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Batch Removal Of Heavy Metals By Biosorption Onto Marine Algae-Equilibrium And Kinetic Studies

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Abstract: Water pollution owing to the release of heavy metals from industries has become a major issue throughout the world. Cadmium (Cd) is one of the heavy metals found in the wastewater discharges from the electroplating industries, manufacture of nickel-cadmium batteries, fertilizers, pesticides, pigments and dyes and textile operations. Several toxic but nonfatal symptoms are reported in the cadmium concentration range of 10-326mg/lit Cd^{2+}. The disorders caused by cadmium on human beings are renal dysfunction and hypertension. This paper deals with the experimental investigation on removal of cadmium [Cd(II)] ions from an aqueous solution using marine algae, *Sargassum tenerrimmum,* in batch condition. The influence of pH, agitation rate, sorbent dosage and initial metal ion concentration on the metal uptake by the pre treated algal biomass was studied. It was seen that there is no considerable difference in metal uptake in the pH range 4-6. The maximum value of the adsorption capacity is obtained at the speed of 150 rpm. Sorbent dosage study showed that increasing the adsorbent concentration up to 4 g/l resulted in rapid increase in the percentage of cadmium uptake (0-80%). The equilibrium data on cadmium uptake was found to fit the isotherm models, namely Langmuir, Sips and Redlich-Peterson isotherms with reasonable accuracy. Kinetic studies were also carried out using pseudo-first order equation, pseudo-second order equation and Elovich equation and it was found that Elovich equation gave the best fit (R^2=0.9891).
Keywords: Biosorption, Cadmium, *Sargassum tenerrimmum.*

Introduction

Water, the main source of life on the planet and due to the influence of advanced technologies, water is being polluted. Water pollution owing to the release of heavy metals from industries has become a major issue throughout the world. If these discharges are emitted without treatment, they may have an adverse effect on the environment. One of the main goals in heavy metal removal from wastewater is the reduction of these pollutants to a minimum possible level. Cadmium is one of the heavy metals found in the wastewater discharges from the electroplating industries, the manufacture of nickel-cadmium batteries, fertilizers, pesticides, pigments and dyes and textile operations. Several toxic but nonfatal symptoms are reported in the cadmium concentration range of 10-326mg Cd^{2+}/l. The disorders caused by cadmium on human beings are renal dysfunction and hypertension. Conventional methods are not useful when metals are present in the concentration range of 1-100mg. The application of microorganisms as biosorbents for the removal of heavy metals offers a potential alternative to

the existing methods. In the present investigation a marine algae, *Sargassum tenerrimum* has been used as the biosorbent for the sorption process of cadmium from aqueous solution. The investigation includes batch equilibrium studies to determine the optimum working conditions in terms of pH and the sorption capacity of the algae. In addition, the present study employed an up-flow packed column to investigate cadmium removal as a function of bed height and flow rate.

Materials And Methods

Preparation of Biosorbent and Chemicals

The raw biomass of the marine alga, *Sargassum tenerrimum*, was harvested from the coasts in Mandapam (Tamilnadu, India) and then sun-dried. It was then grounded to particles of size fraction 200 - 1180 µm. The sieved biomass was soaked in 0.1 M HCl for 4 h in order to protonate it. After washing in distilled water the algal matter was dried at 60º C overnight. A weight loss of approximately 15% was observed. All chemicals including $Cd(NO_3)_2$ purchased from Sd fine chemicals Ltd. (India) were of analytical grade. The $Cd(NO_3)_2$ stock solution was diluted with distilled water to specified concentrations. In the sorption equilibrium experiments, a borate buffer solution prepared by dissolving HNO_3 and NH_4OH was used to maintain the pH. The analysis for residual cadmium concentration was accomplished by atomic absorption spectrophotometer[1]. The amount of cadmium adsorbed by algae was calculated from the differences between the amount added to the biomass and the cadmium content after adsorption using the following equation:

$$Q = \frac{V(C_o - C_f)}{M}$$

(1)

where Q is the cadmium uptake (mg/g), C_0 and C_f are the initial and final cadmium concentrations in the solution respectively (mg/l), V, the solution volume (l) and M is the mass of biosorbent (g).

Experimental

Preliminary experiments

Adsorption of metal ions onto biosorbents greatly depends on the particle size and dosage of sorbents. To study the effect of the particle size on Cd^{2+} uptake batch experiments were performed with different particle size fraction (< 0.3, 0.3 – 0.5, 0.5 – 0.8, 0.8 – 1.0, 1- 1.25, 1.25 – 1.5, 1.5 – 2.5 mm) of the alga. The analyses were carried out with 0.2 g of biomass and 50 ml of the metal solution (100 mg/l). The mixtures were agitated at 125 rpm for 12 h in a rotary shaker and the algal biomass from each sample was separated from cadmium solution by centrifugation at 3000 rpm for 10 min. The influence of adsorbent dosage on the sorptive capacity was investigated by agitating 50 ml of metal solution (100 mg/l) with 0.0025, 0.05, 0.075, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4 g of adsorbent for 3 hr. The effect of agitation rate on the removal of metal was studied by agitating 50 ml of metal solution (1 mmol/l) with 0.2 g of the sorbent at different rotation speeds (0 – 250 rpm). All these experiments were carried out at room temperature and a pH of 5.The analysis for residual cadmium concentration was accomplished by atomic absorption spectrophotometer. The amount of cadmium adsorbed by algae was calculated from the differences between the amount added to the biomass and the cadmium content after adsorption using the following equation:

$Q=V(C_o-C_f)/M$ (1)

where Q is the cadmium uptake (mg/g), C_0 and C_f are the initial and final cadmium concentrations in the solution respectively (mg/l), V, the solution volume (l) and M is the mass of biosorbent (g)[2].

Influence of pH

The optimal pH level for the effective removal of the metal ions was studied in batch experiments by taking in contact 50 ml of cadmium nitrate solution (100 mg/l) with 0.2g of biomass for 3 h under different pH conditions viz. 2 to 6.

Effect of agitation rate

The impact of the agitation rate on the sorption performance was investigated by agitating the sorbent (0.2 g) and sorbate solution (50 ml, 100 mg/l) with the pH maintained at 6 in the range of 0 – 250 rpm.

Effect of contact time

The contact time is of greater importance in the adsorption for the assessment of the suitability of the biosorbents to serve in the continuous flow systems[3]. The effect of contact time was studied by taking 50 ml of the cadmium solution of initial concentration 100 mg/l and 0.2 g of the sorbent and analyzing the sample in predetermined time intervals. The agitation rate was maintained at 150 rpm.

Effect of Temperature

The temperature effect on the biosorption was studied by conducting the sorption process in the temperature range from 20 to 50° C by contacting 50 ml of the cadmium solution of initial concentration 100 mg/l and 0.2 g of the sorbent with the agitation rate maintained at 150 rpm.

Equilibrium Study

There are many theoretical models to describe the adsorption process of heavy metals by using active and inactive microorganisms. To carry out the equilibrium study in the present investigation 0.2 g of biomass was added to Erlenmeyer flasks containing 50 ml of metal solution in the concentration range of 20 – 500 mg/l. Adsorption isotherms were obtained at a pH of 6.

Kinetic studies

To study the kinetics of the biosorption 5 g of the biomass and 1 l of cadmium solution (100 mg/l) are agitated in Erlenmeyer flasks at room temperature (pH 4, 5 and 6). Samples collected using 20 cc syringes at predetermined intervals are filtered immediately through glass fibre prefilters and the filtrate was analyzed to determine the concentration of left out cadmium.

Modeling

Equilibrium isotherm models: An adsorption isotherm describes the relationship between the amount of metal adsorbed and the metal ion concentration remaining in the solution. The equilibrium model equations for isotherms often provide some insight into both the adsorption mechanism and the surface properties and affinity of the sorbent [4].

Langmuir isotherm:

The Langmuir isotherm is given by:

$$Q = \frac{Q_{max}\, bC_f}{(1 + bC_f)} \qquad (2)$$

Where C_f is the final copper concentration (mmol/l), Q_{max} is a Langmuir constant that expresses the maximum metal uptake (mmol/g) and b is also a Langmuir constant related to the energy of adsorption and affinity of the sorbent.

The Freundlich isotherm:

The Freundlich isotherm is an exponential equation and therefore assumes that the concentration of adsorbate on the adsorbent surface increases with the adsorbate concentration. This equation is widely applied in heterogeneous systems and formulated as :

$$Q = K(C_f^{\,(1/n)}) \qquad (3)$$

where K (l/g) and n are the Freundlich constants characteristic of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

Sips isotherm: The Sips model is given as :

$$Q = \frac{Q_{max}\, bC_f^{\left(\frac{1}{n}\right)}}{1 + bC_f^{\left(\frac{1}{n}\right)}} \qquad (4)$$

At low substrate concentrations it effectively reduces to a Freundlich isotherm, while at high sorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm[5].

Redlich-Peterson isotherm: This empirical equation is represented as:

$$Q = \frac{K_{RP} C_f}{1 + a_{RP} C_f^{\beta}}$$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (5)

where K_{RP} (l/g) , a_{RP} (l/mg) are Redlich-Peterson isotherm constants and   the exponent, lies between 0 and 1. This equation reduces to a linear isotherm in the case of low surface coverage and to a Langmuir isotherm when   = 1.

Kinetic Models:

The adsorption kinetic shows the evolution of the adsorption capacity with time. To examine the potential rate controlling step several kinetic models were used to test the experimental data

Pseudo first order equation:

The pseudo first order equation is expressed as:

$$\frac{dQ_t}{dt} = k_1(Q - Q_t)$$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (6)

where Q and Q_t (mmol/g) are the amount of cadmium adsorbed at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the pseudo first order equation[6].

Pseudo second order equation:

The pseudo first order equation is expressed as:

$$\frac{dQ_t}{dt} = k_2(Q - Q_t)^2$$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (7)

where k_2 is the equilibrium rate constant of the pseudo second order equation (g/mmol min).

The Elovich equation:

The Elovich equation is of general application to chemisorption kinetics. The equation has been applied satisfactorily to some chemisorption processes and has been found to cover a wide range of slow adsorption rates. The same equation is often valid for systems in which the adsorbing surface is heterogeneous and is given as:

$$\frac{dQ_t}{dt} = e^{-\ q_t}$$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (8)

where   (mmol/g min) is the initial adsorption rate and   is related to the extent of surface coverage and the activation energy involved in chemisorptions[7] (g/mmol).

Intraparticle diffusion equation:

The intraparticle diffusion equation is given as:

$$q_t = kt^{1/2}$$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (9)

where k (mmol/g min$^{1/2}$) is the intraparticle diffusion rate constant.

Results And Discussions:

Effect of particle size and sorbent dosage

The influence of particle size on cadmium removal is shown in Fig. 1. In the range studied, there were no significant differences in the Cd^{2+} sorption with varying particle size. The sorption capacity of the marine alga with the different particle size fraction studied varies form 0.19 to 0.21mmol/g. The sorption capacity of sample, <1.5mm, was 0.25 mmol/g. Therefore, all the subsequent experiments were performed with the samples in this range of size[8].

Fig. 2 shows the trend of the effect of sorbent dosage on the removal of cadmium wherein it can be inferred that increasing the adsorbent concentration up to 4 g/l dosage resulted in a rapid increase in the percentage of cadmium uptake (0-80% cadmium uptake). Sorbent dosages more than 4 g/l did not show significant improvement in the cadmium uptake.   Hence this dosage level was selected was further investigations.
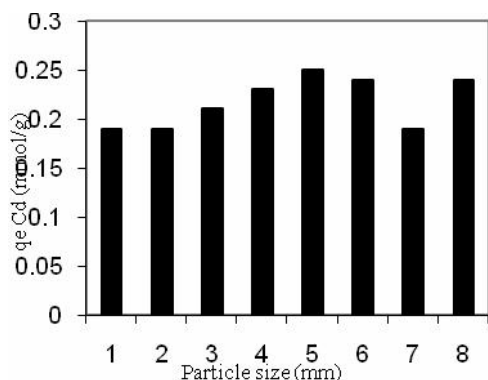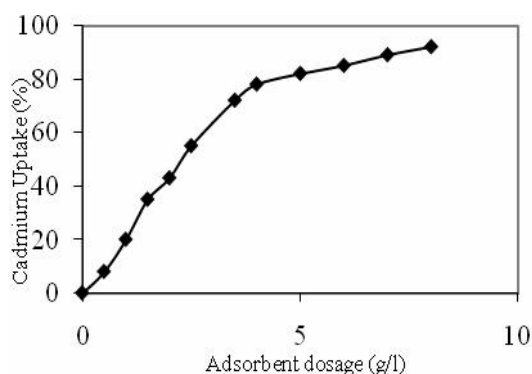

Fig. 1 Effect of particle size on cadmium removal

Fig. 2 Effect of sorbent dosage on cadmium removal

Effect of pH

The metal ion adsorption on both specific and non-specific sorbents in pH dependent as the solution pH affects the chemistry of the metals and the activity of functional groups and the competition of metallic ions for the binding site.At pH values below 8, cadmium is in its free ionic form (Cd^{2+}) [37, 38] and, as such, the increase in metal uptake cannot be described by the change in metal speciation, which leads to the hypothesis that the cell wall functional groups and their associated ionic state are responsible for the extent of adsorption .

The minimal adsorption (Fig. 3) at low pH may be due to the higher concentration and high mobility of the H+, which are preferentially adsorbed rather than the metal ions (11, 35). At higher pH values, the lower number of H^+ and greater number of ligands with negatives charges results in greater cadmium adsorption. For example, carboxylic groups (-COOH) are important groups for metal uptake by biological materials (33, 39). At pH higher that 3 - 4, carboxylic groups are deprotonated and negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced[9].
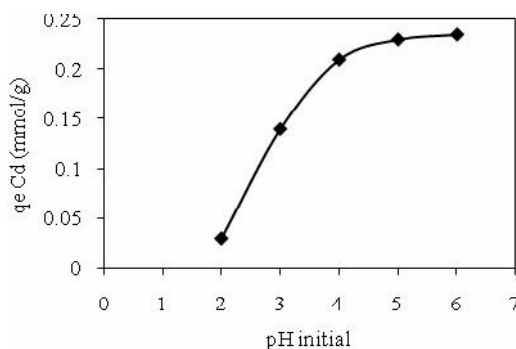

Fig. 3 Influence of the pH on sorption capacity onto biomass

Effect of Agitation Rate

This study shows (Fig. 4) depicts the influence of shaker speed on the sorption performance and the maximum value of the adsorption capacity is obtained at the speed of 150 rpm and agitation rate more than that shows negative effect. This is due to the best homogeneity of the mixture suspension at the moderate speed and lack of the same at higher speed due to vortex formation which makes the adsorption difficult.
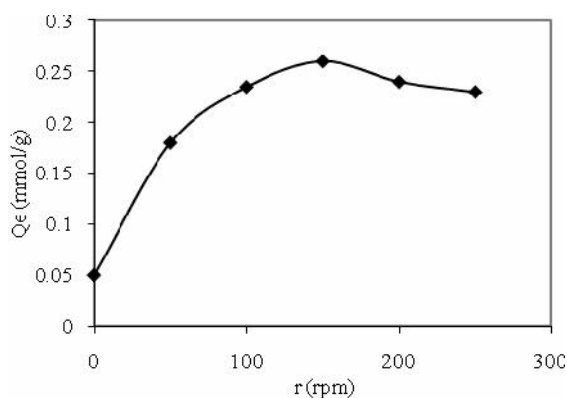
Fig 4. Effect of agitation rate on biosorption of cadmium

Effect of Contact Time:

The representation of the adsorption profile with respect to contact time. It can be seen from the graph that there exists two phases of biosorption: a primary rapid phase that accounts for the major part in the total biosorption wherein most of the metal ions are adsorbed from aqueous solution within first 8 h and a second slow phase that contributes to a relatively small part and there is no more uptake of metal after 20 h. This trend suggests that the uptake may be due to the interaction with functional groups located on the surface of the algal biomass at the first rapid stage and interior accumulation in the second phase.
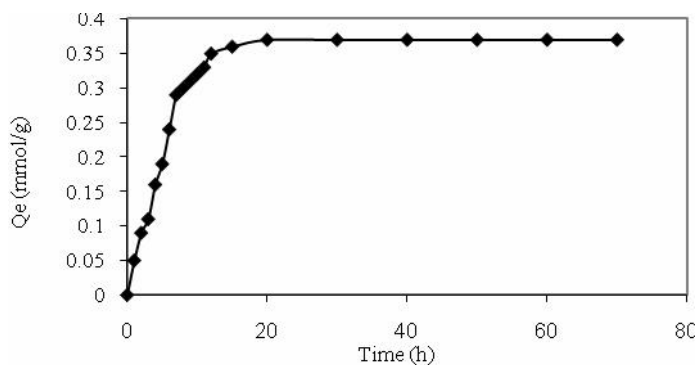

Fig. 5 Effect of contact time on biosorption of   Cd (II) ions
(pH=6, Initial concentration: 100 mg/l,   r = 120 rpm)

Effect of Temperature

It can be seen from Fig.6 the dependence of the biosorption rate of cadmium ions on the temperature of the process. Maximum adsorption was obtained in the temperature of 25 – 30°C. Pronounced efficiency at higher temperatures may be due to the reasons: The energy of the system facilitates higher affinity of the sorption sites on the metal ions and more binding sites on the relevant biomass.
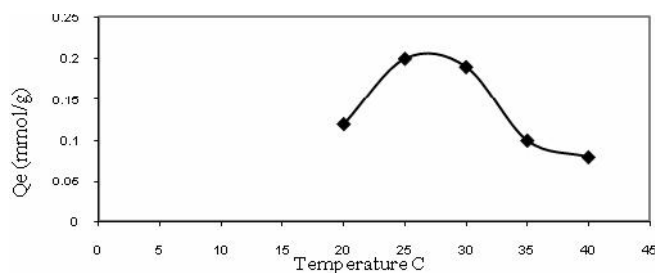
Fig. 6 Effect of temperature on biosorption of Cd
(II), pH=6, Initial conc.= 100 mg/l, t=72 h, r=120 rpm

Adsorption isotherm

The equilibrium experimental data was modeled using four isotherm models, namely, Langmuir, Freundlich, Sips and Redlich Peterson equations. The comparison between the experimental data and the predicted values from these models is presented in fig 4. The parameters of each model are evaluated using 'cftool ' kit available in MATLAB 7 software and presented in Table 1 along with the correlation coefficients. From the R^2 it can be seen that the Sips equation fits the experimental appreciably when compared to the other equations.
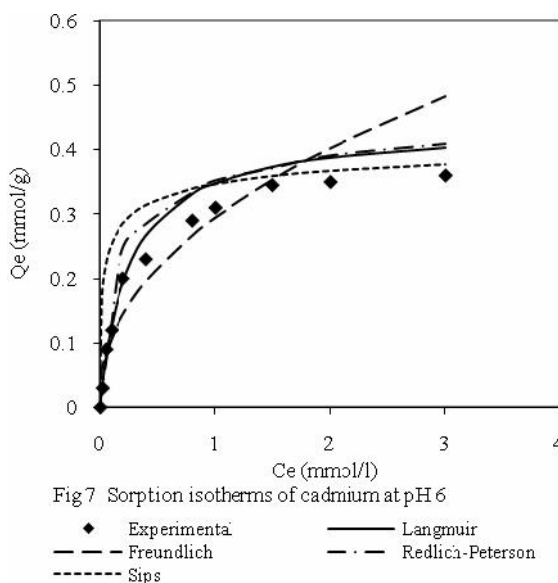

Fig 7 Sorption isotherms of cadmium at pH 6

♦ Experimental   ——— Langmuir
— — — Freundlich   — · — Redlich-Peterson
- - - - - - - Sips

Table 1 Parameters of the isotherms:

Model	Parameters	R^2
Langmuir	Q_{max} = 0.3813; b = 4.75	0.9931
Freundlich	k = 0.2853; n = 3.174	0.9536
Sips	Q_{max} = 0.4079; n = 3.219; b = 3.219	0.9950
Redlich Peterson	a_{RP} = 6.19; k_{RP} = 2.221; b = 0.9282	0.9282

Adsorption kinetics

The equilibrium experimental data was modeled using four kinetics models, namely, Pseudo first order, Pseudo second order, Elovich and Intraparticle diffusion equations. The comparison between the experimental data and the predicted values from these models is presented in fig 5. The parameters of each model are evaluated using 'cftool' kit available in MATLAB 7 software and presented in Table 2 along with the correlation coefficients. From the R^2 it can be seen that the Elovich equation fits the experimental appreciably when compared to the other equations.
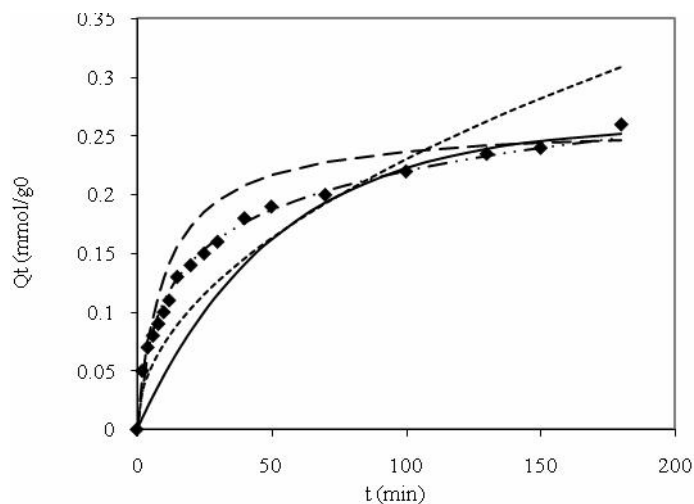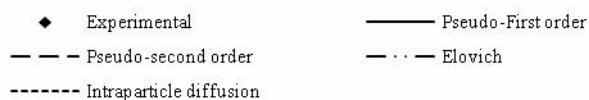
Fig 8 Sorption kinetics of cadmium at pH 6

♦   Experimental   —— Pseudo-First order
— — — Pseudo-second order   — ·· — Elovich
------- Intraparticle diffusion

Table 2 Parameters of the kinetics:

Model	Parameters	R^2
Pseudo first order	$Q_e = 0.223$; $k_1 = 0.101$	0.9215
Pseudo second order	$Q_e = 0.27$; $k_2 = 0.6$	0.9318
Elovich	$\alpha = 4.71$; $\beta = 15.2$	0.9891
Intraparticle diffusion	$k = 0.022$	0.9561

Conclusion:

S. tennerrimmum has ben found to a very effective biosorbent for the removal of Cd (II) ions form aqueous solutions. Cadmium uptake has strong influence on pH, which can be seen from the abrupt rise in the percentage uptake of cadmium (from 8 to 80 %) when the pH was increased from 2 to 6. The adsorption rate is rapid and the equilibrium can be considered to be reached at 60 min, at pH values of 4-6. The Elovich equation is the best choice for describing the adsorption kinetic of cadmium ions onto the alga since this offers heterogeneous surface and the presence of various types of binding site. The equilibrium results have been modeled and evaluated suing for different isotherm models at pH 6. The Sips model provided the best fit of the equilibrium data. According to this model, the maximum cadmium uptake was 0.3773 mmol/g at pH 6.

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