

BIOSORPTION OF HEAVY METALS USING FRESH WATER AND MARINE ALGAE

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ABSTRACT: Heavy metals are the most toxic substances found in aquatic ecosystems. These metals tend to accumulate in photosynthetic plants and fish and are transferred to humans causing many diseases. It has to be removed from our environment to reduce any health risks. Dry biomass of the microalgae *Spirulina* (freshwater algae) and seaweed (*Euchema cottonii*) were used as a biosorbent for the removal of heavy metals from electroplating wastewater. The effects of different levels of pH (2–10), contact time (30–150 min) were tested. Batch process was carried out in triplicate in an orbital shaker at 120 rpm. After centrifuging the biomass, the remaining levels of heavy metal ions were measured in the supernatant by Atomic Absorption Spectrometer. Very high levels of removal, reaching up to 80.78% and 87.47% for *Spirulina* and seaweed respectively were obtained. The highest percentage of removal was reached at pH 6, 15 g of biosorbent, after 120 min of contact time for *Spirulina* and for seaweed at pH 10, 20g of biosorbent, after 120 minutes of contact time. The equilibrium isotherm Results of this study indicated that both seaweed and *Spirulina* follows Langumir isotherm with $R^2 = 0.979$ and $R^2 = 0.967$. This study denoted that Seaweed is a very good candidate for the removal of heavy metals from aquatic environments. The process is feasible, reliable and eco-friendly.

KEYWORDS: Seaweed, *Spirulina*, Biosorption, Heavy metals, Electroplating wastewater

1. Introduction

Heavy metal pollution has posed a serious threat to the aqua-tic environment. At high concentrations, metals are toxic to animals and plants alike, as they could be dispersed in water and consequently in human beings through food chain biomagnifications that could cause serious health hazards. Chromium water pollution has become of considerable concern due to the fact that chromium has been widely used in metal finishing, electroplating, leather tanning, stainless steel production, textile industries, and chromate preparation (Abdel-Jawad et al., 2002). Chromium exists in the environment in either its hexavalent form (Cr) or trivalent form (Cr (III)). The metal species Cr is considered as highly toxic in that it could act as a carcinogen, mutagen, and teratogen in the biological system (Abu Al-Rub et al., 2002). It has also been noted that prolonged exposure to the metal species could cause skin allergies and cancer in human beings (N. et al., 2002). Additionally, Cr (III) should be oxidized to the state of a more carcinogenic and mutagenic Cr by some bacteria in the environment under certain conditions (Ahalya et al., 2006). Recently, the commonly used method applied to remove excessive chromium from aqueous solutions have included ion exchange, chemical precipitation, activated carbon adsorption, evaporation and membrane processes. However, these methods were found to be either inefficient or expensive when metal ions exist in low concentrations (<100 mg/L) and may also be associated with the generation of secondary environmental problems from waste disposal (Ahalya et al., 2003). The list of the advantages of biosorption includes competitive performance, heavy metal selectivity, cost-effectiveness, regeneration and no sludge generation. Sources of biomass include seaweeds, microorganisms (bacteria, fungi, yeast, and molds), activated sludge and fermentation waste. Studies using Biosorbents have shown that both living and dead microbial cells are able to uptake metal ions and offer a potentially inexpensive alter-native to conventional absorbents (Khoo and Ting, 2001; Knorr, 1991). However, the living cell is subject to toxic effects of the heavy metals, resulting in cell death. Moreover, living cell often requires the addition of nutrients and hence increase the BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) in the effluent. For these rea-sons, the use of non-living biomaterials or dead cells as metal binding compounds has been gaining advantage because toxic ions do not affect them. In addition, dead require less care and maintenance, and is cheaper (Mofa, 1995). Furthermore, dead biomass could be easily regenerated and reused. The capability of some living microorganisms to accumulate metallic elements has been observed at first from the toxico-logical point of view (Volesky, 1990a,b; Introduction, 1990). However, further researches have revealed that inactive/dead microbial biomass can passively bind metal ions via various physicochemical mechanisms. Research on biosorption has become an active field for the removal of metal ions or or-ganic compounds. Biosorbent behavior for metallic ions is a function of the chemical make-up of the microbial cells of which it consists (Volesky and Holan, 1995). Mechanisms responsible for biosorption, although understood to a limited extent, may be one or a combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and micro precipitation (Veglio and Beolchini, 1997; Vijayaraghavan and Yun, 2008; Wang and Chen, 2006).

1.1 Biosorption

Biosorption is a term that describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution. This implies that the removal mechanism is not metabolically controlled. In contrast, the term bioaccumulation

describes an active process whereby removal of metals requires the metabolic activity of a living organism.

1.2 Biosorbent

Biosorbent is a material obtained from various biological materials. Several biosorption processes carried out using microbial systems such as bacteria, algae, fungi, agricultural wastes such as rice husks and straws, soya bean, sawdust, walnut and cotton seed hull, corn cobs, banana peels.

1.3 Batch biosorption studies

The sorption of heavy metal in wastewater is affected by various parameters, including the solution pH, biomass dosage, temperature, contact time and heavy metal concentration. The effect of pH will be studied under different pH regimes. Similarly effect of dry weight of algal biomass on adsorption will be studied by using different dry weight of biomass. The effect of contact time will be examined by incubation for different periods of time. The rotary shaker is to be used for the agitation of solution at 120 rpm. The supernatant will be collected for the analysis of heavy metal using AAS.

1.4 Electroplating wastewater

Electroplating involves the deposition of a thin protective layer (usually metallic) onto a prepared surface of metal, using electrochemical processes. The process involves pretreatment (cleaning, degreasing, and other preparation steps), plating, rinsing, passivating, and drying. The cleaning and pretreatment stages involve a variety of solvents (often chlorinated hydrocarbons, whose use is discouraged) and surface stripping agents including caustic soda and a range of strong acids, depending on the metal surface to be plated. The use of halogenated hydrocarbons for degreasing is not necessary as water based systems are available. In the plating process, the object to be plated is usually used as the cathode in an electrolytic bath. There are three main types of plating solutions: are acid or alkaline solutions and may contain complexing agents such as cyanides.

1.5 Waste Characteristics

Any or all of the substances used in electroplating (such as acidic solutions, toxic metals, solvents, and cyanides) can be found in the wastewater, either via rinsing of the product or due to spillage and dumping of process baths. The solvents and vapors from hot plating baths result in elevated levels of volatile organic compounds (VOCs) and in some cases, volatile metal compounds (when may contain chromates). Approximately 30 percent of the solvents and degreasing agents used can be released as VOCs when baths are not regenerated. The mixing of cyanide and acidic wastewaters can generate lethal hydrogen cyanide gas and this must be avoided. The overall wastewater stream is typically extremely variable (1 liter to 500 liters per square meter of surface plated) but usually high in heavy metals (including cadmium, chrome, lead, copper, zinc, and nickel), cyanides, fluorides, and oil and grease, all of which are process dependent. Air emissions may contain toxic organics (such as trichloroethylene and trichloroethane). Cleaning or changing of process tanks and the treatment of wastewaters can generate substantial quantities of wet sludge containing high levels of toxic organics and/or metals.

2.LITERATURE REVIEW

Abbas ali a, Mohamed sihabudn m, Zahir hussain a(2016)[1]: Biosorption of heavy metals by pseudomonas bacteria Heavy metals are discharged into the environment through natural and anthropogenic activity, creating serious environment problems. Biosorption is an effective method used for removing heavy metals from environment. In the present study, spirogyra has been examined for biosorption for the removal of heavy metals from ground water. The biosorption capacity was determined from atomic absorption spectroscopy. The bacteria in media supplemented with metals showed higher tolerance and was able to degrade 80% of initial concentration of metals. The ability of Pseudomonas sp. to decrease various metals concentration was examined in both media within 7 days. Maximum degradation of metals was observed in 15th day of incubation. For Pseudomonas sp. ability in degrading of Pb, Cr, Cu, Fe and Mn showed that this bacterium could degrade average of 54% in 7 days and average of 76% in 15 days. The findings prove the capacity of Pseudomonas sp. in Bioremediation of PAHs. The uptake of copper by Pseudomonas sp. was impressive and almost 50% of Pb, Cr, Cu, Fe and Mn were degrading in 7th day. This is probably due to the availability of bacterial species and their cell wall surfaces. The metal sorption tends to reverse the negative charges on bacterial cells and numerous studies have reported that the phosphoryl residues on the outer membrane of bacterial cells are the most likely binding sites for metals for most Gram-negative bacteria. The minimum inhibitory concentration (MIC) of metals (Pb, Cr, Cu, Fe & Mn) in the growth cycle of Pseudomonas sp. was observed to be highly dependent on the composition of culture media and incubation temperature. It was found from the results of this study that metal toxicity and cell growth rate depends on the combination of media composition, substrate concentration, and incubation temperature. The cells might compete with the components in the medium for metals binding sites. In 15th day, Pb, Cr, Cu, Fe and Mn can form more metal complexes and help the cells to grow in higher concentrations compared to that in 7th day. The cells then provide more metal binding sites for and thus show less toxic to metals in 15th day. It was concluded that Pseudomonas sp biosorbed almost 75% of heavy metals in 15 days.

Anamika Kushwah, JK Srivastav et al., (2015)[2]: “Biosorption of Copper Ions by Green Algae spirogyra” The removal of toxic heavy metal ions from waste water is of great importance from an environmental view point. Biosorption is an effective technology, using non-living biomass to remove heavy metals from aqueous solutions. In this paper, the biosorption of

copper ions onto the dead biomass of *Spirogyra*, a green algae, was investigated in batch mode. The results indicated that the biomass of *Spirogyra* sp. is an efficient biosorbent for the removal of Copper ions from aqueous solutions and pH dependent. The maximum removal rate was achieved at a solution of pH of 8.5.

Akbar Esmacili et al., (2015)[3]: “Removal of mercury(II) from aqueous solutions by biosorption on the biomass of *Sargassum glaucescens* and *Gracilaria corticata*” The objective of this research is to study the batch removal of Hg^{2+} from aqueous solution, and wastewater using marine dried red algae *G. corticata* (red algae) and *S. glaucescens* (brown algae). Marine alga was used as a low-cost absorbent. The effects of pH, biosorption time and the concentration of the Hg^{2+} solution were examined in the adsorption process with *S. glaucescens* and *G. corticata*. Results showed that when we used *S. glaucescens* as the biosorbent, optimum conditions of pH, Hg^{2+} concentration and equilibrium time were at 5, 200 ppb and 90 min, and when *G. corticata* was used, these conditions were at 7, 1000 ppb and 30 min. The equilibrium adsorption data are fitted to the Freundlich isotherm model, by both *S. glaucescens* and *G. corticata*. The Hg^{2+} uptake by *S. glaucescens* was best described by the first-order rate model and *G. corticata* was best described by the second-order model.

Ali A. Al-Homaidan et al., (2015)[4]: “Biosorption of copper ions from aqueous solutions by *Spirulina platensis* biomass” In this study, the economically important micro-alga (cyanobacterium) *Spirulina platensis* was used as biosorbent for the removal of copper from aqueous solutions. The cyanobacterium was exposed to various concentrations of copper and adsorption of copper by the biomass was evaluated under different conditions that included pH, contact time, temperature, concentration of adsorbate and the concentration of dry biomass. Increased adsorption of copper by the non-living biomass was recorded with gradually increasing pH, and a maximal uptake by the biomass was observed at pH 7. The adsorption of copper was found to increase gradually along with decrease in biomass concentration. Biosorption was found to be at a maximum (90.6%), in a solution containing 100 mg copper/L, at pH 7, with 0.050 g dry biomass and at 37°C with 90 min of contact time. Analysis of the spectrum obtained with atomic absorption spectrophotometer (AAS), indicated that the adsorbent has a great potential to remove copper from aqueous media contributing to an eco-friendly technology for efficient bioremediation in the natural environment.

S Kanchana et al., (2014)[5]: “Biosorption of heavy metals: A Review” Various algal species can be used for removing heavy metals like Cd, Cu, Ni, Pb, and Zn from aqueous solutions successfully. Biological removal of metals is possible by both living and non living algal biomass. Algal biosorption is dependent on various parameters such as pH, biomass concentration, temperature, contact time and initial concentration of metal ion in the solution. The potential metal binding groups present on the cell surface of the algal species are carboxylate, amine, imidazole, phosphate, sulfhydryl, sulphate and hydroxyl. Algae found in large quantities in sea as well as in fresh waters serve as basis for newly developed metal biosorption process, as a very competitive means for the detoxification of metal bearing industrial effluents. Higher uptake capacity has been found for brown algae than for red and green algae. In the batch studies, *Sargassum* seaweed has been found to biosorb chromium. pH had an important effect of the biosorption capacity. Biosorbent size did not affect the biosorption capacity and rate. Cadmium and copper uptake by six different *Sargassum* species was studied by Davis et al. (2003). Maximum biosorptive capacities were found to be 0.9 m.mol/g for *Sargassum* sp. 0.89 for *S. filipendula*, 0.93 for *S. vulgare* and 0.8 for *S. fluitans*. Cu uptake by *Ascophyllum nodosum* showed a q_{max} of 0.037 m.mol/g.

Khalid M. El-Moselhy et al., (2014)[6]: “Removal of cadmium from aqueous solution using marine green algae, *Ulva lactuca*” The present study aimed to evaluate the efficiency of marine algae for removal of metals from the aqueous solution. The green alga, *Ulva lactuca*, collected from the intertidal zone of the Suez Bay, northern part of the Red Sea was used to reduce cadmium levels from the aqueous solutions. The biosorption mechanisms of Cd^{2+} ions onto the algal tissues were examined using various analytical techniques: Fourier-transform infrared spectroscopy (FT-IR) and Scanning electron microscopy (SEM). Results indicated that at the optimum pH value of 5.5; about 0.1 g of *U. lactuca* was enough to remove 99.2% of 10 mg L^{-1} Cd^{2+} at 30°C in the aqueous solutions. The equilibrium data were well fitted with the Langmuir and Freundlich isotherms. The monolayer adsorption capacity was 29.1 mg g^{-1} . The calculated RL and ‘n’ values have proved the favorability of cadmium adsorption onto *U. lactuca*. The desorption test revealed that HCl was the best for the elution of metals from the tested alga. In conclusion, the seaweed *U. lactuca* was the favorable alternative of cadmium removal from water.

R.Santhi et al., (2014)[7]: “Biosorption of Hexavalent Chromium Using *Aspergillus niger* dead biomass and its optimization studies” The use of fungal biomass as a biosorbent for the removal of toxic and heavy metal ions from different industrial effluents has received much attention in the recent years. In the present study dried biomass of the fungal strain *Aspergillus niger* MTCC 281 was exploited as a biosorbent for the removal of hexavalent chromium ions Cr^{6+} . The metal tolerance ability (Ti) and the Minimum Inhibitory Concentration (MIC) of the test strain *Aspergillus niger* were determined by amending different concentrations of Cr^{6+} ions in the potato dextrose agar medium. From the present study, pH 3 was found to be optimum for the fungal biosorption of Cr (VI) with biosorption of 67.5%. Maximum biosorption of 70.28% was observed at a temperature of 27°C and 71.94% with an incubation period of 24 hours. Experimental results also showed maximum biosorption percentage of 75.36% and 72.2% for a biomass concentration of 3 mg/ml and metal concentration of 1 mg/ml respectively. The findings of the present study revealed that fungi from metal polluted sites could show higher metal tolerance and biosorption efficiency and hence could be exploited for heavy metal biosorption.

Xiu-Feng Yan et al., (2014)[8]: “Equilibrium and Kinetic Studies of Cd^{2+} Biosorption by the Brown Algae *Sargassum fusiforme*” A fundamental investigation of the biosorption of Cd^{2+} from aqueous solution by the edible seaweed

Sargassum fusiforme was performed under batch conditions. The influences of experimental parameters, such as the initial pH, sorption time, temperature, and initial Cd²⁺ concentration, on Cd²⁺ uptake by *S. fusiforme* were evaluated. The results indicated that the biosorption of Cd²⁺ depended on the initial Cd²⁺ concentration, as well as the pH. The uptake of Cd²⁺ could be described by the Langmuir isotherm model, and both the Langmuir biosorption equilibrium constant and the maximum biosorption capacity of the monolayer decreased with increasing temperature, thereby confirming the exothermic character of the sorption process. The biosorption kinetics follows the pseudo-second-order kinetic model, and intraparticle diffusion is the sole rate-limiting step for the entire biosorption period. These fundamental equilibrium and kinetic results can support further studies to the removal of cadmium from *S. fusiforme* harvested from cadmium-polluted waters.

3. EXPERIMENTAL STUDIES :

3.1. MATERIALS

All the laboratory grades chemical were used for analysis. The fresh water algae was purchased from Auroville Spirulina farm, Auroville, Vellore and seaweed was collected from Oceanography Department, Alagappa university, Thondi. The electroplating wastewater is collected from workshop of southern railways, Trichy, India and preserved at 18 °C until used.

3.2. EXPERIMENTAL METHODS

A biosorption process can be performed via several modes; of which, batch and continuous modes of operation are frequently employed to conduct laboratory scale biosorption processes. Although most industrial applications prefer a continuous mode of operation, batch experiments have to be used to evaluate the required fundamental information, such as biosorbent efficiency, optimum experimental conditions, biosorption rate and possibility of biomass regeneration, batch system shown in fig

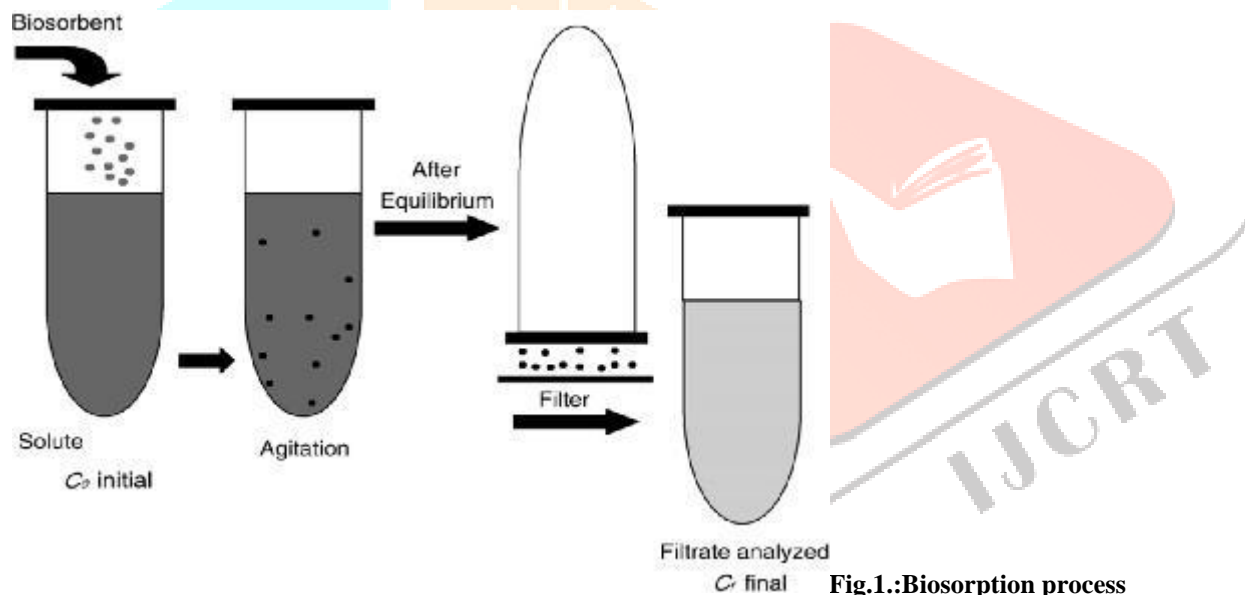


Fig.1.:Biosorption process

3.3 EQUILIBRIUM ISOTHERMS

The biosorption equilibrium uptake capacity for each sample will be calculated according to mass balance on the ions expressed in the equation:

$$q_e = \frac{c_0 - c_e}{M} \times V$$

Where V – sample volume (L); C₀- initial ion concentration (mg/L)

C_e- equilibrium or final ion concentration (mg/L)

M – Biomass dry weight (g)

q_e – biomass biosorption equilibrium ions uptake capacity (mg/g)

Langumir and Freundlich isotherms, the two classical adsorption models, will be used to describe the equilibrium between adsorbed ions on the biomass cell and ions in the solution in the study.

3.3.1 Freundlich Isotherm

The empirical Freundlich equation based on sorption on a heterogeneous surface, is as follows:

$$q_e = k_f (c_e)^n$$

The equation can be linearized in the following logarithmic form:

$$\ln q_e = \ln k_f + \left(\frac{1}{n}\right) \ln c_e$$

These values n and k_f can be obtained from the slopes and the intercept of the linear plots respectively, where experimental data of $\ln q_e$ as the function of $\ln C_e$.

3.3.2 Langmuir Isotherm

$$q_e = \frac{q_{max} C_e b}{1 + C_e b}$$

Then after arrangement we have

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max} b} \right) + \left(\frac{C_e}{q_{max}} \right)$$

These values q_{max} and b (where b , is the adsorption equilibrium constant) can be obtained from the slopes and the intercepts of the linear plots respectively, where experimental data of C_e/q_e as the function of C_e .

3.5 INITIAL CHARACTERISTICS OF WASTE WATER

The following tables shows the initial characteristics of electroplating waste water

TABLE 1(a): Characteristics of the wastewater used for this study

SL.NO	PARAMETERS	OBTAINED VALUE
1	pH	4.35
2	TSS	277mg/l
3	TDS	138500mg/l
4	OIL & GREASE	5 mg/l
5	CHLORIDES	160 mg/l
6	SULPHATE	6680 mg/l

TABLE 1 (b): list of heavy metals present in waste water

SL.NO	HEAVY METALS	QUANTITY (mg/l)
1	HEXAVALENT CHROMIUM	1967

2	COPPER	2.5
3	NICKEL	0.21
4	ZINC	1.7

The removal of chromium was concentrated mainly on this study because the other metal ion concentration was less and nearly to the permissible limit.

4.RESULT AND DISCUSSION

4.1 EFFECT OF pH

Results on the effect of pH of Cr concentration by spirullina and seaweed are shown in fig 2(a) and 2(b). Maximum percentage of biosorption obtained at the time of 120 min at pH 6 for spirullina and at pH 10 for seaweed was 64.33% and 72.83%. The biosorbent dosage was fixed as 2 g/100ml.

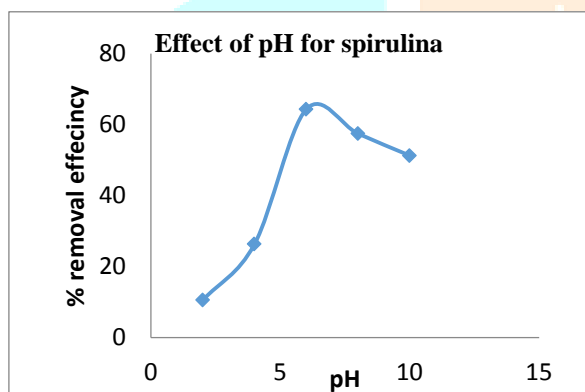


Fig 2 (a) Effect of pH for spirulina

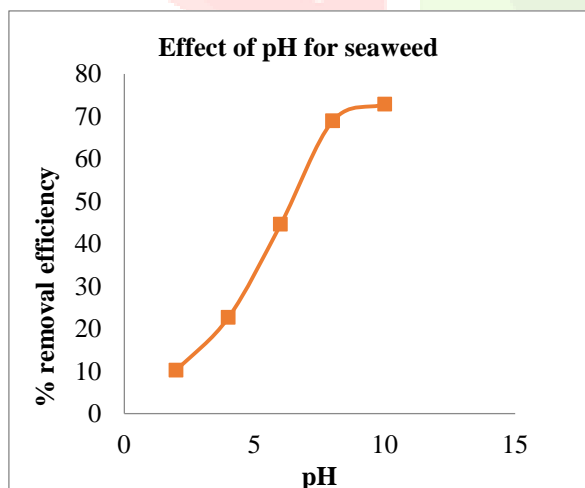


Fig 2(b) effect of pH for seaweed

4.2 EFFECT OF CONTACT TIME

Results on the effect of contact time of Cr concentration by spirullina and seaweed are shown in fig 3(a) and 3(b). Maximum percentage of biosorption obtained at the time of 120 min at pH 6 for spirullina and at pH 10 for seaweed was 64.24% and 74.66%. The biosorbent dosage was fixed as 2 g/100ml.

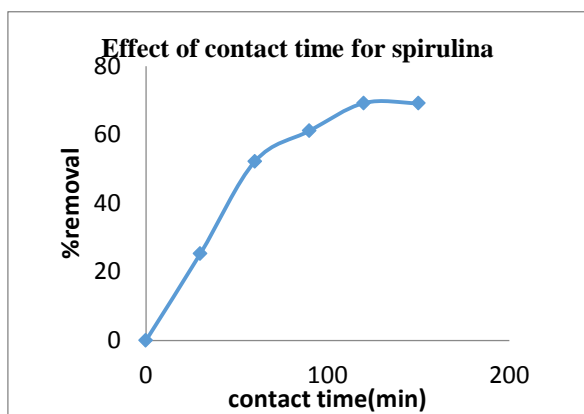


Fig 3(a) Effect of contact time for Spirulina

4.3 EFFECT OF ADSORBENT DOSAGE

Results on the effect of contact time of Cr concentration by spirulina and seaweed are shown in fig 4(a) and 4(b). Maximum percentage of biosorption obtained at the time of 120 min at pH 6 for spirulina and at pH 10 for seaweed was 80.78% and 85.47%. The biosorbent dosage was raised from 2 g/100ml to 20 g/100ml.

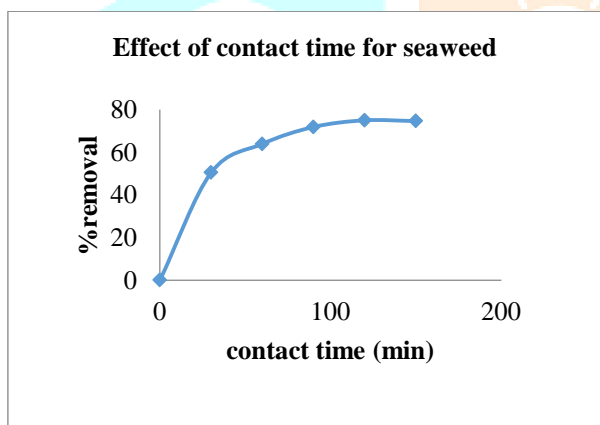


Fig 3(b) Effect of contact time for seaweed

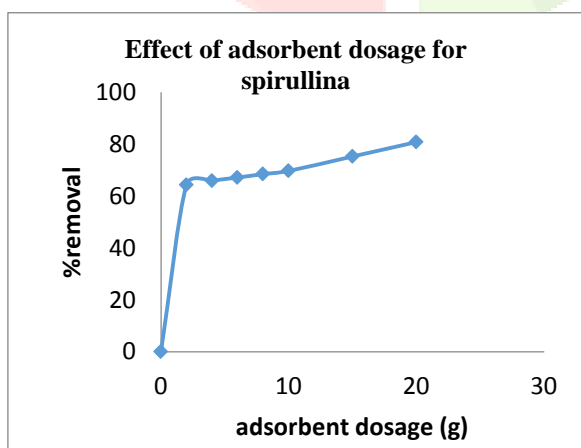


Fig 4 (a) Effect of adsorbent dosage for Spirulina

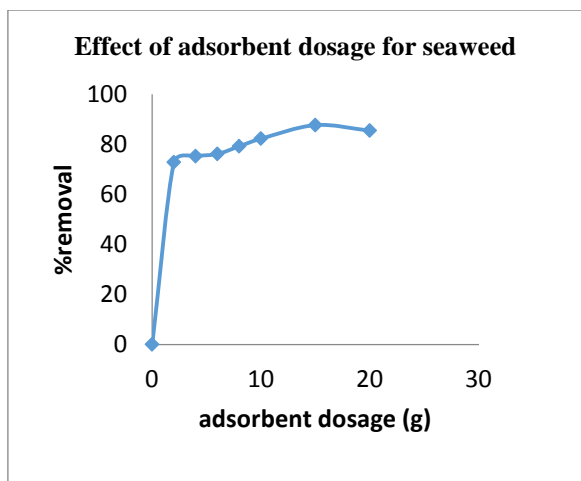


Fig 4(b) Effect of adsorbent dosage for seaweed

4.4 EQUILIBRIUM ISOTHERM

The equilibrium experimental results of chromium ions have been fitted in the Langmuir and Freundlich models. For biosorption of chromium using Spirulina and seaweed the coefficient of determination (R^2) of both models was mostly close to 1 as shown in Fig. 5(a), 5(b), 5(c), 5(d).

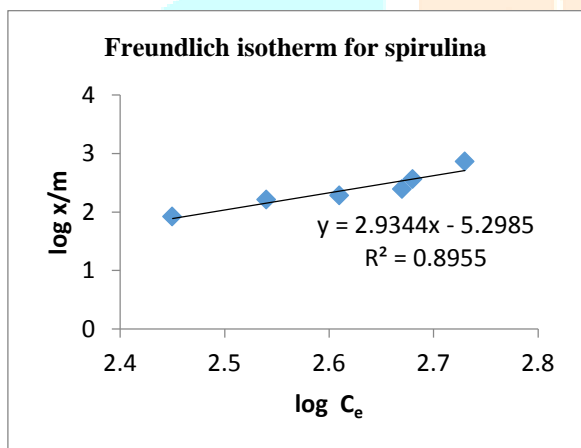


Fig 5(a) Freundlich isotherm for spirulina

This indicates that both models adequately describe the experimental data of the biosorption of chromium. In the biosorption of chromium by Spirulina sp., most of the metal ions were sequestered very fast from the solutions in the first phase of contact time of 120 min and almost no increase in the level of bound metal having occurred after this time interval.

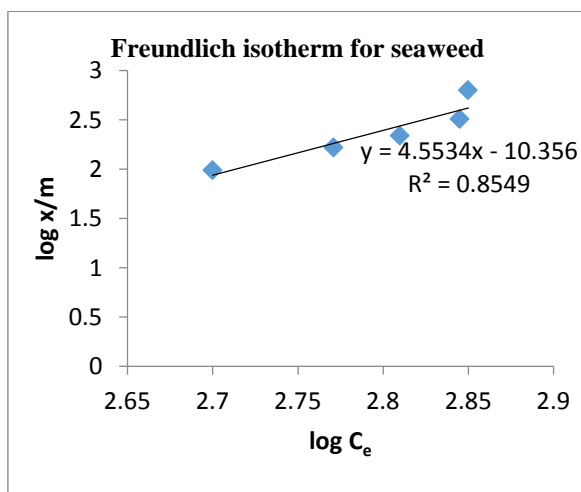


Fig 5(b) Freundlich isotherm for seaweed

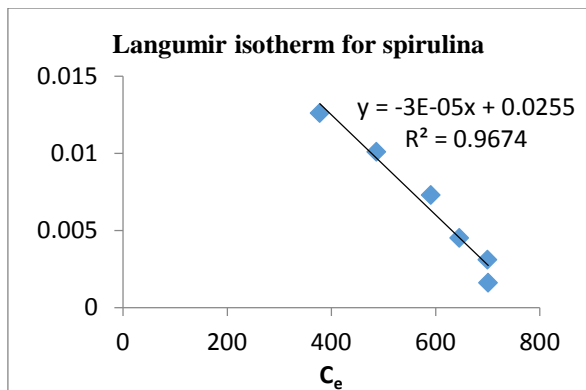


Fig 5 (c) Langumir isotherm for spirulina

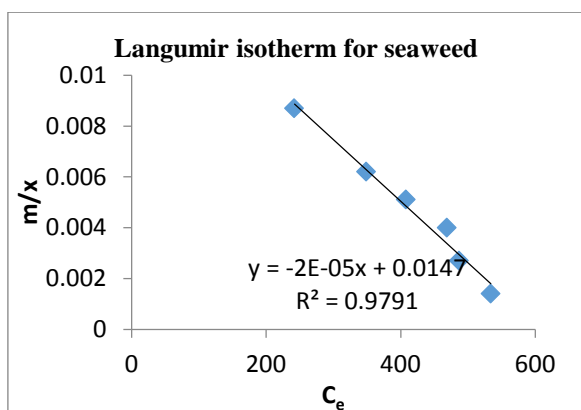


Fig 5(d) Langumir isotherm for seaweed

5. SUMMARY AND CONCLUSION

The influence of various experimental parameters such as pH, contact time and adsorption dosage on the removal of pollutants from electroplating wastewater was studied. The results of this study have shown the applicability of biosorption in the treatment of electroplating wastewater. The biosorption process is feasible and economical.

According to the obtained results, the following can be concluded: The removal of chromium using the biosorbents such as dry biomass of Spirulina and seaweed was gained the removal efficiency up to 80.78% and 85.47% respectively. The biosorption process followed both the Langmuir and Freundlich isotherm models but the Langmuir isotherm model was better than the Freundlich with $R^2 = 0.969$ for Spirulina and $R^2 = 0.979$ for seaweed.

6. REFERENCE

- [1] Abbas ali a, Mohamed sihabudn m, Zahir hussain a(2016): 'Biosorption of heavy metals by pseudomonas bacteria' *International Research Journal of Engineering and Technology* 08 (2016) 1446-1450
- [2] Ali A. Al-Homaidan et al.,(2015): 'Biosorption of copper ions from aqueous solutions by Spirulina platensis biomass' *Saudi Journal of Biological Sciences* 22 (2015) 795-800
- [3] Anamika Kushwah, JK Srivastav (2015): 'Biosorption of Copper Ions by Green Algae spirogyra' *International Journal of Chemical Studies* 3 (3) (2015) 36-38
- [4] Fadel M, Naziha M. Hassanien, Maha M. Elshafei (2014), 'Biosorption of manganese from groundwater by biomass of Saccharomyces cerevisiae' *Housing and Building National Research Journal* 13 (2014) 106-113
- [5] Hassan Rezaei (2013): 'Biosorption of chromium by using Spirulina sp' *Arabian Journal of Chemistry* 9 (2013) 846-853
- [6] Kanchana S, Jeyanthi J, Kathiravan R, Suganya K(2014): 'Biosorption of heavy metals: A Review' *International Journal of Pharma Medicine and Biological Sciences* 3 (2014) 9

- [7] **Khalid M. El-Moselhy (2014):** 'Removal of cadmium from aqueous solution using marine green algae, *Ulva lactuca*' *Egyptian Journal of Aquatic Research* (2014) 40, 235–242
- [8] **Sabreen alfarra R, Eman Ali N, Mashita Mohd Yusoff (2014),** 'Removal of heavy metals by natural adsorbent: review' *International Journal of Biosciences* 4 (2014) 130-139
- [9] **Santhi R, Guru V (2014) :**'Biosorption of Hexavalent Chromium Using *Aspergillus niger* dead biomass and its optimization studies' *International Journal of Current Microbiology and Applied Sciences* 3(10) (2014) 669-678
- [10] **Xiu-Feng Yan et al.,(2014):**'Equilibrium and Kinetic Studies of Cd²⁺ Biosorption by the Brown Algae *Sargassum fusiforme*' *Plos One* 9 (4)
- [11] **Zacharia Kariuki, Jackson Kiptoo, Douglas Onyancha (2016),** 'Biosorption studies of lead and copper using rogers mushroom biomass *Lepiota hystrix*' *South African Journal of Chemical Engineering* 23 (2017) 6

