Art - Botany Anil 2018-19

ADSORPTION OF HEAVY METALS FROM AQUEOUS SOLUTIONS USING MANGROVES FROM MUMBAI MANGROVES.

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ABSTRACT

Bio-adsorption of heavy metals by mangrove biomass has been valued as a potential alternative to the existing physiochemical technologies for detoxification and recovery of valuable heavy metals from waste waters.

In this context the efficacy of mangrove leaf powder *Avicennia marina* (MLP) as bio adsorbent for removal of divalent metal ion Chromium was investigated. The particle size of the powder was kept constant at 1mm. Adsorption of the heavy metal was studied under varying MLP amount and Time while pH (4.0) and a temperature (37° C) were kept constant.

With a defined calibration curve adsorption of chromium was estimatedwith diphenyl carbazide absorption method using colorimeter (visible).

Increase in concentration of MLP paralleled with time showed maximum adsorption of chromium. These results indicated that mangrove leaf powder (MLP) can be used as low cost adsorbent for the removal of chromium from aqueous solutions.

Keywords: *Adsorption,, Heavy metal ions, Mangroves and Mangrove leaf powder*

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Introduction

Heavy metal release to the environment has been increasing continuously as a result of industrial activities and technological development, posing a significant threat to the environment, public and soil health (Cerbasi and Yetis;2001). Among the heavy metals released into environment, chromium is an important pollutant. Chromium is a redox active element, with oxidation states from –2 to +6, but only the +3 and +6 states are prevalent in the aqueous environment. Cr(III) and Cr(VI) are environmentally stable oxidation states and exhibit different types of toxicity mechanism on biota. Chromium is released into the environment by a large number of industries such as mining, iron sheet cleaning, chrome plating, leather tanning and wood preservation (Krishna and Philip;2005). These industries contains Cr(III) and Cr(VI) at a concentration ranging from 10 to 100 mg/L (Park *et al*;2005). Long-term release of such wastewater may result in the accumulation of heavy metals in soil exerting a selection pressure on soil micro-biota. Cr(VI) is a highly soluble and toxic chromate anion, and is a suspected carcinogen and mutagen (Costa;2003). Alsothe wide use of chromium (Cr) by modem industries has resulted in a large quantity of this element being discharged into the environment via air emission, waste water or land disposal. One of the important sources of the Cr in the waste water is due to the use of chromates in cooling water for corrosion control. Cr may exist in water in both hexavalent and trivalent states. Trivalent Cr has a lower toxicity than that in the hexavalent state. Important sources which add chromium (Cr) to the environment are: Ferro-chromium production units, refining of ores, chemical industries and the combustion fossil fuels. In rural areas chromium content in ambient air is usually less than 0.1 ~g/cubic meter, while in industrial areas it may range from 0.01-0.03 pg/cubic meters. Particulate ejected from coal fired power generation plants may contain 2.3-32 ppm of chromium. Waste waters from tanneries may contain 10-50 ppm, textile wastes up to 32 ppm while spent chrome liquors may contain up to 4500 mg/litre of Cr. Only trivalent and hexavalent forms of Cr are of biological significance. Trivalent Cr is the most common form of the metal in nature and it is in this state the metal almost always occurs in a living system. Hexavalent Cr is capable of crossing the cell membrane and is rapidly reduced to trivalent state inside a living cell. Small quantities of trivalent Cr are essential to carbohydrate metabolism in mammals while it is also a co-factor for action of insulin. A little amount of Cr is helpful in improving glucose tolerance in diabetic patients, weak and old individuals. Most of the mammals can tolerate almost a hundred times more Cr in trivalent state than their usual body burden without any toxic effects. Acute Cr toxicity causes serious renal tubular necrosis. Exposure to hexavalent Cr has been found to cause dermatitis, allergic skin reactions, chronic ulceration and injury to nasal septum, gastrointestinal ulcers etc. Chronic Cr toxicity has been associated with incidence of cancers of respiratory track in occupationally involved workers. Both forms of Cr (hexavalent and trivalent) are considered equally potent carcinogenic agent. In view of the paradoxical role of the Cr, as an essential micronutrient in human and animal nutrition at low concentrations, and a known carcinogen at the elevated levels, there is a growing concern about the fate and effects of Cr in the environment. The conventional methods for removing Cr (VI) ions from wastewater are based on the combination of different physical and chemical reduction processes (Kurniawan *et al*; 2006). However, such processes are becoming undesirable due to the use of expensive and toxic chemicals.

Further these methods are also inefficient in the removal of Cr(VI),particularly with wastewater containing with a low Cr concentration and also associated with the production of secondary effluents (Baral and Engelken,2002). Prakasham *etal.*,(1999) and Kadimpati *etal.*(2013) suggested that the removal of heavy metals by adsorption on various biomass surfaces is the best alternative to the physic and chemical methods. In recent years, many researchers used the various bio-materials such as tea factory waste (Cay*etal.*2004;Malkoc and Nuhoglu 2005, 2006),sawdust (Acar and Malkoc2004;Yu *etal.*2003); soya cake (Daneshvar *etal*; 2002), sugarcane bagasse (Gupta and Ali 2004),green algae (Gupta *etal.* 2001; Malkoc and Nuhoglu 2003), distillery sludge (Selvaraj *etal.*2003)for removal of heavy metals from wastewaters. Most of the low-cost sorbents have the limitation of poor sportive capacity, and thereby, for the same degree of treatment it generates more solid waste (pollutant laden sorbent after treatment) leading to disposal problems. Therefore, there is a need to explore low cost, economically viable and effective sorbent, having high pollutant sorption capacity (Ho*etal.*2005).

Mangrove belt of Mulund-Vikhroli area (+19°4'45.83", +72°55'7.26")is a marsh tract from Thane extends towards the south along Thane creek, where the small channels of the creek in this region form a network among the continuous stretches of mangrove vegetation and comprises a diversity of species. The vegetation is spread over 730ha with about 105 different plant species of Mangroves and associates (Avhad A E 2011).

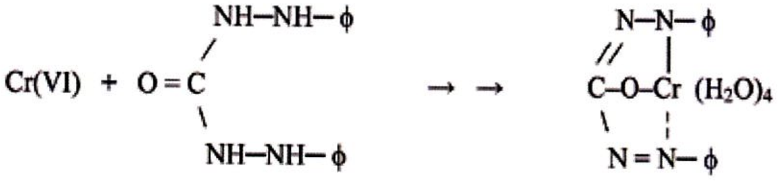
Avicennia marina was found to be abundant source of mangrove, hence was taken as source for leaf powder as a bio adsorbent in this current study. All the estimation of heavy metals for in this context chromium +6 was quantitatively determined by Diphenyl carbazide absorption metrical method using colorimeter (DIGITAL COLORIMETER EQ 650A) as inspecting device.

The project purpose was to explore the possibility of using mangrove biomass for phytoremediation. Thus the study entitled "Adsorption of heavy metals by mangrove leaf powder" was chosen to explore the adsorption capacity of mangrove biomass.

II) MATERIALS AND MEHODS

Determination of Chromium with Diphenylcarbazide

For the determination of chromium,colorimetric method with diphenylcarbazide (DPC) was adopted. Chromium (VI) reacts with DPC to form reddish violet complex. The reaction is selective for chromium and very sensitive. One tenth to five microgram of chromium could be determined with an error less than +2%.This efficiency to obtain chromium complex made the procedure to be more precise in detecting quantitatively the amount of chromium in the solution. (ATSDR (1993), toxicological profile for chromium and chromium compounds)(Quantitative determination of chromium by diphenylcarbazide method by - Environmental solution book)



1,5-diphenylcarbazide **Cr-diphenylcarbazone complex**

2.1 Mangrove leaves collection and preparation

For the present investigation plants of *Avicennia marina* were selected. Leaves of same were obtained from mangrove belt of Mulund-Vikhroli area (+19°4'45.83", +72°55'7.26").

The leaves were oven dried for overnight at 40°C. The samples were washed with distilled water to remove soil and soluble particles. Cleaned roots samples were then oven dried at 80 0C for 24 hours in order to obtain biomass in completely dried form. The dried mangrove samples were then ground into fine powder using mechanical grinder after which the powder was soaked and washed severally with both cold and hot tap water until clean. The leaves were crushed to obtain 1mm size with the help of motor grinder and stored in plastic containers awaiting adsorption experiments.

2.2 Reagents

All reagents used were of analytical grade. Special grade chemicals $K_2Cr_2O_7$was used as a source of chromium. The amount of chromium was detected by Diphenylcarbazide Reagent method using colorimeter. Solutions from 0.010 to 1.5 mg/L were prepared with the standard stock solution of 25.0 mg/L [Cr(VI)]. Solutions from 0.0010 to 0.0075 mg/L were prepared with standard solution of 0.25mg/L.

Solution of diphenylcarbazide – 2ml of diphenylcarbazide solution dilute to 100ml with distilled water.

2.3 Instrumentation

All pH measurements were made using pH meter. Solutions were constantly agitated using an orbital shaker SELEC RC5100 – Neolab Instruments(Rotatory shaker). The absorbance was recorded with Equiptronics – Digital colorimeter EQ 650A.

Chromogenic Reaction and Reaction time

Chromogenic reaction was processed at the room temperature (37°C). The reaction was maintained at constant pH of 4.0 for each solution flask by using 1N H_2SO_4.The flasks were agitated by hand for 60 seconds after addition of diphenylcarbazide solution.

Series of flask were prepared using 1ml of stock solution and 24ml of distilled water, 5µL of 1N H_2SO_4 for pH maintenance and 1ml of diphenylcarbazide for complex formation. Variation of Time and concentration of MLP was considered in each experiment.

After incubation in rotatory shaker and normal incubation the MLP was filtered out with a Whatman no 1 filter paper. The reaction time for Cr (VI) was obtained using colorimetric technique. All nine flasks, after addition of 5uL of 1N H_2SO_4 and diphenylcarbazide was to detected calorimetrically.Hence a filter was to be chosen to detect all the flask therefore a random selection was done of 0.60mg/L concentration of chromium containing flask and was read at every filter.

From the pilot studies it was found that the reaction gives optimum results when processed at the room temperature (37ºC), at constant pH of 4.0 and continuous agitation for 60 seconds after addition of diphenylcarbazide solution. The optimum time was found to be as 5 mins for complete color change form colorless to wine red (Cr-diphenylcarbazone Complex).(Fig 1), with maximum absorption at 470nm (Fig 2) and the standard value was obtained to be 0.26 ΔOD= 0.125mg of chromium/L. (fig 4).

Considering these values the experiment was set up to find out the time bound effective use of MLP for removal of chromium. Series of flask were prepared using 1ml of stock solution and 24ml of distilled water, 5μL of 1N H_2SO_4 for pH maintenance and 1ml of diphenylcarbazide for complex formation. As shown in the table 1, 2, 3 & 4 the working of the experiment was conducted.

Variation of Time and concentration of MLP was considered in each experiment. After incubation in rotatory shaker and normal incubation the MLP was filtered out with a Whatman no 1 filter paper.

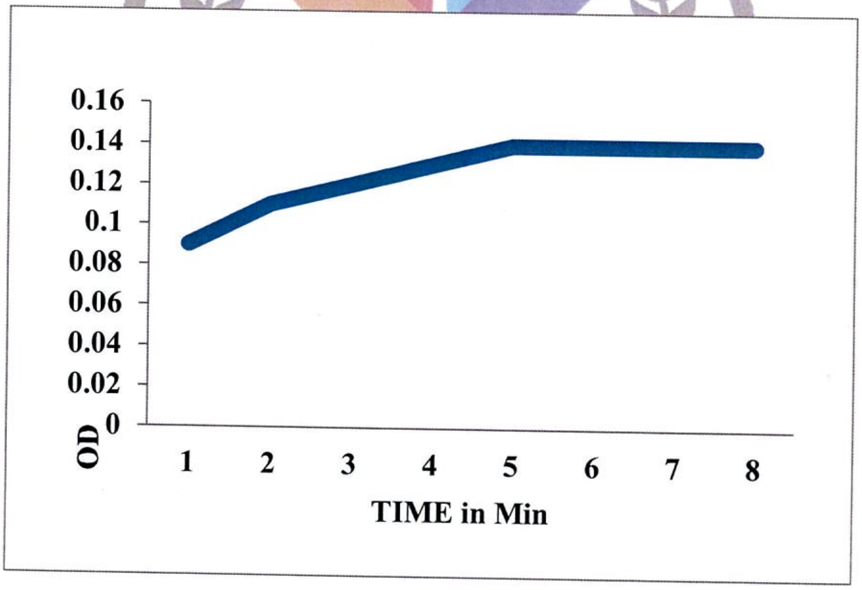


Figure 1: Optimum time for colour formation

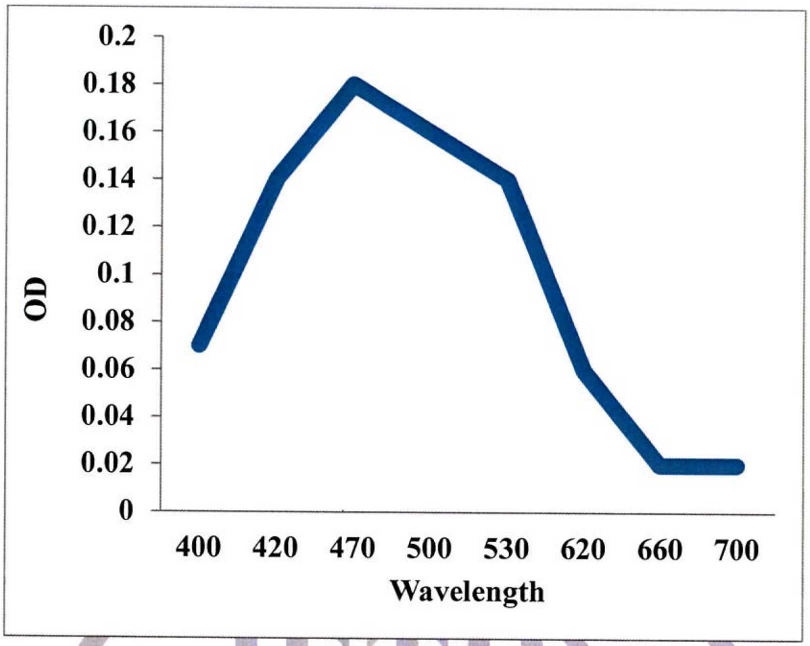


Figure 2: Maximum absorbance found at 470nm

Figure3: Standardisation for Chromium detection

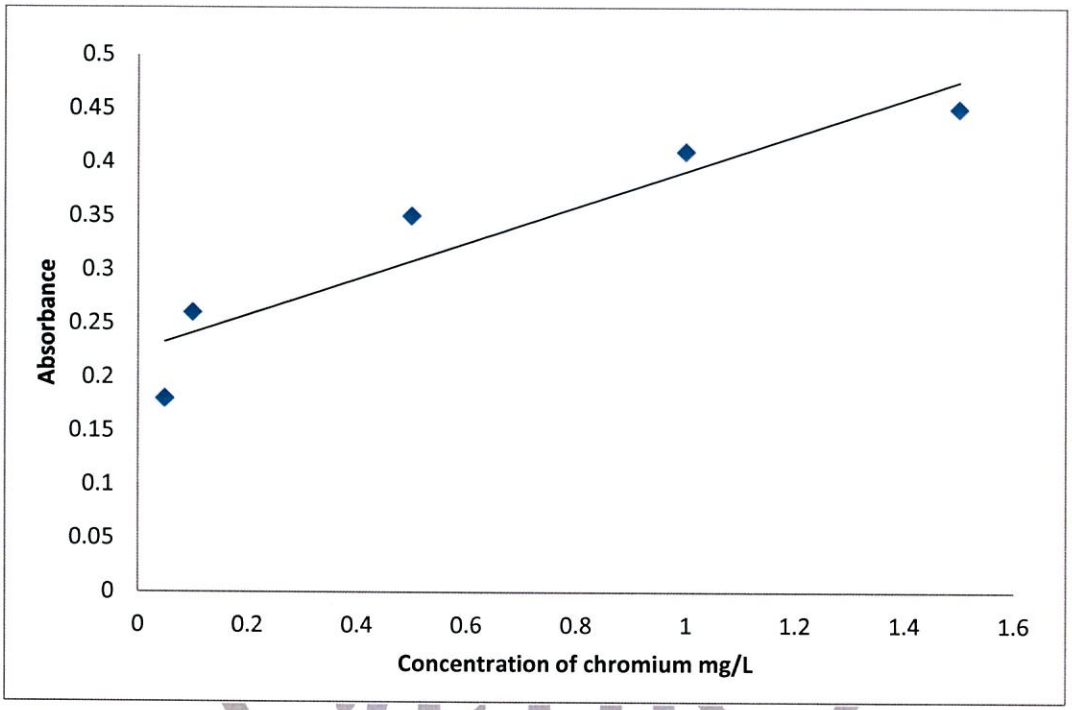


Figure 4: Standard value of chromium

Figure 5: Showing adsorption of chromium at varying time with constant 1 gm of MLP.

III) RESULTS AND DISCUSSIONS

Maximum adsorption of chromium (VI) was observed when the plant material (*Avicennia marina*) leaf powder was subjected to rotatory shaker at constant rpm 70 than normal incubation.

Maximum adsorption was observed when the heavy metal solution along with 1gm of MLP was kept for 24 hrs of incubation in the rotator shaker as per calculated values.

The adsorption was observed to be increased as concentration of MLP was also increased paralleled with time.

A least amount of chromium was left after complete 24 hrs of incubation in the rotatory shaker with 1 gm of MLP – 0.028mg of chromium/L ,whichshowedthat the efficacy to adsorb heavy metal in our study chromium(VI) was upto 90% which was truly worth experimenting .

Due to progressive adsorption of chromium (heavy metal) by MLP*Avecinnia marina* leaf powder, it could be concluded that it is highly capable of adsorbing heavy metals if exposed for optimum period of time along with enough amount of MLP. Hence instead of using Physio-chemical methodologies which are not only expensive but also time consuming, we can buildup a good heavy metal sink by using these mangrove biomass.

This study significantly demonstrated that MLP can be used as an important component for the remediation of hexavalent chromium. It is an environmental friendly technology for cleaning up the chromium contained waste water which normally show chromium oxidation state as +6 which can be toxic to the microbiota of the waste water drainage system.

Evaluation in soil and water samples is important as it has the potential to put environmental and human health at risk, changes in heavy metal concentration above acceptable levels whether due to natural or anthropogenic factors can significantly contribute to serious environmental and human health challenges. The emergence of unplanned housing structures in the creek area of Thane and Mumbai has led to depletion of mangrove forest as more and more land is used for building or construction as well as firewood.

From our experimental studies carried out for this project we can conclude that depletion of the mangrove species such as *Avicenniamarina*can be hazardous to the environment as these plants are important sponges for adsorption of heavy metals like chromium. On this basis we can suggest that if the industries allow these mangroves to be conserved and propagated, they would help us in creating a good heavy metal sink.

However, it should be noted that these mangroves need not be defoliated to obtain MLP. On the other hand the senescent foliage can be harvested and converted to MLP.

This MLP can be used in effluent tanks of polluting industries for chromium adsorption and the treated effluent can be filtered and released in the creeks. While the MLP can be washed, chromium can be recovered and MLP can be reused.

IV. CONCLUSION

MLP is the environmentally friendly potential adsorbent for heavy metals especially Chromium. This work examined the efficiency of MLP in removal of Chromium ions from aqueous environment. However, this work can be considered as a preliminary study to conclude that mangrove roots biomass is suitable and efficient material for the adsorption of Cr ions from aqueous solution.

Acknowledgement

My gratitude goes to the BCUD, University of Mumbai for funding this Minor Research Project in 2016-17.

V) REFERENCES

- **ATSDR (1993),** toxicological profile for chromium and chromium compounds)(Quantitative determination of chromium by diphenylcarbazide method by - Environmental solution book)
- **Acar FN, Malkoc E (2004)** The removal of chromium(VI) from aqueous solutions by Fagus orientalis L. BioresourTechnol 94(1):13–15
- **Avhad Anil E (2011)**Studies on mechanisms of Nitrate uptake and assimilation in *Sesuviumportulacastrum*L.Ph. D. Thesis, Univ. of Mumbai.
- **Baral A, Engelken RD (2002)** Chromium-based regulations and greening in metal finishing industries in the USA. Environ Sci Policy 5:121–133 .
- **Cay S, Uyanık A, O¨ zas¸ık A (2004)** Single and binary component adsorption of copper (II) and cadmium(II) from aqueous solutions using tea-industry waste. Sep PurifTechnol 38:273–280
- **Cerbasi IH, Yetis U (2001)**Biosorption of Ni (ii) and Pb (ii) by Phanerochaetechrysosporium from binary metal system— kinetics. Water Res 27:15–20
- **Costa M (2003)** Potential hazards of hexavalent chromate in our drinking water. ToxicolAppl Pharm 188:1–5
- **Daneshvar N, Salari D, Aber S (2002)** Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake. J Hazard Mater 94(1):49–61
- **Gupta VK, Ali I (2004)** Removal of lead and chromium from wastewater using bagasse fly ash-a sugar industry waste. J Colloid Interface Sci 271:321–328
- **Gupta VK, Srivastava AK, Jain N (2001)**Biosorption of chromium(VI) from aqueous solutions by green algae Spirogyra species. Water Res 35:4079–4085.
- **Ho YS, Chiang TH, Hsueh YM (2005)** Removal of basic dye from aqueous solution using tree fern as a biosorbent. Process Biochem 40(1):119–124
- **Kadimpati KK, Mondithoka KP, Bheemaraju S, Challa VRM (2013)** Entrapment of marine microalga, Isochrysisgalbana, for biosorption of Cr(III) from aqueous solution: isotherms and spectroscopic characterization. Appl Water Sci 3:85–92
- **Krishna KR, Philip L (2005)** Bioremediation of Cr(VI) in contaminated soils.
J Hazard Mater B 121:109–117 (Park *et al*; 2005).

- **Kurniawan TA, Chan GYS, Lo W-H, Babel S (2006)** Physicochemical treatment techniques for wastewater laden with heavy metals. ChemEng J 118:83–98
- **Malkoc E, Nuhoglu Y (2003).** The removal of chromium (VI) from synthetic wastewater by Ulothrixzonata. Fresenius Environ Bull 12:376–381
- **Malkoc E, Nuhoglu Y (2005)** Investigations of nickel (II) removal from aqueous solutions using tea factory waste. J Hazard Mater 127(1–3):120–128
- **Malkoc E, Nuhoglu Y (2006)** Removal of Ni (II) ions from aqueous solutions using tea factory waste: adsorption on a fixed-bed column. J Hazard Mater 135(1–3):328–336
- **Prakasham RS, Merrie JS, Sheela R, Saswathi N, Ramakrishna SV (1999)**Biosorption of chromium VI by free and immobilized Rhizopusarrhizus. Environ Pollut 104:421–427
- **Selvaraj K, Manonmani S, Pattabhi S (2003)** Removal of hexavalent chromium using distillery sludge. BioresourTechnol 89(2):207–211