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OPTIMIZATION OF PROCESS PARAMETERS FOR THE REMOVAL OF COPPER METAL USING BROWN ALGA PADINA *GYMNOSPORA*

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ABSTRACT

The biosorption of copper on Padina gymnospora was investigated in a batch system. The relationship between the response and the independent variables was developed via the quadratic approximating function of copper sorption capacity of sorbent. From this study, it can be concluded that the copper can be removed by using a brown alga P.gymnospora which is abundant and cheaply available alga. Dry biomass of P.gymnospora proves to be cost effective and efficient to eliminate heavy metal especially copper for aquatic effluents and the process is feasible, reliable and eco-friendly. This brown alga can be recommended for the removal of copper from industrial effluents.

Keywords: Padina gymnospora, copper metal, biosorption.

1. INTRODUCTION

Heavy metal pollution has become one of the most serious environmental problems in the recent years. Presence of heavy metals even in traces is toxic and detrimental to both flora and fauna. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in the living tissues, thus becoming concentrated throughout the food chain. The expanding technological activities have especially accelerated the addition of numerous poisonous metal pollutants to the environment resulting in their immobilization and accumulation in various microbial ecosystem and even threatening human life [25]. The major source of metals into the environment is through discharges from industries such as allow, pigments, tannery, fertilizers, pesticides, pharmaceuticals, chemical etc. Heavy metals modify the structure and productivity of aquatic ecosystem. Though heavy metals are essentially needed by living organisms for various metabolic process [26], their excess concentration showed lethal effect. The physiological as well as toxicological effects imparted by metal irons are considered to be biological continum, since algae are considered to be basic in food chain as a primary producer.

Bio accumulation is defined as the transport of pollutants (organic and inorganic) cellular interior [1]. The mechanism of heavy metal ions binding and toxic effect caused by them differ between microbial species and heavy metal ions [11]. Also, chemical nature of pollutants has the fundamental effect on the bioaccumulation process. Water sediments and the biota are generally metal reservoirs in aquatic environments [15].

The heavy metals such as cadmium, arsenic bismuth, copper, zinc, chromium, cobalt, selenium, etc., contaminate the environment. Environmental pollution due to Cu arises from industrial and agricultural emissions. Even though the literature present papers using algal cells [16] and other biomaterials [12,17], little is known about the behaviour of a continuous system for this kind of treatment. The purpose of the present work was to investigate the behaviour of continuous serial reactors for the uptake of copper. The brown seaweed, *Padina gymospora* is made up of polysaccharide alginate, usually calcium and sodium with a high potential for the accumulation of heavy metals, as compared to other algae [2]. The polysaccharides are produced due to the interaction between alginic acid and alkaline and alkaline-earth elements from seawater. The present work is aimed to remove the copper from industrial waste waters by using marine macro algae, *P.gymnospora* utilizing biosorption techniques. Copper is one of the frequently used metals in the production of steel. High concentration of copper has been observed in waste water of pharmaceuticals, galvanizing, paints, etc. Traditional methods such

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as chemical precipitation, evaporation etc, are most suitable in situations where the concentrations of the heavy metal ions are relatively high. They are either in effective on expensive when heavy metals are present in waste water at low concentrations. Biological approaches especially application of sorbents have been suggested in the last decade. Marine algae have been found to be potential suitable sorbents became of their cheap availability, relatively high surface algae and high binding affinity. The use of marine algae for heavy metal removal has been reported by Umamaheswari and Rajasulochana [23].

2. MATERIAL AND METHODS

The brown alga *Padina gymnospora* was collected from post monsoon season (2019) Pudumadam coast (lat. 9°45'N; long. 79°15'E) during low tide, handpicked and washed thoroughly with seawater to remove adhering sand particles, etc. The washing process was continued till the wash water contain nodirt. The metal salt $CuS0_4.5H_20$ used as stock solution was suitably dissolved in distilled water to obtain the working concentrations (10-200 mg/l) of the metals. The pH of the solution is not adjusted but measured. This solution is used for metal biosorption experiments. Concentrations of standard and process solutions are evaluated by atomic absorption spectometry (Perkin-Elmer, model analyst 300). Then the samples were shade-dried for 10 days and completely bleached. Further oven-dried at 60°C for 24 h [2] the dried alga was coupled into small pieces and was powdered using domestic mixer. In the present study, the powdered materials in the range of 500-700 particle size then directly used as sorbents without any pretreatment is used for the kinetic study.

Batch experiments were carried out with and without agitation in different initial concentrations (10, 25, 60, 100, 200 mg/l) of copper (II) solution. 100 ml of each of the solution with 1 g of P.gymnospora biomass without adjusting pH was placed in 250 ml stoppered conical flask, equilibrated for 6 h and after the lapse of this period, the solutions were analyzed to establish the amount of Cu(ll) removed. The experiments with agitation in a mechanical shaker of a constant speed of 50 rpm, were carried out at room temperature (25°C).

3. RESULTS AND DISCUSSION

Batch studies without shaking indicate that at low concentrations of 10 mg/l, removal upto 87% was achieved with 1 g of alga for 100 ml of the copper solution, whereas with shaking upto 93.5% removal was achieved. In batch studies with and without shaking the linearized Freundlich and Langmuir sorption isotherms of copper (ii) ions and constants from the isotherms were evaluated (Tables 1-6).

Table -1
The linearized Freundilich adsorption Isotherms for Cu(ii) ion

Log C_{eq}	Log q_{eq}
0.1146	-0.0610
0.9980	0.1772
1.4651	0.3191
1.8210	0.5290
2.1802	0.6865

Table -2
The linearized Freundilich adsorption Isotherms for Cu(ii) ion

$1/C_{eq}$	$1/q_{eq}$
10.768	0.151
0.100	0.665
0.034	0.479
0.15	0.295
0.006	0.206

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Table -3
Freundlich and Langmuir adsorption constants obtained from the Freundlich and Langmuir adsorption isotherms of copper.

Metal	Freundlich Constants		Langmuir constants	
	K	N	Qmx (mg/g)	b
Copper	0.8	2.8	5	0.0938

Table -4
The linearlized Freundlich adsorption Isotherms for Cu (I) ions

Log C_{eq}	Logq_{eq}
-0.1911	-0.028
0.6996	0.3008
1.0734	0.5816
1.5810	0.7915
2.0458	0.948

Table -5
The linearlized Freundlich Langmuir adsorption isotherms for Cu(II) ions

1/C_{eq}	1/q_{eq}
1.553	1.068
0.199	0.503
0.084	0.262
0.026	0.162
0.009	0.113

Table -6
Freundlich and Langmuir adoption constant obtained from the Freundlich and Langmuir adsorption isotherms of copper

Metal Ion	Freundlich Constants		Langmuir Constants	
	K	**N**	**Qmx(mg/g)**	**b**
Copper	1.288	2.309	9.09	0.0573

The Freundlich constants, K and n, showed easy uptake of copper from copper solution. The Langmuir and Freundlich (1918) sorption models, for batch studies with and without shaking, with the sorption parameters, obtained specific for Cu(II) *P.gymnospora* was represented as equation.

Without shaking : (Table-; 1-3)

$$q_2 = \frac{0.469C_e}{1+0.0938C_e}$$

$$q_2 = 0.8C_e^{1/2.8}$$

where

q_e - amount of adsorption at equilibrium (mg/g)

C_e- equilibrium concentration of solution (mg/l).

The essential features of a Langmuir isotherm constant 'b' can be expressed in terms of a dimensions constant separation factor or equilibrium parameters R_L, which is defined as:

$$R_L = 1/(1+bc_o)$$

where :

C_o - Initial metal concentration (mg/l)

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b - Langmuir constant

R_L - Values obtained (0.0506 - 0.5159) were between 0 and 1, which indicate "favourable isotherm shape" for Cu(II) *P.gymnospora* biomass system in the concentration range studied.

With shaking : (Tables 4-6)

$$q_e = \frac{0.5209C_e}{1+0.0573C_e}$$

$$q_e = 1.288C_e^{(1/2.309)}$$

$$R_L = 1/(1+bc_0)$$

R_L - Values obtained (0.0803 - 0.6357) were between 0 and 1, which indicate "favourable isotherm shape: for Cu(II) *P.gymnospora* biomass system in the concentration range studied. It is concluded that biosorption with agitation is the effective removal of copper and sorption isotherm follow Langmuir and Freundlich equation.

Literature reports that microalgae ae more efficient in heavy metal ions binding than bacteria or fungi. Probably because the process carried out by living microalgae is associated with metablic activity and photosynthesis [3,6,7,8,9]. Microalgae possess high tolerance towards elevated concentration of heavy metal ions. In the presence of these ions, over-expression of specific metal-binding peptides and proteins (i.e. phytochelatins) occurs, that results from their physiological adaptation, since these organisms frequently live in salty environment [14,24,28].

The majority of studies on bioaccumulation of heavy metal ions by microalgae (similarly as the majority of works on bioaccumulation itself) report only the final concentration of metal ions. However, only few works provide quantitative kinetric description of the process and investigate its mechanism. The majority of works only report the quantity of metal ions bounded by the biomass without quantitative equilibrium and kinetic data, and cocnern mainly the following microalgal strains: *Chlorella vulgaris* [1], *Chlamydomonas reinhardil* [10] as the model algae [6]. Bioaccumulation of Cr(III) ions by Blue green alga *Spirulina* sp. Part II Methematical Modelling was reported by Katarzyna Chojnacka and Piotr M. Wojciechowski [5].

There are only few models describing bioaccumulation in the literature. The most thoroughly documented was the model elaborated by Prince and Ting [13,20,21,22] that assumed two steps of bioaccumulation process: 1) preliminary, quick binding of metal ions to cellular wall; 2) slower transport through cellular membrane. The suitability of this model was confirmed for the following stains of unicellular algae: *Chlorella pyrenoidosa*, *Chlorella vulgaris* and *Chlamydomonas reinhardti*.

In the first stage, metal ions present in the solution, are reversibly bound with the free surface of the biomass. The equilibrium between the concentration of metal ions in the solution at the surface of a cell C_{Me} and the concentration of metal adsorbed on its surface c_{pas} can be described with Langmuir equation.

$$q = \frac{q_{\max}.C_{Me}}{1+b.C_{Me}}$$

for low concentration of metal ions, the above equation can be simplified to the following linear dependence:

$$C_{Me} = a.C_{pas}$$

where a is dimensionless adsorption coefficient and C_{pas} is the concentration of Cu ions adsorbed on the surface on the biomass

Algae are potential indicators of environmental conditions. This is supported by the fact that there exist highly significant correlations between the concentrations of some metals in algae and in water. This is in line with the study carried out by Whitton et al., [27] using Cladophora glomeratea. From the mean metal concentraiton for zinc, iron, copper, cadmium and aluminum calculated, the four different algae used in this study showed different absorption potentials for each metal. Jain et al., [4] reported similar result using duckweed and water velvet. Markina and Aizdaicher [15] using 0.13 and 0.25mg /1 of copper on Phaedactylum lricornutum (Bacillariophyta) found an inhibitory effect of copper on growth parameter was greater with increased concentration of copper in the medium.

Various studies have been carried out to show the role of algae in the bioremediation of heavy metals. Some metals such as Cu, Pb, Cd, Co are removed by Cladohpora glomerata and by Oedognium rivulare as short term uptake and others such as Ni, Cr, Fe, Mn as continuous uptake (Vymazal, 1984). Studies a heavy metal

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removed by immobilized cells of chlorella vulgiris Buyerinck was made by Umamaheswari and Rajasulochana [23].

4. ADSORPTION ISOTHERM STUDY

Adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by coal fly ash. Adsorption isotherm is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of absorbable solute between the liquid and solid phases at various equilibrium concentrations.

Adsorption from aqueous solution at equilibrium is usually described by the Langmuir isotherm, Freundlich isotherm or BET isotherm. In the present study, the results obtained from batch adsorption experiments were fitted to Langmuir, Freundlich and BET adsorption isotherms using lest square fit method. Adsorption isotherm equations include constants which indicate the surface properties and affinity of the absorbent are usually described by the Langmuir isotherm [13], Freundlich isotherm or BET isotherm as indicated by Eq (1), Eq (2) and Eq (3) respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a . q_m} \quad (1)$$

where, C_e is equilibrium concentration of Ni^{+2} ions ($mg.L^{-1}$), q_e is solid phase concentration of Ni^{+2} ions ($mg.g^{-1}$), q_m ($mg.g^{-1}$), and K_a ($L.mg^{-1}$) are empirical constants, can be evaluated from the slope and intercept of the linear plot of C_e/q_e against C_e.

The standard model of Freundlich Equation (Freundlich, 1906) used is represented below:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

where, K_f is the Freundlich characteristic constant [$(mg.g^{-1})(L.g^{-1})^{1/n}$] and 1/n is the heterogeneity factor of sorption, obtained from intercept and slope of In q_e versus In C_e linear plot respectively.

The BET isotherm model [3] in the linear form as used is represented as

$$\frac{C_e}{q_e (C_S - C_e)} = \frac{1}{q_s C_{BET}} + \frac{(C_{BET} - 1)}{q_s C_{BET}} \left(\frac{C_e}{C_S} \right) \quad (3)$$

Where

C_e = equilibrium concentration (mg/l)

C_s = adsorbate monolayer saturation concentration (mg/l)

C_{BET} = BET adsorption isotherm relating to the energy of surface interaction (l/mg)

The resists obtained in batch adsorption experiment were fitted to Langmuir adsorption isotherm, Freundlich adsorption isotherrnjand BET adsorption isotherm.

Since many water bodies are used for effluents discharge, some of which contain these toxic heavy metals, the algae used for this study are native to his water bodies and were subjective to the most occurring five heavy metals usually present in polluted water bodies. Additionally, algae are first link in the aquatic environments food chain and as such any effect on them has ripple effects on subsequent members of the food chain or trophic levels. The specific objectives of this study are to determined a metal concentrations in the algae and their surrounding water.

The results obtained in these studies reveal the potential of applying *P.gymnospora* in bioremediation of waste waters containing heavy metals. Batch studies with agitation indicate that 93% removal of copper at concentration 10 mg/l was higher when compared to without agitation. Equilibrium studies indicate that, the maximum uptake of metal is 8.9 mg/g at 200 mg/l of metal concentration with agitation. The equilibrium of the process was fitted into the well known adsorption models, Freundlich & Langmuir and equilibrium for the metals are found to be best described by both the models.

5. CONCLUSION

Generally an algorithm of artificial neural network can be applied in forecasting evolution of concentration of metal ions in the system during the process, separately from the description of reaction kinetics itself. This type of methods can be applied in interpolation, but frequently it fails in the case of extrapolation.

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Kinetic model however makes it possible to analyze various aspects of the course of bioaccumulation and can be easily interpreted through the assessment of physical nature of all the constants. Finally, reaction rate constants, determined in the model might be used to quantitatively assess the applicability of *Padina sp.* for the application in bioaccumulation of Cu ions and modelling that would finally lead to commercial applications.

The development of microbial metal recovery systems, depend on many factors including capacity, efficiency and selectivity at the case of recovery, equivalence to existing physical and chemical treatments in the performance, economics and immunity from interference by other effluent components or operating conditions. Further studies on the recovery of metals from the algal biomass by employing improved methods will be useful for extending the use of this laboratory level experiment with Padina gymnospora to large scale and field level removal systems.

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