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TABLE OF CONTENTS

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Control of microbiologically influenced corrosion (MIC) of mild steel exposed to sulphate reducing bacteria(SRB) in marine environment by using nanostructured polyaniline

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Abstract

Microorganisms have the capacity to connect their metabolic products to solid surfaces, directly exchanging electrons with them through membrane-bound redox compounds, thus accelerating the electrochemical activities and results in microbial corrosion. Biocidal coatings exhibit characteristics to kill microbes and fungi by slowly and steadily releasing biocide from the coating. Generally, the biocidal activity lasts within two years due to leaching of biocides from the coatings which requires reapplication of coating to regain antibacterial and antifungal protection.

In the present communication we have developed a new biocidal coating system that prolongs biocidal activity by immobilizing biocidal additive nanopolyaniline in epoxy resin.

It was synthesized by using cyclic voltametry technique and characterized by particle size analyzer, infrared spectroscopy and atomic force microscopy.Biocidal property of the coating was measured by open circuit potential and potentiodynamic polarization techniques.

Keywords: Microbiologically Influennced Corrosion(MIC), Mild steel, Polyaniline, Cyclic voltametry and Potentiodynamic polarization

Introduction

Mild steel is one of the most widely used structural and engineering material for infrastructure, transportation, aviation, ships and naval structures [1]. Sea water contains 3.5% sodium chloride and the amount of sodium chloride present in atmosphere of coastal area is about 1.5%[2]. Chloride ions are highly detrimental for corrosion of mild steel and it create severe corrosion hazards to onshore and offshore structures. Apart from the sodium chloride, microbes present in sea water corrode the surface of mild steel. Biocidal coatings are used to kill microbes and fungi by slowly releasing the biocide from the dried film, but once all the biocide is leached out or washed out of the coating all protecting action against the microbe is lost. New coating has to be applied to regain the antifungal protection[3].

Acetylacetonate complexes of Co, Cu, Mn and Zn have been used as corrosion inhibitor of mild steel in 3.5% Nacl [4]. Some polymeric compounds such as poly(N-methylamine)[5], poly(N-ethyl

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aniline)[6], polypyrole phosphate [7] and polypyrole [8] has been studied as a corrosion inhibitor of mild steel. In 1990 it was proved that polyaniline is a flexible and highly useful polymer. Polyaniline is a unique polymer because it is a type of semiconductor. Polyaniline can be configured to conduct across a wide range, from being utterly non-conductive for insulation use to highly conductive for other electrical purposes. Polyaniline is widely used in different areas of research including electronics, solar cells, batteries, electromagnetic shielding devices, sensors and anticorrosive coatings [9-10].

Polyaniline is in granular form which can be mixed with an organic chemical and painted or sprayed onto a substance to form a smooth layer of polyaniline [11]. The aim of the present investigation was to find out inhibition performance and biocidal activity of polyaniline for control of microbiologically influenced corrosion of mild steel exposed to cultures of *Desulfovibrio desulfuricans* with 3.5% sodium chloride solution.

Experimental Procedure

Chemicals used in preparation of culture media were obtained from and Himedia (India).

The bacteria used in the present study were obtained from National Collection of Industrial Microorganisms,(NCIM), Biochemical science Division, National Chemical Laboratory,Pune,411088,Maharashtra. The bacteria used in the present study was *Desulphovibro Desulphuricans*. Composition of the culture medium is given below:

Name of organism	NCIM No.	Maintenance medium
Desulphovibrio desulfuricans	2047	Barr's medium(Sulphur bacteria) K_2HPO_4 0.05g, NH_4Cl 0.1g, $CaSO_4$ 0.2g, Sod.lactate 0.7g, $MgSO_4.7H_2O$ 0.2g, Fer.ammon.sulphate 0.05g, Distilled water 100 cm^3.(Medium is sterilized for three consecutive days at 121^0C for 20 min and the final pH is adjusted to 7.0-7.5.

Synthesis of Polyaniline by cyclic voltammetry.

Polyaniline was synthesized by using electrochemical techniques at room temperature in a standard three electrode cell. The working electrode was mild steel and the counter electrode was spectroscopic grade graphite rod. Saturated calomel electrode (SCE) was used as reference electrode.

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Mild steel of commercial grade in sheet form having composition as follows: C - 0.16%, Si - 0.10%, Mn - 0.40%, P - 0.013%, S - 0.02% and Iron- balance, were used in the present investigation. For electrochemical techniques, 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 Sianor, 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.

During a CV experiment, the potential is increased linearly from an initial potential to a final potential and back to the initial potential again, while the current response is measured. Polyaniline were deposited from 1 M sulphuric acid solution containing 0.5 M aniline, by cyclic voltammetry . The cyclic voltammetry was sweep between -400 mV and 100 mV/SCE, at 50 mV s^{-1}. Polyaniline was deposited on mild steel (working electrode) which was removed and washed thoroughly with distilled water. Cyclic voltammograms of Polyaniline, recorded at different sweep rate is shown in Fig 1.

Particle size analysis

For confirming the size of polyaniline, Particle size analysis was performed on Motic digital microscope (Model No. DMWB3-223ASC) with software Motic Image plus version 2.0ML. Polyanile were found to be in nano range As shown in Fig. 2. Characterization of polyaniline by IR Fig.3.

Open circuit potential (OCP) measurement

Inhibition efficienct of polyaniline was determined by electrochemical techniques. A molecular structure of polyaniline is shown in Fig.4. Pure NaCl obtained from S.D.Fine Chemicals was used to prepare its 3.5% solution with double distilled water. 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 mild steel sheet. The samples were polished with emery papers of grades 1 / 0, 2 / 0, 3 / 0, and 4 / 0 to obtain a scratch free mirror finish surface. The samples were coated with epoxy resin and polyaniline leaving a small portion at the tip for providing electrical contact

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

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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 in 3.5% Nacl solution containing *Desulfovibrio desulfuricans* with samples uncoated, coated with blank epoxy resin and with epoxy resin containing polyanilne.

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 analyzing the nature of the OCP curve. The variation of open circuit potential of Mild Steel coated with blank epoxy resin and with epoxy resin containing polyanilne in 3.5% NaCl solution containing *Desulfovibrio desulfuricans* is shown in Fig. 5. The steady state potential is obtained after 1.5 to 2.0 Ks of the exposure period. In the presence of blank epoxy resin and with epoxy resin containing polyanilne in 3.5% NaCl solution containing *Desulfovibrio desulfuricans*, OCP is shifted towards the positive potential direction and get stabilized thus indicating the inhibition of corrosion on the metal surface. Maximum shift of the corrosion potential in the positive direction is obtained in the presence of epoxy resin containing polyanilne as shown in Fig.5.

The value of inhibition efficiency in terms of corrosion current density was determined by using the following equation:

$$E = 100 \times (i_o - i) / i_o \qquad \dots (1)$$

where i_o and i are the corrosion current density of the uninhibited and inhibited samples respectively.

Potentiodynamic polarization

The anodic and cathodic polarization curves of mild steel coated with blank epoxy resin and with epoxy resin containing polyanilne in 3.5% NaCl solution containing *Desulfovibrio desulfuricans* are shown in the Fig. 6. Potential was swept at a scan rate of 10 mV/s. The Potentiodynamic polarization shows that the epoxy resin containing polyanilne caused a remarkable potential shift in the corrosion potential (Ecorr).The positive shift in Ecorr confirms the best protection of the mild steel when its surface is covered by the polyaniline. It clearly show that a substantial reduction in the corrosion current density (Icorr) occurs for the mild steel coated with epoxy resin containing polyanilne - with respect to the mild steel coated with blank epoxy resin. The effect of these coatings on various electrochemical parameters like corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel constant (β_a), cathodic Tafel constant (β_c), corrosion rate and % inhibition efficiency etc. is shown in Table. 1.

Polyaniline coating is strongly adherent and it provides a better corrosion inhibition on mild steel surface.The corrosion rate of mild steel coated with epoxy resin containing polyanilne is

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found to be 1.248 m/year and corrosion rate of mild steel coated with blank epoxy resin is found to be 7.170 m/year.

The % Inhibition efficiency is calculated from potentiodynamic polarization.

The % Inhibition efficiency (%IE) is calculated by using the following expression

$$\%IE = \frac{Icorr_o - Icorr_i}{Icorr_o} \times 100 \qquad \dots (2)$$

Where $Icorr_0$ and $Icorr_I$ denotes the corrosion current density of uninhibited and inhibited samples respectively.

The % IE calculated from potentiodynamic polarization for mild steel coated with epoxy resin containing polyanilne and mild steel coated with blank epoxy resin is found to be 98.85% and 98.8% respectively.

Scanning Electron Microscopic Analysis (SEM)

The SEM micrographs were taken for uncoated mild steel samples , epoxy resin samples and epoxy resin containing polyaniline samples after completion of potentiodynamic polarization shown in Fig.7.

SEM micrograph shows that epoxy resin containing polyaniline shows a smooth surface whereas many pits are observed on the surface of the uncoated sample.

Atomic force microscopy (AFM) studies

The AFM analysis was performed for the closer examination of the mild steel samples.

AFM measurements were taken for uncoated mild steel samples , epoxy resin samples and epoxy resin containing polyaniline samples as shown in Fig.8. AFM measurements were performed with diInnova from Veeco Instruments. The quantitative analyses were carried out using Veeco software. All the AFM measurements have been performed in tapping mode (for both trace and retrace information) using a silicon nitride tip at ambient temperature.

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AFM micrographs confirms that surface of mild steel with epoxy resin containing polyaniline is smooth and shows more corrosion inhibition.

Table 1. Electrochemical parameters for inhibition of corrosion of Mild Steel exposed to 3.5% sodium chloride containing *Desulfovibrio desulfuricans* with samples uncoated, coated with blank epoxy resin and with epoxy resin containing polyanilne.

Conc. (PPM)	βa (V/dec.)	βc (V/dec.)	Icorr (μA. cm^{-2})	Ecorr (mV)	Corr. Rate (mpy)	% of Inhibition Efficiency
Uncoated	115.3e-3	531.4e-3	30	-600.0	13.71	
Blank epoxy resin	97.30e-3	538.8e-3	15.70	-625.0	7.170	47.66
Epoxy resin with polyaniline	82.50e-3	520.5e-3	2.730	-654.0	1.248	90.9

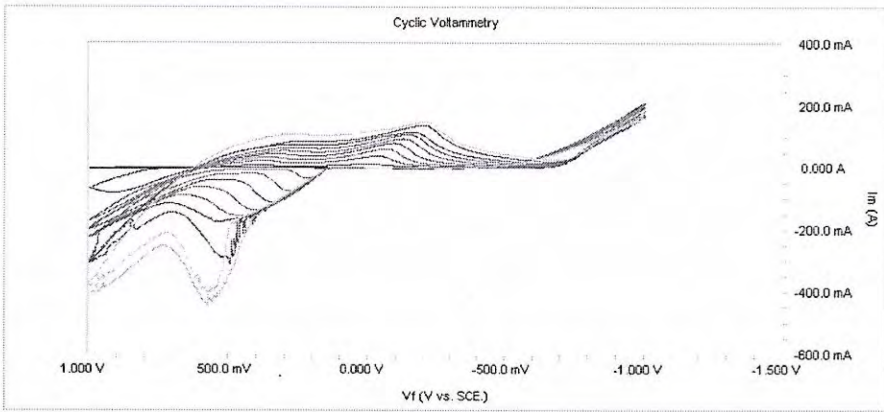

Fig.1. Cyclic voltammetry of polyanilne.

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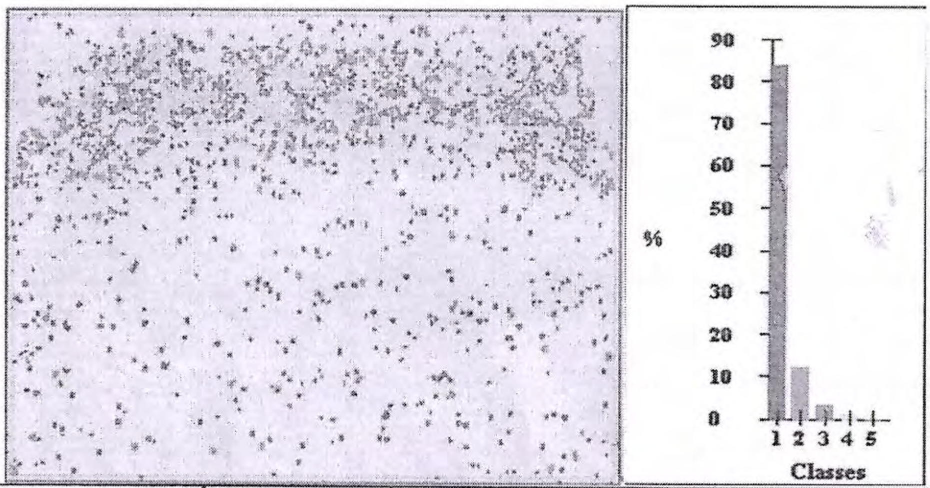

	Count	%Count	%Count(Total)	Count/area mm
#1: 0-1	1217	84.2215	84.2215	1841260
#2: 1-2	168	11.6263	11.6263	254175.6
#3: 2-3	45	3.1142	3.1142	68082.74
#4: 3-4	12	.8304	.8304	18155.4
#5: 4-5	3	.2076	.2076	4538.85

Fig.2. Particle size analysis of polyaniline.

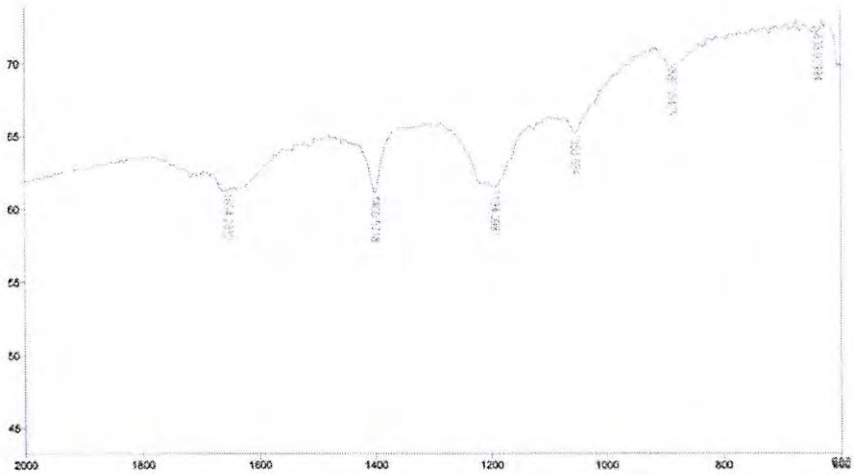

Fig3. Characterization of polyaniline by IR

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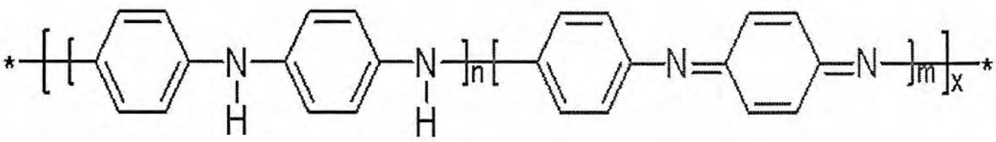

Fig 4. Molecular structure of Polyaniline

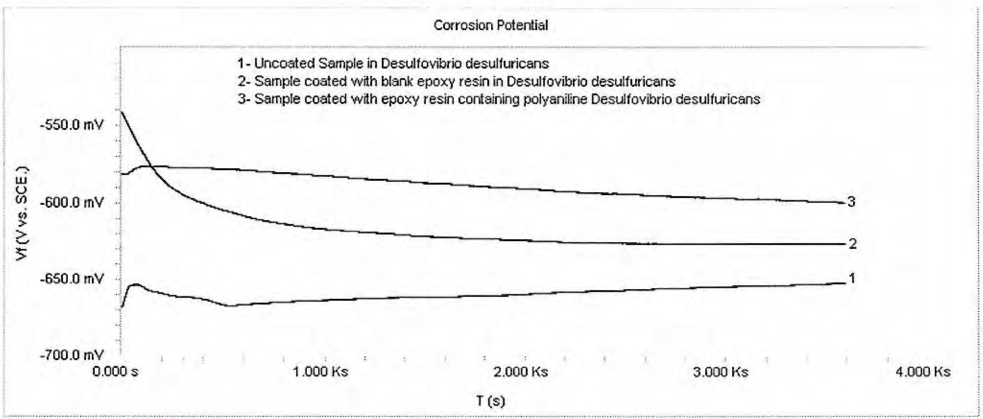

Fig.5. Corrosion potential of Mild steel exposed to 3.5% NaCl solution containing *Desulfovibrio desulfuricans* with samples uncoated, coated with blank epoxy resin and with epoxy resin containing polyanilne .

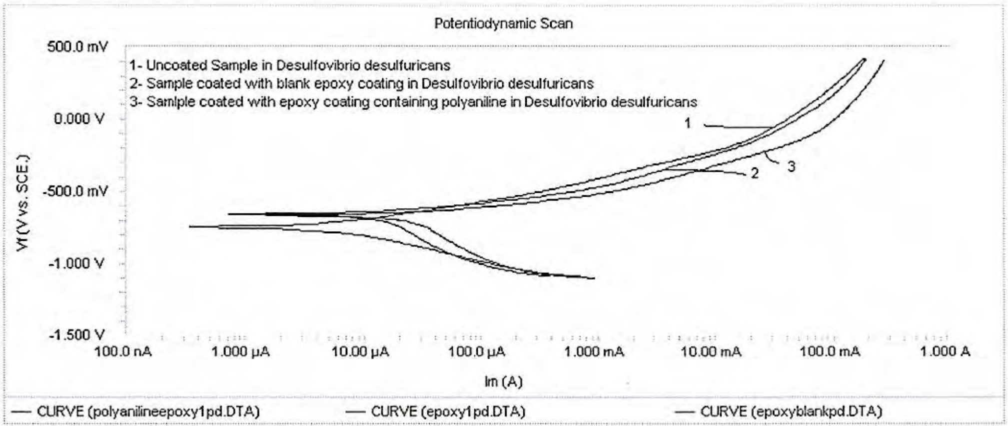

Fig.6. Potentiodynamic polarization curve of Mild steel exposed to 3.5% NaCl solution containing *Desulfovibrio desulfuricans* with samples uncoated, coated with blank epoxy resin and with epoxy resin containing polyanilne .

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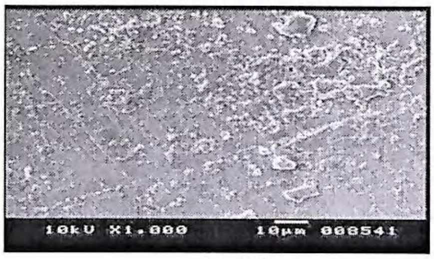
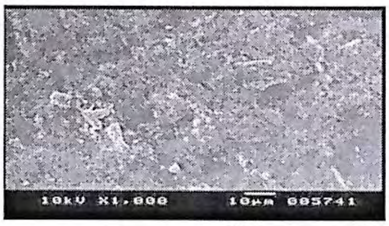


(a)



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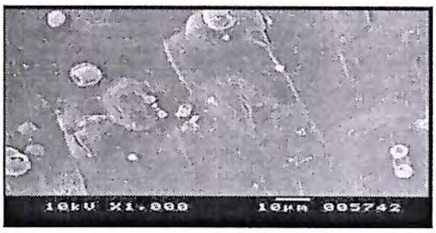
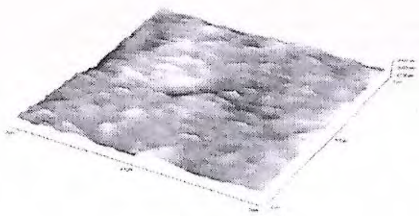
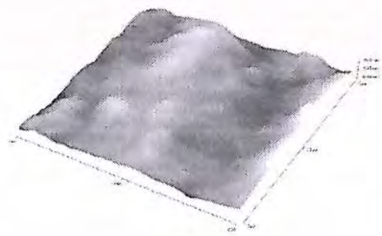


(c)

Fig.7. SEM micrographs for the (a) uncoated mild steel sample (b) epoxy resin samples and (c) epoxy resin containing polyaniline samples after completion of potentiodynamic polarization in 3.5% Nacl solution containing *Desulfovibrio desulfuricans*.



(a)



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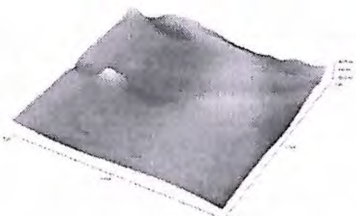

(c)

Fig.8. AFM micrographs for the (a) uncoated mild steel sample (b) epoxy resin samples and (c) epoxy resin containing polyaniline samples after completion of potentiodynamic polarization in 3.5% Nacl solution containing *Desulfovibrio desulfuricans*.

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Conclusions

Polyaniline in epoxy resin acts as a good corrosion inhibitor for mild steel in 3.5% sodium chloride solution containing *Desulfovibrio desulfuricans*.

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