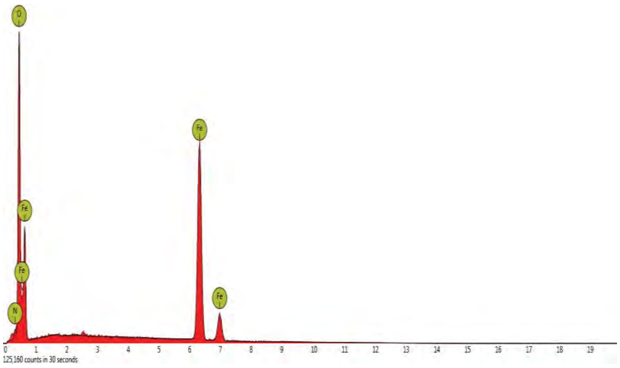


Figure 5(c). EDX spectra of mild steel after one day of immersion in 1 M HCl +500 ppm of 8-hydoxy Quinoline.

V. MECHANISM OF INHIBITION

Corrosion inhibition of mild steel in acid solution can be described on the basis of adsorption phenomenon.8-hydroxy Quinoline contains various functional groups such as –OH,C=C and C=N through which it can adsorb on metal surface. The adsorption can be chemisorption or physisorption and some time both processes can take place. 8-hydroxy Quinoline can absorb onto metal surface by three different ways.

1. Sharing of electrons of nitrogen and oxygen with iron surface.
2. Interaction between pi electrons of benzene ring of 8-hydroxy Quinoline with the metal surface.
3. It is also possible that the N atom of 8-hydroxy Quinoline can be easily protonated in acid medium. This protonated N atom can show electrostatic interaction with negatively charged metal surface.

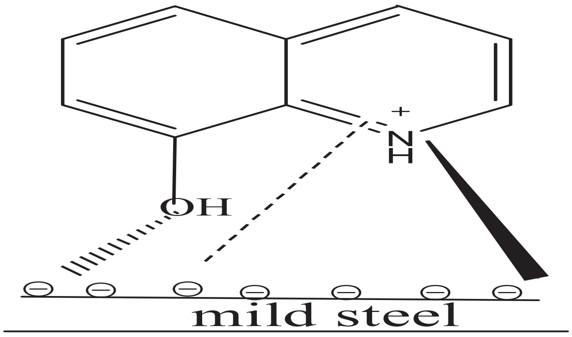


Figure 6. Pictorial representation of adsorption behaviour of the 8-hydroxy quinolone on mild steel in 1M HCl

VI. CONCLUSION

On the basis of the above results the following concision can be drawn.

1. 8-hydroxy Quinoline acted as an effective corrosion inhibitor for mild steel in 1M HCl solution.
2. The corrosion process was inhibited by adsorption of inhibitor molecule on the mild steel surface.
3. The inhibition efficiency increased with increase in the concentration of the inhibitor.

4. Adsorption study showed that the inhibition mechanism obeyed Langmuir adsorption isotherm.
5. The negative value of free enegy of adsorption indicated strong and spontaneous adsorption of inhibitor on mild steel surface.
6. Potentiodynamic polarization studies shown that inhibitor retards both the anodic and cathodic partial reactions. Thus 8-hydroxy Quinoline acted as mixed type inhibitor.
7. SEM/EDX studies revealed that corrosion inhibition is due to the adsorption of 8-hydroxy Quinoline at mild steel/acid solution interface.

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CORROSION CONTROL OF MILD STEEL USED IN OIL AND NATURAL GAS INDUSTRIES BY TRIAZOLE DERIVATIVES IN 1 M HCI

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ABSTRACT:

Corrosion behaviour of mild steel and its control by bezotriazole and benzoyl benzotiazole in1M HCI has been investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization techniques. Microstructure of surface was analyzed by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (E-DAX).The polarization curves revealed that both the compounds behaved as mixed-type inhibitors. The inhibitors efficiency increased with increase in the concentration of both the inhibitors .The adsorption of inhibitor molecules on mild steel surface obeyed Langmuir adsorption isotherm .The presence of thin film formed due to adsorption may be responsible for decrease in corrosion rate of the mild steel.

Key words: *corrosion inhibition, Mild steel, HCI, triazole derivatives.SEM, E-DAX.*

INTRODUCTION:

Mild steel is the most common choice of material which is extensively used in the production and transportation of crude oil in the oil and natural gas industry[1].The main problem concerning mild steel application is its relatively low corrosion resistance in acidic solutions[2].The most commonly used media is hydrochloric acid. Hydrochloric acid solutions are widely used for acid cleaning, industry acid pickling,oil well acidizing and acid rescaling [3].The strong acid medium can cause structural damage to mild steel . Therefore the use of inhibitors is one of the most practical methods for the protection of metal against corrosion in acid media [4].There are several types of corrosion inhibitors which are widely used to control corrosion problem of mild steel. Usually, an organic compound that exerts significant influence on the extent of adsorption on the metal surface can be used as effective corrosion inhibitors. Regarding the adsorption of inhibitors on the metal surface, Two types of interaction are possible .First is physical adsorption which involves electrostatic force between ionic charges or dipoles of the adsorbed species and electric charge of metal /solution interface and the second is chemical adsorption which involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form coordinated types of bonds[5].Organic compounds containing hetero atoms, pi electrons in the form of double and triple bonds and aromatic rings in there structures are mostly used as inhibitors. Several heterocyclic compounds such as Quinoline derivates, pyrazole derivatives, Imidazole derivatives, pyridine derivatives, pyridazine derivatives, Schiff base compounds can be used as effective corrosion inhibitors in various corrosion environments [6]

In present investigation an attempt have been made to study the inhibitive effects of Two synthesized triazole derivatives, benzotriazole and benzoyl benzotriazole ,on corrosion of mild steel in 1M HCL using weight loss and electrochemical techniques such as open circuit potential, potentiodynamic polarization. The passive film formed on the surface is further confirmed by SEM and EDX.

2. EXPERIMENTAL PROCEDURE:

2.1. MATERIAL AND SAMPLE PREPARATION

The weight loss and electrochemical experiment were performed on mild steel specimen having chemical composition, C-0.16%, Si-0.10%, Mn-0.40%, P-0.013%, S-0.02% and remaining iron. The exposed dimensions were 1cmx3cmx0.025cm and 1cm^2 for the weight loss and electrochemical experiment respectively. Before exposure to test solution exposed areas were cleaned with different grades of metallographic emery paper,1/0,2/0.3/0,and 4/0, washed with doubled distilled water, degreased with acetone and finally dried and stored in desiccators.

TEST SOLUTION

1 M HCL was prepared by dilution of 36% HCI (analytical grades) in bi-distilled water.

2.2. SYNTHESIS OF INHIBITORS

Procedure for synthesis of benzotriazole:

10.8 gm of O-phenylenediamine was added to a mixture of 12 gm (11.5 ml) of glacial acetic acid and 30 ml of water, which was cooled to 15^{0}C.solution of 7.5 gm of sodium nitrite in 15 ml water was added all at ones, the mixture being stirred with the glass rod or by slow mechanical stirrer .The temperature increased slowly to 85^{0}C and then cooled slowly. When temperature was 45^{0}C the mixture was chilled in an ice bath for 30 minutes. A pale brown solid separated by filtration. Recystallisation was done using benzene as the solvent.

Procedure for synthesis of benzoyl benzotriazole:

To a solution of benzotriazole (11.9 g ,0.1 mole) in anhydrous dichloromethane (200 ml) at 0^0 C under nitrogen, triethyl amine (17 ml ,0.12 mol) was added drop wise, followed by addition of Benzoyl chloride (0.11 mol).The resulting mixture was stirred at room temperature for 1-2 hours. The reaction was quenched at this temperature with hydrochloric acid (2 N,200ml), and the organic phase was separated with hydrochloric acid (2N,2x50 mi) and water (50 ml) sequentially .The organic extract were dried over anhydrous magnesium sulphate , filtered and evaporated to dryness to give a white powdery solid which was purified by recrystallisation from water.

The characterization data, IUPAC name, structure and abbreviation used for the synthesized compound are given below in Table 1.

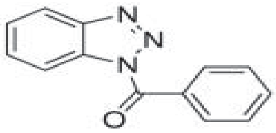
Sr.no	**IUPAC name**	**Chemical structure**	**Analytical data**
1	1,2,3-Benzotriazole		**MP** – 98^0C - 100^0C. **FT-IR-** υ **max/cm^3.** 1208,870,775,745,729,1615,1360.
2	Benzoyl bezotriazole		**MP** – 140^0C - 142^0C. **FT-IR-** υ **max/cm^3.** 1208,870,775,1775,750, 740,1355,1600.

Table 1: IUPAC name, molecular structure, melting point and analytical data of studied inhibitors.

2.3. Weight loss measurement:

The weight loss experiment was performed by immersing mild specimen in 50 ml of test solution with and without different concentration of inhibitors. After 24 h immersion time, the mild steel specimen were taken out, cleaned with distilled water, dried and accurately weighed. Each experiment was performed in triplicate to obtain good result and the mean value is reported. The inhibition efficiency was calculated by using the following relation.

$$\eta\% = \frac{W_0 - W_{corr}}{W_0}$$

Where W_0 and W_{corr} are the weight loss in absence and presence of inhibitors .The surface coverage is given by following relation

$$\theta = \eta\%/100.$$

2.4 Electrochemical measurement:

Polarization studies were carried out using electrochemical measurement system, DC 105, containing software of DC corrosion technique from M/S Gamery instrument, 734 Louis Drive, Warminster, PA, USA. For polarization studies, mild steel specimens having surface area of 1cm^2 were exposed to acid solution .Mild steel as working electrode, saturated calomel (SCE) as reference electrode and graphite as auxiliary electrode were used for all electrochemical measurement. Before each measurement the specimen were allowed to corrode freely, and their OCPs were measured as a function of time to obtain a steady-state potential. The anodic and cathodic Tafel curve were obtained by changing the electrode potential automatically from 0.5 and 0.5 v. at the scan rate of 5mv/s. polarization study was done with and without inhibitors in 1M HCl.

2.5 Surface measurement:

The surface film formed on the metal specimen was evaluated by SEM-EDX analysis. This was carried out by SEM/EDX model QUANTA-200 from the Netherlands. The spectra were recorded for a period of 24 hours in 1M HCl in the absence and presence of 500 ppm inhibitors. The energy of acceleration beam employed was 20 kv.

3. RESULT AND DISCUSSION

3.1 Weight loss experiment:

The loss in the weight of mild steel coupons in 1M HCl in absence and presence of different concentration of benzotriazole and benzoyl benzotriazole was determined after 24 hours immersion period at 25^0C+1^0C.The percentage inhibition efficiency (%E) and degree of surface coverage (θ) were calculated and presented in Table.2.In the two cases it can observed from the table that the inhibition efficiency increased with increase in concentration of inhibitors and the compounds acted as very good corrosion inhibitors for corrosion of mild steel in 1M HCl. The maximum efficiency for each compound was achieved at 500 ppm concentration. The parameter (θ) which represents the part of the metal surface covered by the inhibitors molecules increased as the inhibitors concentration increased. The corrosion inhibition can be attributed to the adsorption of inhibitors at the metal /acid interface.

Inhibitor	Concentration (ppm)	Weight loss(mg)	Surface coverage	Inhibition efficiency (%E)
Blank	**-**	**235**	**-**	**-**
Benzotriazole	**100**	**184**	**0.217**	**21.70**
	200	**136**	**0.419**	**41.90**
	300	**92**	**0.608**	**60.80**
	400	**51**	**0.784**	**78.40**
	500	**12**	**0.949**	**94.90**
Blank	**-**	**431**	**-**	**-**
Benzoyl Benzotriazole	**100**	**190**	**0.559**	**55.90**
	200	**135**	**0.687**	**68.70**
	300	**102**	**0.762**	**76.20**
	400	**88**	**0796**	**79.60**
	500	**71**	**0.835**	**83.50**

Table 2: The weight loss parameter obtained for mild steel in 1 M HCl containing different concentrations of Benzotriazole and Benzoyl Benzotriazole.

3.2. Adsorption isotherm:

The values of surface coverage θ were evaluated using the value of %IE resulted from weight loss experiment in 1M HCl .Figure 1 shows a plot C/θ v/s C gave a straight line with a coefficient $(R)^2$ value very close to unity. It indicates that corrosion control take place via adsorption. The adsorption of inhibitors molecules on mild steel surface obeys Langmuir adsorption isotherm. The equation can be represented as:

$$K_{ads} = \frac{\theta}{C(1-\theta)}$$

The equation can be rearranged to

$$C_{inh} / \theta = 1/K_{ads} + C_{inh}$$

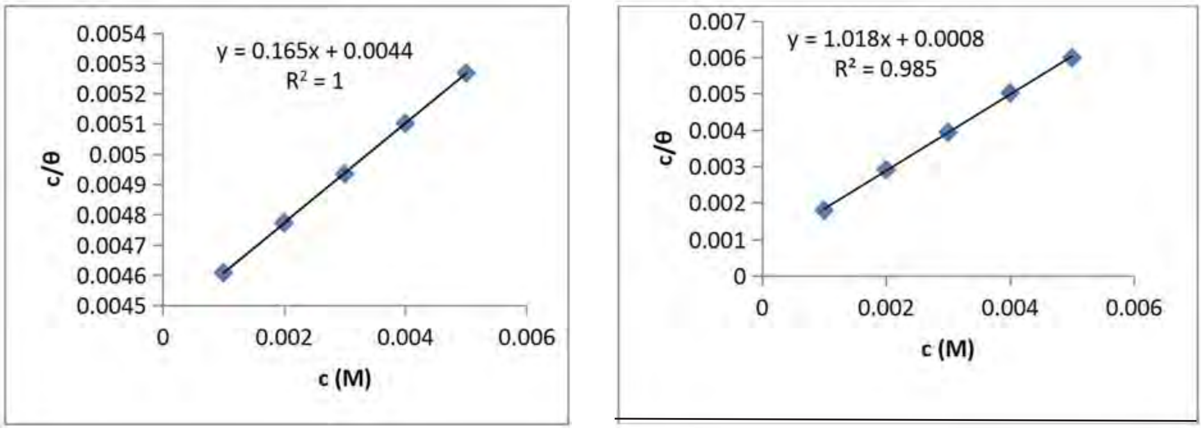
Where, C_{Inh} is the concentration of inhibitor, θ is surface coverage and K_{ads} is the equilibrium constant for adsorption – desorption process. The K_{ads} is related to standard free energy ($\Delta G^0{}_{ads}$) of adsorption by following relation.

Free energy of adsorption: ($\Delta G^0{}_{ads}$) =- 2.303 RT log (55.5 K_{ads}).

Where R is the universal gas constant, T is the absolute temperature in K ,and the numerical value 55.5 represent the molar concentration of water in acid solution.The calculated values of K_{ads} and $\Delta G^0{}_{ads}$ at studied temperature is listed in Table 3.

Compound	slope	K_{ads}	Regression coefficient	$\Delta G^0{}_{ads}$ (KJ.mol)
Benzotriazole	0.004	250	1	-23.635
Benzoyl Benzotriazole	0.0008	1250	0.985	-27.6232

Table 3: slope, equilibrium constant, regression coefficient and free enthalpy of adsorption of benzotriazole and benzoyl bezotriazole in 1 M HCl.



(a) (b)

Fig 1:Langmuir isotherm plot for adsorption of Benzotriazole (a) and Bezoyl Bezotriazole (b) on mild steel surface in 1 M HCl

Generally the magnitude of ΔG_{ads} around -20 kJ/mol less negative indicates physisorption and those around -40kJ/mol or more negative indicate chemisorptions. In the present case calculated values for both the inhibitors benzotriazole and benzoyl benzotriazole are – 23.635 and – 27.6232 respectively. This indicated the adsorption of inhibitors on the mild steel surface involved both physical and chemical process (7-8).

3.4Open circuit potential:

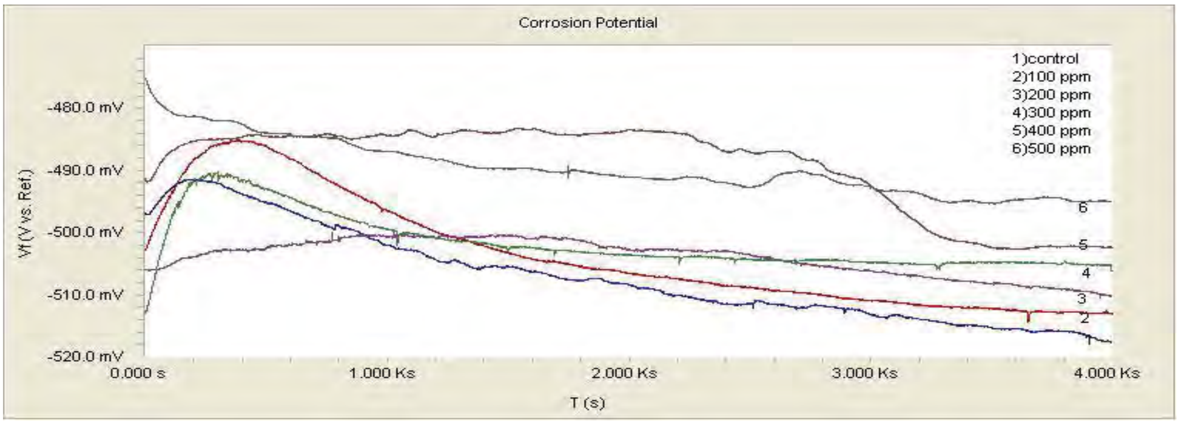


Fig 2(a): Open circuit potential diagram for mild steel in 1 M HCl without and with different concentrations of benzotriazole.

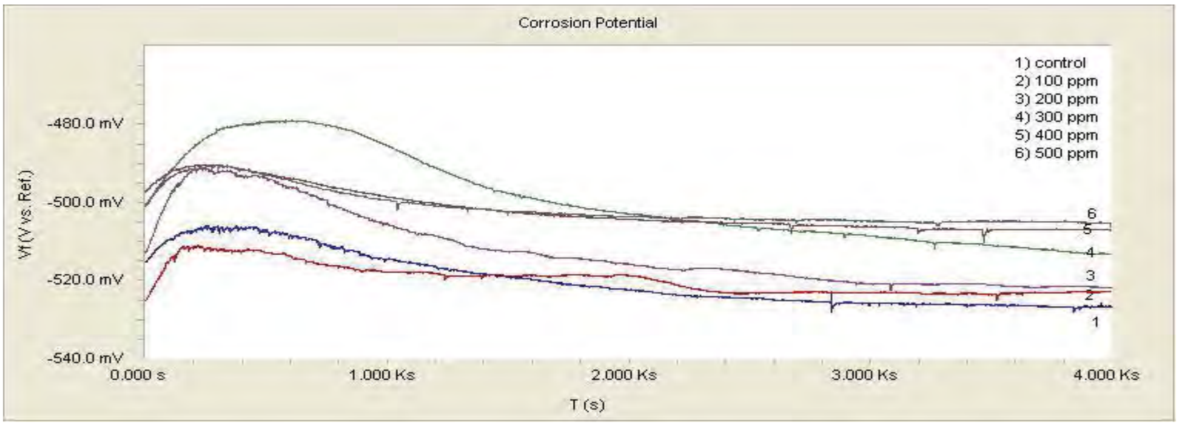


Fig 2 (b): Open circuit potential diagram for mild steel in 1 M HCl without and with different concentrations of benzoyl benzotriazole.

The evolution of open circuit potential with time for mild steel in 1M HCI solutions without and with benzotriazole and benzoyl benzotriazole is shown in figure 2(a) and figure 2 (b) respectively. The plot shows a clear change in the OCP curve due to the presence of the inhibitors.It is clear that the curve shifts in positive direction in the presence of benzotriazole and benzoyl benzotriazole. The inhibited solution exhibited higher positive open circuit potential value ,when compare with those obtained in blank solution, indicating formation of the protective film due to the adsorption of inhibitor on the mild steel surface. The continuous shift to the positive direction can be attributed to the formation of protective and inhibitive film,which increase with increasing the inhibitor concentration and immersion time[9].

3.5 Potentiodynamic polarization studies:

Polarization measurement were carried out in order to get information regarding kinetics of anodic and cathodic reactions. The obtained polarization curves for mild steel in 1M HCI in absence and presence of different concentration of benzotriazole and benzoyl benzotriazole are shown in figure3.corrosion kinetic parameter E_{corr}, I_{orr} ,Tafel (β_a ,β_c) and inhibition efficiency depicted in table

3.The lower current density (I_{corr}) values in the presence of inhibitors without causing significant changes in corrosion potential (E_{corr}) suggest that compound were mixed type inhibitors and adsorbed on the surface thereby blocking the corrosion reaction . The Tafel constants β_a and,β_c were both affected and there were no definite trends in the shift of E_{corr} values. This indicates that compounds are mixed type inhibitors [10].

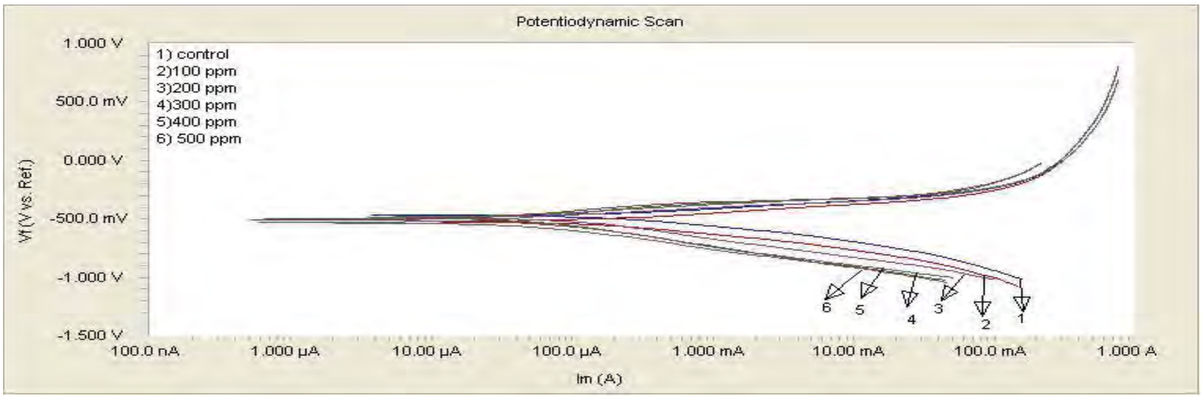


Fig. 3 (a): potentiodynamic polarization curve for mild steel in 1 M HCl without and with different concentrations of benzotriazole.

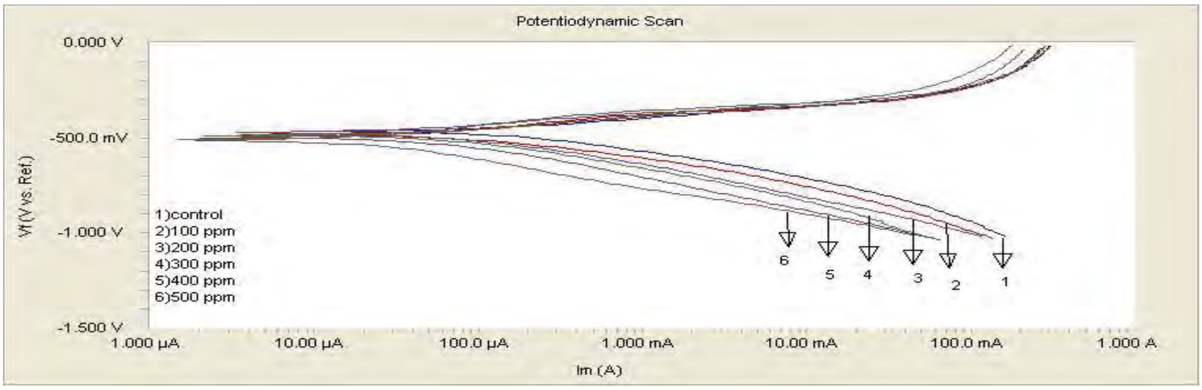


Fig. 3 (b): potentiodynamic polarization curve for mild steel in 1 M HCl without and with different concentrations of benzoyl benzotriazole.

Acid Medium	Concentration (ppm)	$-E_{corr}$ (mv)	I_{corr} ($\mu A/cm^2$)	β_a (v/dec)	β_c (v/dec)	IE %
1 M HCl	-	-471.0	197.0	91.30	163.4	-
	100	-524.0	157.0	86.80	142.8	20.30
	200	-488.0	108	70.40	160.2	45.18
	300	-495.0	74.60	66.10	155.8	62.13
	400	-483.0	46.70	85.60	100.8	76.29
	500	-504.4	12.50	82.40	109.3	93.65

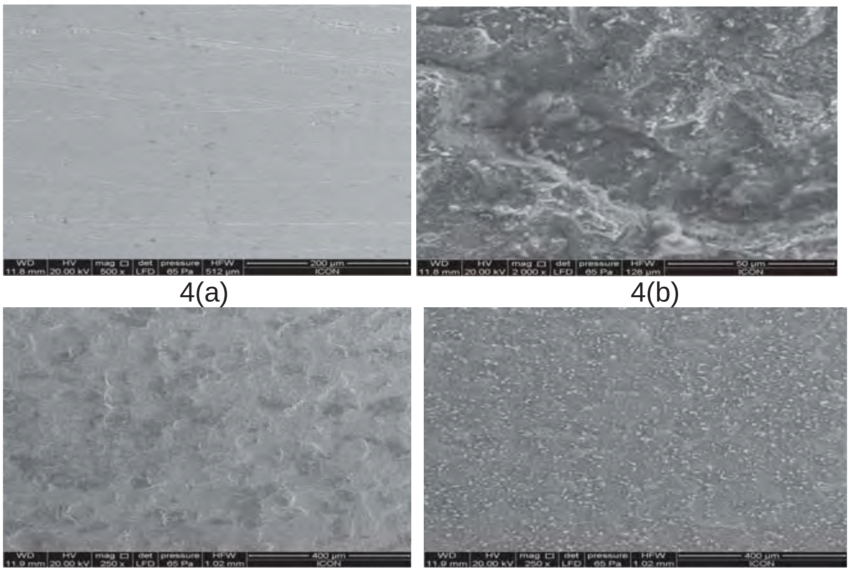
Table 4(a):potetiodynamic electrochemical parameter obtained for mild steel in 1 M HCl containing different concentration of benzotriazole.

Acid Medium	Concentration (ppm)	$-E_{corr}$ (mv)	I_{corr} ($\mu A/cm^2$)	β_a (v/dec)	β_c (v/dec)	IE %
1 M HCl	-	-464.0	178.0	78.00	157.2	-
	100	-483.0	76.30	94.10	129.6	57.13
	200	-487.0	58.60	83.30	142.5	67.07
	300	-471.0	46.90	80.00	139.4	73.65
	400	-499.0	38.00	84.00	138.2	78.65
	500	-513.0	25.40	111.2	151.6	85.73

Table 4(b): potentiodynamic electrochemical parameter obtained for mild steel in 1 M HCl containing different concentration of benzoyl benzotriazole.

3.6 SEM studies:

A photograph of the polished mild steel surface before immersion in 1M HCI is shown in figure 4aThe photograph shows the surface was smooth and without pits. The photograph of mild steel after immersion in 1M HCI is shown in figure 4b. The photograph indicates that surface was strongly damaged in absence of inhibitors. A photograph of mild steel after immersion in 1M HCI solution containing 500 ppm of benzotriazole and benzoyl benzotriazole is shown in figure 4(c-d) It is found that surface is free from pits and it was smooth. Thus we can conclude that in presence of both the inhibitors corrosion was inhibited strongly.



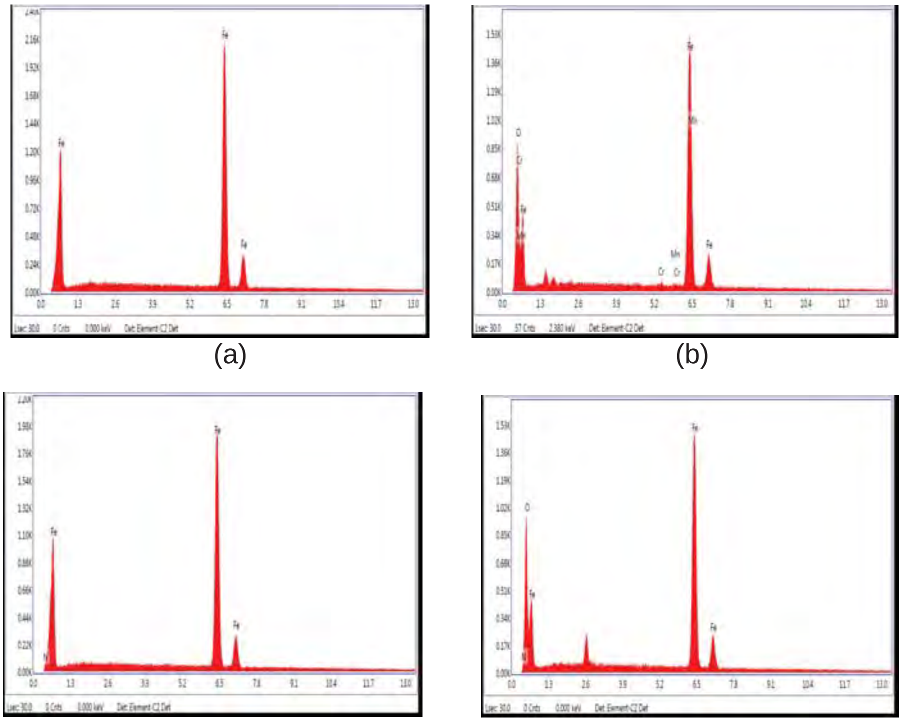
4(a) 4(b)

4(c) 4(d)

Fig.4 SEM micro graphs of mild surface-4(a) before immersion in 1 M HCl, 4(b) after one day immersion in 1 M HCl and 4(c) after one day of immersion in 1 M HCl+500 ppm of benzotriazole, 4(d) after one day immersion in 1 M HCl + 500 ppm benzoyl benzotriazole.

3.7 EDX studies:

Figures 5(a – d) show the EDX spectrum in the absence and presence of bezotriazole and benzoyl benzotriazole .Figure 5(c) show and additional peak characteristic for existence of nitrogen (N). Figure 5(d) shows additional peaks characteristic of N and O, indicating that the inhibitors molecule adsorbed on the metal surface.EDX investigation thus confirms the polarization data, that the presence of Triazole derivatives inhibits the corrosion of mild steel in 1M HCl due to adsorption of its molecules on the mild steel surface preventing it from being corroded easily.



(a) (b)

(c) (d)

Fig.5 EDX of mild surface (a) before immersion in 1 M HCl, (b) after one day immersion in 1 M HCl and (c) after one day of immersion in 1 M HCl+500 ppm of benzotriazole, (d) after one day immersion in 1 M HCl + 500 ppm benzoyl benzotriazole.

3.7 MECHANISM OF INHIBITION:

The inhibition effect of benzotriazole and benzoyl benzotriazole derivatives towards the corrosion of mild steel in 1m HCl solution may be attributed to the adsorption of these compounds at the metal-solution interface. The inhibition process is a function of the metal, inhibitor concentration and temperature as well as inhibitor adsorption abilities which depends on adsorption sites[11] .The mode of adsorption (physisorption and chemisorption) observed could be attributed to the fact that inhibitors contains different donating atoms which can be adsorbed chemically and physically [12]. In case of benzotriazole the inhibition effect is due to interaction of pi electrons of benzene and triazole rings as well as the presence of electron-donating atoms such as nitrogen through which benzotriazole form bond with mild steel .similarly the inhibitive effect of benzoyl benzotriazole is because of pi electron of benzene and triazole ring, along with hetero atoms such as nitrogen and oxygen through which the inhibitor adsorbed on mild steel surface to form insoluble ,stable and uniform film.

4 CONCLUSIONS:

1) Benzotriazole and benzoyl benzotriazole were effective corrosion inhibitors and acted as mixed type inhibitors for mild steel corrosion in 1M HCI.
2) The corrosion process was inhibited by the adsorption of these molecules on mild steel surface and the inhibition efficiency increased with increase in concentration of both inhibitors.
3) In determining the corrosion rates, electrochemical studies and weight loss measurement gave similar result.
4) Adsorption of both the inhibitors for mild steel obeyed the Langmuir adsorption isotherm.
5) The value of $\Delta G^0{}_{ads}$ was low and negative, which indicated spontaneity of the adsorption process.
6) SEM-EDX analysis showed that there was improvement in surface morphology of inhibited mild steel as compared with uninhibited mild steel.

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CORROSION INHIBITION OF MILD STEEL USED IN OIL AND NATURAL GAS INDUSTRIES USING 5-PHENYL TETRAZOLE

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ABSTRACT:

The inhibitive action of 5 phenyl tetrazole on corrosion of mild steel in 1 M HCl was studied by weight loss, open circuit potential (OCP) and potentiodynamic polarization technique. The inhibition efficiency increased with increase in concentration of inhibitor. Electrochemical studies support the conclusion that compound is efficient inhibitor for mild steel corrosion. The adsorption of compound obeys Langmuir's adsorption isotherm. Polarization study indicated that the inhibitor acted as mixed type. The protective film formed on surface is confirmed by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDX).Result obtained from weight loss technique are in good agreement with electrochemical and surface analytical results.

Key words: mild steel, corrosion, HCl, Tetrazole, SEM, EDX.

1. INTRODUCTION:

Mild steel is the most widely used metal in industrial application due to its excellent mechanical properties and low cost [1-3]. Acidic conditions were applied in many industrial methods and processing, such as industrial metal cleaning and treating, chemical descaling, and the oil and gas industry[4-6].An organic corrosion inhibitors is a chemical substance that can be applied to liquid or gas within industrial process to decrease a corrosion rate of metal or its alloy [7]. Organic compounds containing atoms with a lone pair of electrons (N, O, S and p) can decrease corrosion process of metal in aqueous acidic solutions [8].

The aim of this work is to evaluate the corrosion inhibition efficiency of 5-phenyl tetrazole for mild steel in 1molar HCl using weight loss, open circuit potential, potentiodynamic polarization and surface analytical techniques such as SEM and EDX**.**

2. EXPERIMENTAL PROCEDURE:

2.1. MATERIAL AND METHODS:

Mild steel refers to low carbon steel which is usually used for structural application in industry. Mild steel coupons having composition (c-o.16%, si-0.10%, Mn-0.40%, P-0.013%, Si-0.02% and remaining iron.) have been used in present investigation**.**

SURFACE TRETMENT OF MILD STEEL:

For electrochemical and polarization and gravimetric analysis, coupons of 1cm x 3cm x 0.025cm were sheared from the commercial grade sheet. The surface of mild steel coupons were abraded successively by different grades of metallographic emery paper 1/0, 2/0, 3/0 and 4/0. So as to get the surface free from scratches and other apparent defects. Polished sample were wash with soap solution, rinsed with doubled distilled water, degreased with acetone and finally dried. The surface treatment was carried out immediately before each experiment of corrosion test.

TEST SOLUTION:

1M HCl was prepared by dilution of 36% HCl (analytical grade) in bi-distilled water. The concentration ranged from 100 to 500 ppm solution of 5- phenyl tetrazole in 1M HCl.

2.2 SYNTHESIS OF INHIBITORS:

The tetrazole used in the present study were synthesized according to previously described procedure [9]. The characterization data, IUPAC name, structure and abbreviation used for the synthesized compound are given below in Table 1.

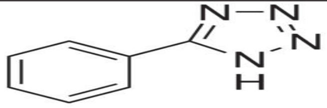
Inhibitor	Molecular Structure	Analytical data
5-amino tetrazole		**MP** – 214^{0}C - 216^{0}C. **FT-IR- υ max/cm^3.** 3120,2970,2830,2760,2606,2575, 2488,1560,1465,1160,720,703.

Table 1: IUPAC name, molecular structure, melting point and analytical data of studied inhibitor.

2.3 WEIGHT LOSS MESUREMENTS

Weight loss measurement was carried out in a test tube containing 10 ml test solution with and without inhibitors solution at the range from 100 to 500ppm.The immersion time was 24 hours at 26^0C $+1^0$C. The coupons were withdrawn from test solution ,rinsed with doubled distilled water, washed with acetone ,dried and weighted .the average value of weight loss were reported**.**

2.4 OPEN CIRCUIT POTENTIAL (OCP) AND POLARISATION MEASUREMENT

Electrochemical measurement system, DC105, containing software of DC corrosion technique from M/S Gamery instrument, USA was used for OCP and potential polarization experimental studies. Above mentioned polished and cleaned mild steel coupons were masked with enamel lacquer by leaving 1 cm^2 working area on one side and a small portion at the tip to provide electrical contact. Finally the coupons were dried in desiccators for further use. A Saturated calomel electrodes and graphite electrodes were used as reference and counter electrode respectively. The working surface area of mild steel electrodes and remaining these electrodes were sufficiently immersed in to the Pyrex glass vessel containing 50ml of test solution and connected to gamery instruments. Potential was swept between -0.5 and 0.5v at the scan rate of 5mv/s. the open circuit potential was carried out for 1 hours to obtained steady horizontal curve and then potentiodynamic polarization was run .The variation in potential and polarization of mild steel with respect to with and without inhibitor was measured against saturated calomel electrode.

2.5 SEM AND EDX ANALYSIS

The composition and surface morphology of corrosion product on mild steel sample after immersion for 24 hours in 1M HCl in absence and a presence of 500 ppm of 5-phenyl tetrazole, was studied using a SEM and EDX .The accelerating voltage for SEM picture as 20.0 kv.

3 RESULTS AND DISCUSSION:

3.1 WEIGHT LOSS MEASUREMENT:

Weight loss data of mild steel in 1 molar HCl in the absence and presence of various concentrations of inhibitors were obtained and are given in table 2. Inhibitors efficiencies were calculated according to following equation.

$$\%\mathrm{IE} = \frac{\mathrm{w}_{0-}\mathrm{w}_{\mathrm{corr}}}{\mathrm{w}_{\mathrm{corr}}}$$

.

W_{corr} and W_0 are weight loss of mild steel in presence and absence of inhibitors respectively. The results showed that the inhibitor efficiencies increase with increasing the concentration of inhibitors. The results obtained from the weight loss measurement were in good agreement with those obtained from electrochemical measurements.

Inhibitor	Concentration (ppm)	Weight loss(mg)	Surface coverage	Inhibition efficiency (%E)
Blank	-	**235**	-	-
5-Phenyl tetrazole	100	61	0.7404	74.04
	200	32	0.8638	86.38
	300	28	0.8808	88.08
	400	21	0.9106	91.06
	500	11	0.9531	95.31

Table 2: The weight loss parameter obtained for mild steel in 1 M HCl containing different concentrations of 5- Phenyl tetrazole.

3.2 ADSORPTION ISOTHERM:

In corrosion field Adsorption isotherm provides basics information regarding interaction between the inhibitors molecules and metal surface [10].To find suitable adsorption isotherm in the present study, several commonly used isotherms were tested, among which Langmuir adsorption isotherms were found to fit well with experimental data. Assumption of Langmuir relates the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage (θ) according to equation: $C/\theta = 1/K + C$, where K is equilibrium constant of adsorption. The graph of C/θ vs C obtained straight line with R^2 value obtained varied close to unity confirming the validity of this approach .The slop of the straight line was almost close to unity, suggesting that adsorbed molecule formed monolayer on mild steel surface.

Free energy of the adsorption (ΔG^0_{ads}) can be calculated using

$\Delta G^0_{ads} = -RT \ln(55.5\, k_{ads})$

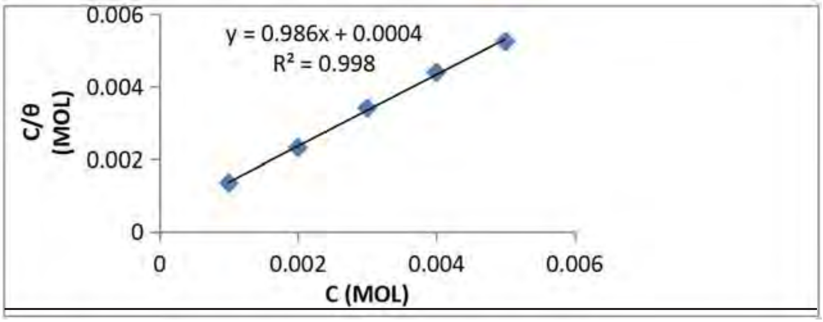


Fig 1: Langmuir isotherm plot for adsorption of 5-Phenyl tetrazole on mild steel surface in 1 M HCl.

Generally, value of ΔG^0_{ads} up to -20 $kjmol^{-1}$ are associated with physisorption while those around -40 $kjmol^{-1}$ or higher are associated with chemisorptions. In present case the value was -29.34. Which was lower than -40 kj mol^{-1} but higher than -20 kj mol^{-1} indicating that the adsorption was neither typical physisorption nor chemisorption but it was complex mix typed. Thus in present case adsorption of inhibitor molecule on the mild steel involved both physisorption and chemisorptions but physisorption was the predominant mode of adsorption. The negative value of ΔG^0_{ads} indicated the spontaneous adsorption of inhibitors on the surface of the metal [11,12]

4 ELECTROCHEMICAL MEASUREMENTS:

4.1 OPEN CIRCUIT POTENTIAL (OCP) CURVES:

The potential developed on the mild steel electrodes relative to the potential of the reference electrodes is term as open circuit potential. The stabilization of OCP is essential before performing electrochemical measurement .The variation of OCP of the working electrodes with respect to time in 1 molar HCl in absence and presence of inhibitors is shown in fig 2. The OCP curves gives straight line in absence and presence of inhibitors, indicating that steady state potential has been established after 30 min. immersion. It can be observed from OCP curves that in presence of tetrazole , the steady state potential (E_{corr}) shifted towards more positive direction without changing common feature of the OCP vs. time curves indicative that a physical barrier form between metal and inhibitors.

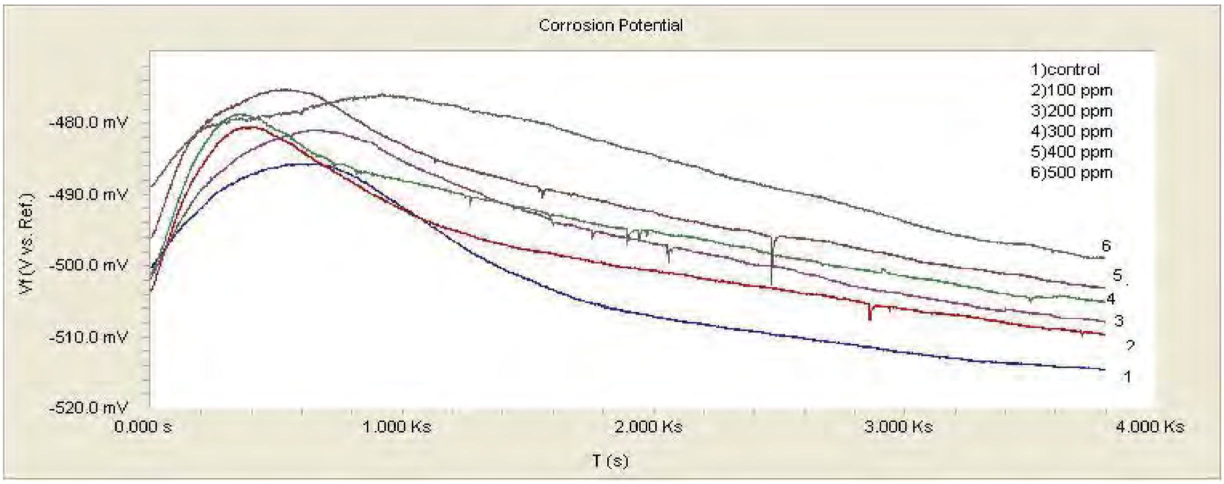


Fig 2: Open circuit potential diagram for mild steel in 1 M HCl without and with different concentrations of 5-Phenyl tetrazole.

4.2 POTENTIODYNAMIC POLARISATION STUDIES

The polarization behavior of mild steel in 1 M HCl in the absence and presence of different concentration of inhibitors are shown in fig.3.

Electrochemical parameters such as corrosion current (i_{corr}), corrosion potential (E_{corr}), and Tafel slopes constant β_a and β_c calculated from Tafel plots are given in table3. From the evaluated i_{corr} value, η% can be calculated using the relation $\eta\% = \frac{i_0 - i_{corr}}{i_0}$ .where i_0 and i_{corr} are the corrosion current densities in the absence and presence of inhibitors. From the table and figure, it is clear that in the presence of tetrazole there was remarkable decrease in i_{corr} value by shifting both anodic and cathodic Tafel slopes towards low current densities [13]. It was further confirmed that the shape of polarization curves were similar in absence and presence of inhibitors, suggesting that 5-phenyl tetrazole inhibited mild steel corrosion by simply adsorbing on the mild steel surface without changing the mechanism of mild steel dissolution[14]. An inhibitor can be classified as anodic, cathodic or mix type depending upon the displacement in E_{corr} value. If the displacement in E_{corr} for the inhibited and uninhibited solution is more than 85mv it can be classified as cathodic or anodic type. But the displacement in E_{corr} is less than 85 mv then it can be classified as mix type. Since the maximum displacement for studied compound was 21mv indicating that tetrazole is mixed type inhibitors [15].

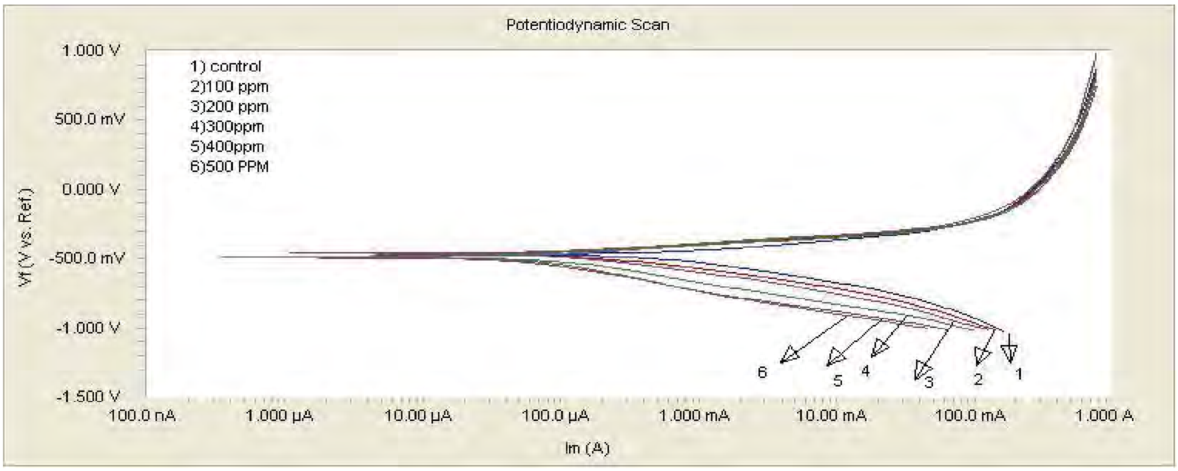


Fig 3: Polarization curve of mild steel in the absence and presence of 5-Phenyl tetrazole.

Acid Medium	Concentration (ppm)	$-E_{corr}$ (mv)	I_{corr} ($\mu A/cm^2$)	β_a (v/dec)	β_c (v/dec)	IE %
1 M HCl	-	-470.0	548.0	$86.60\ e^{-3}$	$171.4\ e^{-3}$	-
	100	-466.0	133.0	$68.20\ e^{-3}$	$133.9\ e^{-3}$	75.73
	200	-462.0	71.0	$61.20\ e^{-3}$	$129.1\ e^{-3}$	87.04
	300	-488.0	67.30	$67.40\ e^{-3}$	$156.8\ e^{-3}$	87.72
	400	-491.0	41.70	$74.50\ e^{-3}$	$171.1\ e^{-3}$	92.39
	500	-491.0	36.90	$66.80\ e^{-3}$	$164.8\ e^{-3}$	93.27

Table 3: Tafel polarization parameters for mild steel in 1 M HCl in absence and presence of 5-Phenyl tetrazole.

4.3 SURFACE STUDIES:

4.3.1Scaning Electron microscope (SEM) studies

5-phenyl tetrazole forms protective film on surface of mild steel is further supported by SEM micrograph of the mild steel surface obtained after immersion in 1 mol HCl for 24 hours in absence and presence of 500ppm of 5-phenyl tetrazole. Figure [3a] represents the surface of mild steel without any addition. From figure [3b] it can be visualized that the specimen surface was rough and strongly damaged in the presence of acid solution. Figure [3c] shows SEM micrographs of the mild steel surface immersed in1M HCl containing 500 ppm of inhibitors. It can be concluded that extent of damaged to the mild steel surface was small and rate of corrosion was greatly reduced in presence of inhibitors. This is due to formation of protective surface film on mild steel, which act as barrier and was responsible for inhibition of corrosion.

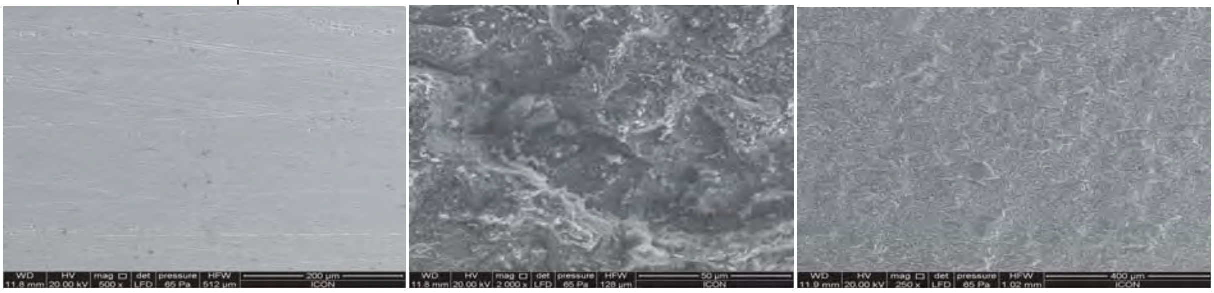
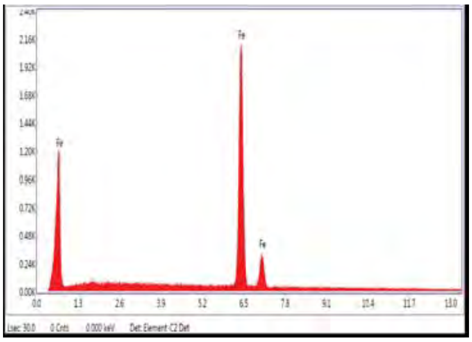


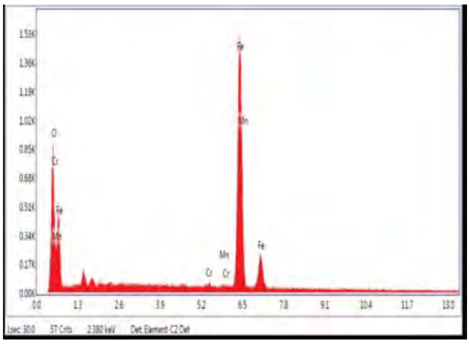
Fig.3 SEM micro graphs of mild surface (a) before immersion in 1 M HCl, (b) after one day immersion in 1 M HCl and (c) after one day of immersion in 1 M HCl+500 ppm of 5-Phenyl tetrazole.

4.3.2 Energy Dispersive X ray spectroscopy (EDX) studies.

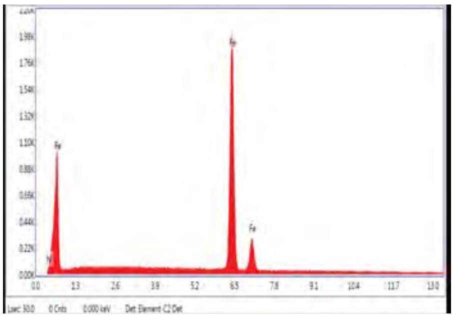
To support weight loss and electrochemical studies, EDX spectra were collected from mild steel in the presence and absence of 500 ppm inhibitors. Figure 4(a) shows EDX spectra of polished mild steel surface with the characteristic peak for Fe. From fig.4[b] it is clear that the EDX spectra in absence of 5-phenyl tetrazole shows characteristic signal for Fe, Mn, Cr, O and Cl due to damage caused by 1 M HCl. However in presence of tetrazole the EDX spectra shown in fig.4[c] indicates signal for nitrogen, confirming the presence of this element on surface, which could be due to adsorption of studied inhibitors on mild steel surface. One can also observe that the damage cause by 1M HCL is curtailed by inhibitors.



a) Polished surface of mild



b) Mild steel in 1M HCl



c) Mild steel + 500ppm inhibitors

Fig.4 EDX spectra of a) Polished surface of mild steel b) Mild steel in 1 M HCl c) Mild steel + 500 ppm of 5-Phenyl tetrazole.

5. MECHANISM OF INHIBITION:

The inhibition effect of tetrazole derivatives on corrosion of mild steel in 1 M HCl solution may be attributed to the adsorption of this compound to the metal solution interface [16]. The extent of adsorption of the inhibitors depends on the nature of metal, chemical structure of inhibitors, nature of electrolyte and temperature. Adsorption on the metal surface was suggested to be via the active center present on inhibitors molecule and relies on their charge density [17, 18].

In case of 5-phenyl tetrazole, the inhibition effect is due to interaction of π electron of phenyl and tetrazole ring as well as the presence of electron donor nitrogen through which it forms a bond with vacant d- orbital of the atom of the metal at the interface.

6. CONCLUSION:

The corrosion behavior of mild steel in 1 M HCl in absence and presence of tetrazole compound was investigated using the weight loss, open circuit potential and potentiodynamic polarization technique and surface analytical techniques. From the result obtained the following conclusion can be drawn:

1. Tetrazole exhibited good inhibition efficiency and shows maximum efficiency at 500ppm.

2. There was good agreement between weight loss and electrochemical techniques to determine the efficiency of corrosion inhibitors.

3 The data obtained from weight loss technique for the studied inhibitor fit well in to Langmuir adsorption isotherm.

4. Polarization studies showed that 5-phenyl tetrazole as mixed inhibitor

5. The surface morphology techniques showed that the mild steel specimen had smoother surfaces in the presence of inhibitors due to formation of protective film of adsorbed inhibitors on the metal surface which prevented corrosion.

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B. Papers Presented in Conferences

Sr. No.	Paper Title	Name of the Conferences	Date and Place
1.	Corrosion inhibition effect Quinoxaline derivatives for mild steel in 1 M HCl	International conference on advances in Chemical science	Shivaji University Kolhapur February 1-3,2018
2.	Investigations of corrosion inhibition effect of Quinoline and its derivatives on mild steel in 1M HCl	International conference on advances in Chemical science	Shivaji University, Kolhapur. February 1-3,2018
3.	corrosion inhibition effect and adsorption behavior of quinoline derivatives on mild steel in 1 M HCl	National Conference on Emerging Trends in Material Science	V.G.Vaze College, Mulund on 13th January,2018
4.	Corrosion inhibition and adsorption mechanism studies of 5-(4-chlorophenyl)-1H-tetrazole on mild steel in 1M HCl	30th Research Scholar's Meet, Jointly Organized by Indian Chemical Society	Jai Hind College, Church gate, Mumbai on 9-10 Feb.2018.
5.	Study of 1,2,4-triazole as effective corrosion inhibitor for mild steel used in oil and gas industries in 1 M HCl	National Conference on Advanced Analytical Tools for Material Characterization	Birla College, Kalyan on 28th Feb.2018.
6.	Inhibitive effect of 8-hydroxy quinoline on the corrosion of mild steel in 1 M HCl	National Conference on Advanced Analytical Tools for Material Characterization	Birla College, Kalyan on 28th Feb.2018.
7.	1-Acetyl-1H-benzotriazole as effective corrosion inhibitor for mild steel in 1 M hydrochloric acid	UGC-SAP sponsored National Conference on Recent Development in Chemical Sciences	Mumbai University during 8-9th March, 2018.
8.	Corrosion inhibition of mild steel used in oil and natural gas industries by 8-nitro quinoline	UGC-SAP sponsored National Conference on Recent Development in Chemical Sciences	Mumbai University during 8-9th March, 2018.
9.	An electrochemical, themodynamical and surface investigation for	National Seminar on Recent Trends in Science and Technology for	The institute of science and National Gallery of Modern Arts, Ministry of Culture,

	corrosion inhibition of mild steel by 5-amino tetrazole	Sustainable Developments	Govt. of India during 22-23 March, 2018.
10.	Corrosion inhibition of mild steel in hydrochloric acid by rhodizonic acid	National Seminar on Recent Trends in Science and Technology for Sustainable Developments	The institute of science and National Gallery of Modern Arts, Ministry of Culture, Govt. of India during 22-23 March, 2018.

Corrosion inhibition effect of quinoxaline derivatives for mild steel in 1 M HCl.

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Abstract:-

The corrosion inhibition efficiency of Quinoxaline (QX) and its derivatives namely 2-methyl quinoxaline (2-MQX), and 2, 3-diphenyl quinoxaline (2,3DPQX) for mild steel in 1M HCl was tested using weight loss, open circuit potential (OCP) and potentiodynamic polarization techniques. All tested inhibitors showed good inhibition efficiency. Potentiodynamic polarization study showed that the inhibitors acted as mixed-type inhibitors. 2,3DPQX exhibited the best performance amongst these inhibitors. On the basis of inhibition efficiency, these inhibitors can be graded in the following order: 2,3DPQX > 2-MQX > QX. The adsorption of inhibitors on mild steel surface obeys Langmuir adsorption isotherm. The activation energy and other thermodynamic parameters for the inhibition process was calculated and discussed. The nature of the protective film formed on mild steel surface was investigated using SEM and EDX techniques.

Keywords:- Inhibitors, mild steel, HCl media, activation parameters.

ICACS-2018

Investigation of the corrosion inhibition effect of Quinoline and its derivatives on mild steel in 1 M HCl solution.

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Abstract:-

Adsorption of Quinoline and its derivative viz.2-chloro-3-quinoline carbaldehyde on mild steel surface in 1M HCl solution and its corrosion inhibition effect has been studied by weight loss, open circuit potential and potentiodynamic polarization techniques. The results obtained for both the compounds showed good inhibition efficiency for mild steel exposed to 1M HCl solution. Inhibition efficiency increased with increase in the concentration of studied compounds but decrease with increase in temperature. The potentiodynamic polarization studies revealed that both the compounds behave as mixed-type inhibitors. Amongst Temkin, Frumkin, Freundlich and Langmuir isotherm, the studied compounds more closely obeyed Langmuir adsorption isotherm. Scanning electron microscopy (SEM) and Energy dispersive x-ray spectroscopy (EDX) were used to investigate the surface morphology of the steel sample in presence and absence of inhibitors.

Keywords:- Mild steel, inhibitors, 2-chloro-3-quinoline carbaldehyde, SEM/EDX.

PP 12

Corrosion inhibition effect and Adsorption behaviour of Quinoline derivatives on mild steel in 1M HCl

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ABSTRACT: The corrosion mitigation effect of quinoline derivatives namely 2-amino quinoline and 2- methyl quinoline has been studied using weight loss, open circuit potential (OCP) and potentiodynamic polarization. The inhibition efficiency increases with increase in concentration of inhibitor and decreases with increasing temperature. The adsorption of inhibitors on mild steel obeyed Langmuir adsorption isotherm. The potentiodynamic polarization showed that both the compounds act as mixed-type inhibitors. The surface morphology of the mild steel specimens was analyzed using scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis.

Keywords: mild steel, HCl, SEM/EDX.quinoline derivatives.

O-1

Corrosion Inhibition and Adsorption Mechanism Studied Of 5-(4-Chlorophenyl)-

1H-Tetrazole on Mild Steel In 1m HCl Solution.

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The effect of 5-(4-chlorophenyl)-1H-tetrazole on corrosion inhibition of mild steel in 1M HCl was investigated by weight loss measurement, open circuit potential(OCP), potentiodynamic polarization and surface measurements. Result showed that the inhibition efficiency increases with increasing concentration of inhibitor and attain the maximum value of 90% at 500 ppm concentration. Polarization study revealed that 5-(4-chlorophenyl)-1H-tetrazole acted as mixed- type inhibitor. Among the several tested isotherms, adsorption of 5-(4-chlorophenyl)-1H-tetrazole on the mild steel surface obeyed the Langmuir adsorption isotherm. The adsorption of corrosion inhibition is well supported by SEM/EDX studies.

Keywords: mild steel, tetrazole, SEM/EDX.

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PP-34

Study of 1,2,4-triazole as effective corrosion inhibitor for mild steel used in oil and gas industries in 1M HCl .

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Abstract

The corrosion inhibition effect of 1,2,4-triazole on mild steel in 1 M HCl solution has been investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization methods. The experimental results revealed that the compound having significant inhibiting effect on the corrosion of mild steel in 1M HCl solution. The inhibition efficiency was found to increase with increasing concentration of inhibitor and attain maximum value of 93% at 500 ppm concentration. Potentiodynamic polarization studies have shown that the compound acted as mixed-type inhibitor retarding the corrosion of mild steel by blocking the active sites of metal surface. The values of inhibition efficiency obtained from weight loss and polarization measurements are in good agreement. The adsorption of the inhibitor on mild steel surface followed Langmuir adsorption isotherm with negative value of the free energy of adsorption $\Delta G^0_{ads.}$The surface morphology of the mild steel specimen was evaluated by using Scanning electron microscope(SEM)and energy dispersive x-ray analysis(EDAX).

Keywords: triazole, mild steel, surface morphology.

PP-68

Inhibitive effect of 8-hydroxy Quinoline on the corrosion of mild steel in 1M HCl

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ABSTRACT

The inhibitive action 8-Hydroxy quinoline on corrosion of mild steel in 1 M HCl was investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization technique.The result showed that the 8-hydroxy Quinoline inhibited mild steel corrosion and inhibition efficiency increased with increase in concentration of inhibitor. The adsorption is spontaneous and followed Langmuir's adsorption isotherm. Polarization study indicated that the inhibitor acted as mixed-type. The protective film formed on surface is confirmed by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDX).Result obtained from weight loss technique are in good agreement with electrochemical and surface analytical results.

Key words: mild steel, corrosion, HCl, SEM, EDX.

PP-66

1-Acetyl-1H-benzotriazole as effective corrosion inhibitor for mild steel in 1 M hydrochloric acid

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1-Acetyl-1H-benzotriazole was tested as a corrosion inhibitor for mild steel in 1M HCl using different techniques: weight loss, open circuit potential (OCP) potentiodynamic polarization. The results showed that the inhibition efficiency increases with increasing inhibitor concentration from 100 to 500 ppm.The maximum inhibition efficiency was observed at 500 ppm concentration. Polarization studies showed that 1-Acetyl-1H-benzotriazole acted as mixed type inhibitor. The adsorption of inhibitor on the mild steel surface obeyed Langmuir adsorption isotherm. The surface morphologies of mild steel were examined by Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX).

Keywords: mild steel, HCl, Benzotriazole derivatives, polarization

PP-69

Corrosion inhibition of mild steel used in oil and natural gas industries by 8-Nitro quinoline

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The effect of 8-nitro quinoline on dissolution of mild steel 1 M HCl solutions has been studied using the weight loss, open circuit potential and potentiodynamic polarization. The results showed that the inhibition efficiency of the investigated compound was found to depend on the concentration and the nature of the inhibitor. The inhibition efficiency was found to increase with increasing the concentration of inhibitor. Polarization result indicated that compound behaves as mixed type inhibitor. The inhibition is assumed to occur via physical adsorption of inhibitor on metal surface, which obeys Langmuir adsorption isotherm. The negative value of ΔG_{ads} showed that the adsorption of inhibitor on surface of the mild steel is spontaneous. The scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDX) results Confirmed the formation of protective layer on mild steel surface.

Keywords: Quinoline, mild steel, acid corrosion.

O1. An electrochemical, themodynamical and surface investigation for corrosion inhibition of mild steel by 5-amino tetrazole in 1M HCl solution.

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Inhibition performance of 5-aminotetrazole as corrosion inhibitors for mild steel in 1M HCl solution at 298 k was studied by weight loss, open circuit potential(OCP),potentiodynamic polarization ,scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy(EDX) techniques. The results revealed that 5-amino tetrazole performed excellently as a corrosion inhibitors for mild steel in this medium .The inhibition efficiency increased with increasing inhibitor concentrations and also with increase in temperature. The maximum efficiency of 84% has been obtained at 500ppm. The Polarization data indicated that the used compound acts as mixed type inhibitors. The adsorption of compound on mild steel surface obeyed Langmuir adsorption isotherms .Both thermodynamic and activation parameters were calculated and discussed. The negative value of ΔG_{ads} indicates spontaneous chemical adsorption. The adsorption of the inhibitor on the mild steel surface is supported by SEM and EDX studies.

Keywords: Mild steel, Acid corrosion, weight loss, SEM/EDX.

P15. Corrosion Inhibition of Mild Steel In Hydrochloric Acid Solution by rhodizonic Acid

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The effect of rhodizonic acid on dissolution of mild steel 1 M HCl solutions has been studied using the weight loss, open circuit potential and potentiodynamic polarization. The results showed that the inhibition efficiency of the investigated compound was found to depend on the concentration and the nature of the inhibitor. The inhibition efficiency was found to increase with increasing the concentration of inhibitor. Polarization result indicated that compound behaves as mixed type inhibitor. The adsorption of these compounds on steel surface followed Langmuir adsorption isotherm. The scanning electron microscope (SEM) results showed the formation of a protective film on the metal surface in the presence of these additives.

Keywords: Rhodizonic acid, Mild steel, Acid Corrosion.

SYNOPSIS

SYNOPSIS
OF
THE THESIS
TO BE SUBMITTED TO
UNIVERSITY OF MUMBAI
FOR Ph. D. (SCIENCE) DEGREE IN CHEMISTRY

Name of the Student	:	**Mr. PRATAP PANDURANG KAMBLE**
Title of the Thesis	:	**"STUDIES ON CORROSION MITIGATION OF MILD STEEL USED IN OIL AND NATURAL GAS INDUSTRIES WITH SUITABLE CORROSION INHIBITORS"**
Degree	:	**Ph.D.**
Subject	:	**Chemistry**
Registration No. **Date of registration**	:	**53, DATED:12/06/2014**
Name & **Designation of the Guide**	:	**DR. R.S.DUBEY, M.Sc. Ph.D.** **ASSOCIATE PROFFESSOR,** **DEPARTMENT OF CHEMISTRY,** **R.J.COLLEGE, GHATKOPAR (W),** **MUMBAI – 400 086.**
Place of Research work	:	**CHEMISTRY RESEARCH LABORATORY,** **DEPT. OF CHEMISTRY,** **RAMNIRANJAN JHUNJHUNWALA** **COLLEGE OF ARTS, SCIENCE & COMMERCE,** **GHATKOPAR – WEST, MUMBAI- 400 086.**
Synopsis submission date	:	**16/05/18**

DR. R. S. DUBEY	**PRATAP PANDURANG KAMBLE**
(RESEARCH GUIDE)	**(RESEARCH STUDENT)**

SYNOPSIS

Of

The Thesis Entitled

STUDIES ON CORROSION MITIGATION OF MILD STEEL USED IN OIL AND NATURAL GAS INDUSTRIES WITH SUITABLE CORROSION INHIBITORS

1. Introduction:

Corrosion is naturally occurring phenomena defined as the deterioration in quality of materials (usually metal) or its properties because of the reaction of material with its environment. Corrosion of material is inevitable due to the fundamental need of lowering of Gibbs free energy[1-2].Corrosion is common problem encountered in the oil and gas industries. Oil and gas pipelines, refineries and petrochemical plants have serious corrosion problems. Internal corrosion in oil and gas industry is generally caused by temperature ,carbon dioxide (CO_2), hydrogen sulfide (H_2S), water,flow velocity, and surface chemistry of steel[3-4].Various factors have to be considered while dealing with corrosion problems of oil and gas industries. The type of reservoir rocks, the acid used for stimulation, the oil well equipments such as tubing and casings and the operating condition are some of the important factors that affects the corrosivity.Oxygen, which plays such an important role in corrosion, quickly react with metal as a very reactive oxident.It is only at drilling stage that oxygen contaminated fluids are first introduced.Drilling muds,left untreated will corrode not only well casing, but also drilling equipment, pipelines and mud handlingequipment. Water and carbon dioxide, produced or injected for secondary recovery, can cause severe corrosion of oil and well structures. Acid used to remove scale, readily attack metals. Hydrogen sulphide (H_2S) poses other problems. Handling all these corrosion situations, with the added complications of high temperature, pressures and stresses involvedin drilling or production requires the expertise of corrosion engineer, an increasing key figure in industries[5-9].

Combating corrosion in oil and gas industry is paramount since the economic loss in these industries due to corrosion is extremely high. Among the various methods to combat corrosion in oil and gas industry, the use of corrosion inhibitor is one of the best and economic methods. There are many types of corrosion inhibitors, andbroadly classified in to anodic, cathodic and mixed corrosion inhibitor.They protect the surface of the metal either by merging with them or reacting with the impurities in the environment that may cause corrosion.

Corrosion inhibitor may act in a number of ways: It may restrict rate of anodic process or cathodic process by simply blocking active sites on metal surface. Alternatively it may act by increasing the potential of metal surface so that the metal enters in passivation region where the natural oxide film isformed. A further mode of action of some inhibitors is that the inhibiting compounds contribute to the formation of a thin layer on the surface which prevents the metal surface[10-12]. Factor to be considered before using a corrosion inhibitor in the oil and gas industry include it'stoxicity, environmentalfriendliness, andthe cost. Organic corrosion inhibitors are more effective than inorganic compounds.Many of the commercial corrosion inhibitors used in oil and natural gas industry are unique mixtures that may contain surfactant, film enhancer,demulsifieror oxygen scavengers in addition to inhibitor moiety[13-15].A variety of organic compounds act as corrosion inhibitors for mild steel during the acidizing procedure in the presence of HCl, including acetylenic alcohols, aromatic aldehydes, amines, amides, nitrogen(N) containing heterocyclic compounds, nitriles, triazoles, tetrazoles, pyridine and its derivatives, Thiourea derivatives and quinolinederivatives[16-19]. In order to use corrosion inhibitors in oil and natural gas industry, the inhibitor must be compatible with the expected environment,economical and not only provide great protection to metal but also should not cause any significant undesirable side effects which might affect the operation/ process[20-22].

In presents investigation, sincere efforts has been made to synthesize,characterize and use the suitable inhibitors for control of corrosion of mild steel in 1 M hydrochloric acid media. Organic compounds like tetrazole, triazole, diazine, quinoline and its derivatives which work as excellent corrosion inhibitor in hydrochloric acid media have been studied.

2. Aim of Present Investigation :

I. To synthesize tetrazole derivatives (5-amino tetrazole,5-phenyl tetrazole and 5-(4-chloro phenyl)tetrazole), Triazole derivatives (benzotriazole,1-benzoyl-1H-benzotriazole,1-acetyl-1H-benzotriazole), quinoline derivatives (2-methyl quinoline,2-amino quinoline,2-chloro-3-quinolinecarboxaldehyde,8-nitroquinoline,8-hydroxyquinolineand 1,4-bezodiazine *i.e.* quinoxaline and its derivatives such as 2-methyl quinoxaline and 2,3-diphenyl quinoxalineby following the procedure available in literature[23-25].

II. To characterize all these synthesized compounds by FTIR technique.

III. To study the inhibition performance of synthesized derivatives on mild steel in 1M hydrochloric acid

IV. To investigate the corrosion control of mild steel by using above inhibitors at different concentration in 1M hydrochloric acid by weight loss, electrochemical measurement techniques such as open circuits potential(OCP), potentiodynamic polarization and surface analytical techniques i.e. scanning electron microscopy(SEM) and energy dispersive X-ray (EDX) spectroscopy.

3. ExperimentalDesign

3.1. Preparation of mild steel specimens: Mild steel refers to low carbon steel which is usually used for structural applications in oil and gas industries. Commercial grade sheets of mild steel were used for the present investigation. It purchased from the local market and analyzed by using X-ray diffractometer for its composition (C-0.16%, Si- 0.10%, Mn-0.40%, P- 0.013%, S- 0.02% and remaining as iron).

For weight loss experiments, rectangular shaped coupons (1 cm x 3 cm x 0.01 cm) were sheared from sheets of mild steel. Specimens with 1 cm^2 working area were used for electrochemical experiments. The surface of specimens was prepared by sequential polishing with 1/0,2/0,3/0 and 4/0 grade Emery paper (John Okay). After polishing the surface by lower grade of emery paper, it was polished with the next higher grade in a direction right angle to the first. After polishing all specimens were washed with triple distilled water, and degreased with 95% ethyl alcohol. Specimens were dried and stored over silica gel in vacuum desiccators. Specimens were weighed on an electronic balance (CONTECH, Model No.CBS-50 least count 0.001g)

Chemicals and solutions

All chemicals used in the present investigation were of AR grade and procured from different chemical companies. The aggressive solution was prepared from AR grade hydrochloric acid obtained from Merck. One molar solution of hydrochloric acid was prepared with double distilled water. Different concentrations (100 – 500 ppm) of inhibitors in 1M hydrochloric acid were prepared to study their inhibition efficiency on mild steel.All the materials were used as received without any further treatment.

Inhibitor

New inhibitorsi.e.tetrazole derivatives (5-amino tetrazole,5-phenyl tetrazole and 5-(4-chloro phenyl)tetrazole), Triazole derivatives (benzotriazole, 1-benzoyl-1H-benzotriazole, 1-acetyl-1H-benzotriazole), quinoline derivatives (2-methyl quinoline, 2-amino quinoline, 2-chloro-3-quinolinecarboxaldehyde, 8-nitroquinoline, 8-hydroxyquinoline and 1,4-bezodiazine *i.e.*quinoxaline and its derivatives such as 2-methyl quinoxaline and 2,3-diphenyl quinoxaline were synthesized,purified and characterized byFTIR spectroscopic technique. Inhibitors were dissolved in 1M HCl to prepare stock solution of 1000 ppm concentration. Desired concentration was obtained by diluting the stock solution with 1M HCl solution.

3.2. Methods

3.2.1 Weight loss measurements: Weight loss measurements were carried out in a test tube containing 10 cm^3 test solution with and without inhibitor at the range from 100-500 ppm inhibitor concentration. The immersion time was 24hrs at 303 k .After 24 hrs of exposure period, coupons were taken out ,rinsed with double distilled water, washed with acetone and dried over silica gel. Specimens were weighed on an electronic balance (CONTECH, Model No.CBS-50. least count 0.001g) before and after immersion tests. After removing the specimens from test solutions the corrosion products were removed from the surface with the help of brush. Each experiment was performed in triplicate to ensure reproducibility, and the mean value was reported. The weight loss was repeated at higher temperature from 313-333k at a concentration of 500 ppm of the inhibitors. Activation energy (E_a), free energy of adsorption (ΔG_{ads}), enthalpy and entropy of activation (ΔH^0&ΔS^0) were also calculated.

.**3.2.2. Electrochemical Experiments:**Electrochemical measurement system, DC105, containing software of DC corrosion technique from M/S Gamry instrument, USA was used for OCP and potentiodynamicpolarization techniques. Above mentioned polished and cleaned mild steel coupons were masked with enamel lacquer by leaving 1 cm^2 working area on one side and a small portion at the tip to provide electrical contact. Finally the coupons were dried indesiccators for further use. A saturated calomel electrode and graphite electrode were used as reference and counter electrodes respectively. The working surface area of mild steel electrodes and remaining these electrodes were sufficiently immersed in to the Pyrex glass cell containing 50ml of test solution and connected to Potentiostat/Galvanostat.

a) Open Circuit Potential measurements: The variation of corrosion potential of mild steel in 1 M HCl was measured against saturated calomel electrode (SCE) in absence and presence of various concentrations of inhibitors. The time dependence of OCP for different experiments was recorded for 1 hour exposure period. Sample period was 1 second and sample area was 1 square centimeter. Then same sample which was used for OCP measurement was used for potentiodynamic polarization experiments. The polarization studies were carried out in unstirred solutions.

b) Potentiodynamic polarization: The potentiodynamic polarization study was performed in the absence and presence of optimum concentrations of inhibitors. For potentiodynamic study potential was swept between -0.5V to 0.5V at the scan rate of 5mV/second. The different electrochemical parameters and corrosion rate of mild steel in 1 M HCl with and without inhibitors were calculated with the help of inbuilt Tafelformula in theGamry instruments software.

3.2.3. SurfaceAnalysis: The surface film formed on the metal specimen was evaluated by SEM-EDX analysis. This was carried out by SEM/EDX model PHENOM PROX from the Netherlands. The spectra were recorded for specimens exposed to 1M HCl for a period of 24 hours in the absence and presence of 500 ppm inhibitors. The energy of acceleration beam employed was 20 kv.

3.3 Result and Discussions:

Chapter 1: The definition, importance, economic impact and environmental hazards of corrosion of mild steel in oil and gas industry are briefly discussed.Acidization of oil well, additives used in acidization, corrosion types and associated agents in oil and gas industry are also given in brief. A brief description with respect to corrosion testing, corrosion monitoring, failure analysis and its management is given. It also throws light on different corrosion protection and prevention techniques. A brief description about passivators, pickling inhibitors, slushing compounds, vapor phase inhibitors has been given. Recent reviews on the use of heterocyclic N and S containing compounds as well as natural occurring substances as low-cost, environment friendly and non-hazardous inhibitors have been discussed.Thus it contains fundamentals, basics and a brief review of corrosion inhibition of mild steel in hydrochloric acid in oil and gas industry.

Chapter 2: This chapter deals with the procedure adopted in the study which covers preparation of mild steel specimens for weight loss and electrochemical experiments, preparation of solution containing different concentration of inhibitors in corrosive media, electrochemical techniques utilized for corrosion measurement such as open circuit potential (OCP) measurements and potentiodynamic polarization. It also describes surface analysis of coupons by SEM and EDX.

Chapter 3: Inhibition performance of 5-aminotetrazole,5-phenyl tetrazole,5-(4-chlorophenyl) tetrazole as corrosion inhibitor for mild steel in 1M HCl was studied by weight loss, open circuit potential(OCP),potentiodynamic polarization ,scanning electron microscopy(SEM) and Energy-dispersive X-ray spectroscopy(EDX) techniques. The results revealed that all tetrazole derivatives performed excellently as a corrosion inhibitors for mild steel in 1M HCl.The inhibition efficiency increased with increasing inhibitor concentrations and maximum efficiency has been obtained at 500ppmconcentration.In the presence of various concentrations of inhibitors the steady state values of OCP of mild steel shifts more towards positive directions. This is due to adsorption of inhibitors on metal surface resulting in passivation of metal.The Polarization data indicated that the presence of tetrazole causes a remarkable decrease in corrosion current density values by shifting both the anodic and cathodicTafel slopes towards low current region. An examination of results also showed that used compounds acts as mixed type of inhibitors. The inhibition efficiency of the studied inhibitors follows the order:5-(4-chlorophenyl) tetrazole>5-amino tetrazole>5-phenyl tetrazole. The adsorption of compound on mild steel surface obeyed Langmuir adsorption isotherm .Both thermodynamic and activation parameters were calculated and discussed. The negative value of ΔG_{ads} indicates spontaneous chemical adsorption. The adsorption of the inhibitor on the mild steel surface is supported by SEM and EDX studies. All the above inhibitors were synthesized according to procedure given in literature and characterized by FTIR spectroscopy.

Chapter4: Benzotriazole (BTA) and its derivatives i.e1-acetyl-1H-benzotriazole and 1-benzoyl-1H-benzotriazoleweresynthesizedby procedure given in the literature and characterized by FTIR spectroscopic technique. Corrosionbehavior of mild steel in 1M HCl and its control by benzotriazole, 1-acetyl-1H-benzotiazole,1-benzoyl-1H-benzotriazolehas been investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization techniques. The results showed that the inhibition efficiency increased with increasing inhibitor concentration from 100 to 500 ppm. The OCP curves give straight line in absence and presence of benzotriazole and its derivatives, suggesting that the steady state potential has been established after 30 minutesof immersion. It can also be observed from OCP curves that in presence of benzotriazole and its derivatives, steady state potential shifts towards more positive direction without changing common features of OCP vs. Timecurves. It is observed that shapes of polarization curves are similar in the absence and presence of benzotriazole and its derivatives suggesting that these derivatives inhibit mild steel corrosion by there absorption on the mild steel surface without changing the mechanism of mild steel dissolution. Polarization curvesalso revealedthat triazole behaved as mixed-type inhibitors. The adsorption of inhibitor molecules on mild steel surface obeyed Langmuir adsorption isotherm. Microstructure of surface analyzed by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (E-DAX) reveled presence of thin film formed due to adsorption may be responsible for decrease in corrosion rate of the mild steel.

Chapter 5: The corrosion inhibition efficiency of Quinoxaline (QX) and its derivatives namely 2-methyl quinoxaline (2-MQX), and 2, 3-diphenyl quinoxaline (2,3DPQX)for mild steel in 1M HCl was tested using above mentioned techniques.

The obtained potential-time curves (OCP) indicate that potential of mild steel immersed in 1M HCl solution (blank) tends towards more negative potential firstly, giving rise to short step. Addition of inhibitors to the aggressive medium produces a positive shift in corrosion potential due to formation of a protective film on the mild steel surface.Potentiodynamic polarization study showed that the corrosion current density was decreased by increasing inhibitor concentration with respect to the inhibitor free solution and hence, formation of good protective layer on the surface of mild steel. The obtained electrochemical parameters showed that the quinoxaline and its derivatives retard both anodic and cathodicreactions act as mixed-type inhibitors. 2,3DPQXexhibited the best performance amongst these inhibitors. All tested inhibitors showed good inhibition efficiency. On the basis of inhibition efficiency, these inhibitors can be graded in the following order:2,3DPQX > 2-MQX > QX. The adsorption of inhibitors on mild steel surface obeys Langmuir adsorption isotherm. The activation energy and other thermodynamic parameters for the inhibition process was calculated and discussed. The nature of the protective film formed on mild steel surface was investigated using SEM and EDX techniques.Quinoxaline and its derivatives used in the present study were synthesized according to previously described procedure and characterized by FTIR spectroscopy.

Chapter 6: The effect of 2–methyl quinoline, 2-amino quinoline,2-chloro-3-quinoline carbaldehyde, 8-nitro quinoline and 8-Hydroxy quinoline on corrosion of mild steel in 1 M HCl was investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization techniques. The result showed that the inhibition efficiency of the investigated compounds was found to depend on the concentration and nature of inhibitors. The inhibition efficiency was found to increase with increase in concentration of inhibitors. In the presence of different concentration of inhibitors, OCP was shifted towards the positive potential direction and gets stabilized thus indicating the adsorption of the inhibitors on the metal surface. Polarization results indicated that addition of all inhibitors affect both anodic and cathodic polarization curves suggesting that these inhibitors could be classified as mixed-type (reduced mild steel dissolution as well as hydrogen evolution). The inhibition is assumed to occur via physical adsorption of inhibitor on metal surface which obeys Langmuir’s adsorption isotherm. The negative values of ΔG_{ads} showed that adsorption of inhibitors on mild steel surface is spontaneous. The protective film formed on surface is confirmed by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDX).Results obtained from weight loss technique are in good agreement with electrochemical and surface analytical results.All the above synthesized compounds were characterized by FTIR spectra.

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INVESTIGATIONS ON CONTROL OF MICROBIAL CORROSION OF MILD STEEL UNDER THE INFLUENCE OF SULPHATE-REDUCING BACTERIA FROM OIL AND NATURAL GAS ENVIRONMENT

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UNDER THE GUIDANCE OF
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MARCH 2022

Statement by the Candidate

As required by the University Ordinance 770, I wish to state that the work embodied in this thesis titled, **“Investigations on control of microbial corrosion of mild steel under the influence of sulphate-reducing bacteria from oil and natural gas environment”** forms my own contribution to the research work carried out under the guidance of **Dr. R. S. Dubey** at the **Department of Chemistry, Ramniranjan Jhunjhunwala College of Arts, Science and Commerce, Ghatkopar (W), Mumbai-400086**. This work has not been submitted for any other degree of this or any other University. Whenever reference have been made to previous works of others, it has been clearly indicated as such and included in the Bibliography.

Signature of candidate
Girase Jitendra Dagesing Ranjankaur

Certified by

Dr. R. S. Dubey
Research Guide

Certificate

I certify that the thesis submitted by **Girase Jitendra Dagesing Ranjankaur** represents his original wok, which was carried out by him in Chemistry Research Laboratory, Department of Chemistry, Ramniranjan Jhunjhunwala College, Ghatkopar (W), Mumbai-400086, from June 2014 to March 2022.

I further certify that I am of the opinion there is a prima facie case for consideration of the thesis.

Dr. R. S. Dubey
Research Guide

DEDICATED TO MY

BELOVED FAMILY

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Girase Jitendra Dagesing Ranjankaur

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List of Abbreviations

AC : Alternate Current

AFM : Atomic Force Microscopy

API : American Petroleum Institute

ARXPS : Angle Resolved X-ray Photoelectron spectroscopy

ASM : American Society for Microbiology

ASTM : American Society for Testing and Materials

Ba : Anodic Beta (Tafel) coefficient

Bc : Cathodic Beta (Tafel) coefficient

Cdl : Double layer Capacitance

CII : Confederation of Indian industry

CMC : Critical Micelle Concentration

CR : Corrosion Rate

CI : Corrosion Inhibitor

CRA : Corrosion Resistance alloy

CSIR : Council of Scientific and Industrial Research

DC : Direct Current

DFT : Density Functional Theory

DST : Department of Science and Technology

EPZC : Potential of Zero Charge

Eop : Open circuit potential

Ecorr : Corrosion potential

EHOMO : Energy of Highest Occupied Molecular Orbital

ELOMO : Energy of Lowest Occupied Molecular Orbital

EDAX : Energy Dispersive Analysis by X-Ray

EDS : Electron Dispersive X-ray spectroscopy

EDX : Electron Dispersive X-ray spectroscopy

EFM : Electrochemical Frequency Modulation

EIS : Electrochemical Impedance Spectroscopy

FTIR : Fourier Transform Infrared Spectroscopy

GDP : Gross Domestic Product

GNP	:	Gross National Product
HIC	:	Hydrogen Induced Cracking
HOMO	:	Highest Occupied Molecular Orbital
Icorr	:	Corrosion Current
IE	:	Inhibition Efficiency
IGA	:	Inter Granular Attack
IR	:	Infra-Red Spectroscopy
IIT	:	Indian Institute of technology
LEED	:	Low Energy Electron Diffraction
LOMO	:	Lowest occupied Molecular Orbital
MC	:	Monte Carlo Simulation
MD	:	Molecular Dynamic Simulation
MIC	:	Microbiologically Influenced Corrosion
MS	:	Mild Steel
MFL	:	Magnetic Flux Leakage tools
NACE	:	National Association of Corrosion Engineers
NLLS	:	Non-linear Least Squares Fitting
NML	:	National Metallurgical Laboratory
NRB	:	Nitrate Reducing Bacteria
OCP	:	Open Circuit Potential
PD	:	Potentiodynamic Polarization
QC	:	Quantum Chemical calculation
Rp	:	Polarization Resistance
Rs	:	Solution Resistance
Rct	:	Charge Transfer Resistance
RED	:	Reflection Electron Diffraction
SCC	:	Stress Corrosion Cracking
SCE	:	Standard Calomel electrode
SEM	:	Scanning Electron Microscopy
SHE	:	Standard hydrogen Electrode
SRB	:	Sulphate Reducing Bacteria

TGA	**:**	Thermo Gravimetric Analysis
TLC	**:**	Thin Layer Chromatography
UGC	**:**	University Grand Commission
VCI	**:**	Volatile Corrosion Inhibitors
WDS	**:**	Wavelength Dispersive X-ray Spectroscopy
XRD	**:**	X-Ray Diffraction
XPS	**:**	X-Ray Photoelectron Spectroscopy