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Batch, Kinetic and Equilibrium Studies of Hexavalent Chromium from Aqueous Phase using Galaxaura Ornate Seaweed

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Abstract: Batch studies have been carried out to study the feasibility of adsorption of hexavalent chromium onto Galaxaura ornate seaweed. The equilibrium data and biosorption capacity of chromium was determined by varying the pH, dosage of adsorbent, contact time and initial metal ion concentration. The maximum adsorptive capacity was obtained at a pH of 2 at an equilibrium time of 120 minutes. Highest removal efficiency for raw biomass was found to be 71% for hexavalent chromium under optimal conditions. The biosorption isotherms were determined using Langmuir and Freundlich models. Based on the correlation coefficient value it was found that the data fits well both to Langmuir (R²=0.99) and Freundlich adsorption isotherm (R²=0.98) representing monolayer adsorption as well as adsorption on heterogeneous surfaces. The findings of the kinetic study infer that pseudo second order model show a better fit for a wider range of concentrations studied than the pseudo first order kinetics. The results indicate that the identified seaweed has the potential to adsorb chromium (VI) from the aqueous solution.

Keywords: biosorption; monolayer; seaweed; Galaxaura; hexavalent chromium.

Introduction

Heavy metals are released into the environment by various industrial and metallurgical processes which tend to persist indefinitely, circulating and eventually accumulating throughout the food chain¹. According to United States Environmental Protection Agency (EPA), hexavalent chromium is one among the 129 most critical pollutants². The major sources of chromium released into the environment are wastewater streams from electroplating, welding, production of chromium–iron alloys, tannery, production of chromates, dichromate, dyes and varnishes, as well as the use in electronic and metallurgy industries³. The currently available technologies to remove the toxic elements are precipitation, chemical reduction, membrane separation, reverse osmosis, ion exchange, adsorption etc, In spite of its huge cost, these methods are not suitable at lower concentrations and also generate unwanted by products⁴. Therefore, an economic and efficient method for the removal of heavy metals from wastewater has become the need of the hour.

Biosorption, the use of dead biomass for the removal of heavy metal pollutants from the aquatic environment⁵, is one such method which could be cost effective and versatile and can be easily adopted to remove heavy metals from large amount of industrial wastewaters⁶. Among the various microbial sources used for biosorption, algae has been proven to have high metal binding capacity, due to the presence of polysaccharides, proteins or lipid on the surface of their cell walls containing functional groups such as amino,

hydroxyl, carboxyl and sulphate, which can act as binding sites for metals^{7,8}. Large amounts of seaweed biomass have been generated from sea weed processing industries. The use of seaweeds reduces the capital cost by 20%, operational costs by 36% and total treatment costs by 28%, compared with existing conventional methods^{9, 10}. First time in literature Galaxura ornate seaweed biomass is studied for the biosorption of chromium and the objective is to determine the maximum adsorption capacity of the biosorbent on hexavalent chromium removal from aqueous solution.

Experimental

Biosorbent

The red seaweed of uniform particle size less than 100 μ m was collected from the Little Rann of Kutch located around Arabian Sea, Gujarat State, India. It was washed several times with deionized water to remove unwanted impurities and subjected to drying in the oven around the temperature of 60°C for three hours. The sample was stored in a glass bottle and preserved in a suitable desiccator for further use.

Stock Solution Preparation

The batch mode biosorption studies were carried out using mechanical shaker. All the chemicals used were of analytical grade and double distilled water was used for the entire processes. Sample solutions of various concentrations (20 - 500 mg/L) were prepared from a stock solution of 1000 mg/L of potassium dichromate. Diluted solutions were taken in 250 ml Erlenmeyer flasks and subjected to shaking at a speed of 120 rpm. pH measurements were made using systronic digital pH meter. All the pH modifications were done with 0.1 N HCl. Determination of unadsorbed chromium ion concentration before and after adsorption were studied by UV-VIS spectrophotometer (Shimadzu) at 540 nm using the diphenyl carbazide reagent.

Batch studies

All the experiments were performed at room temperature $(27^{0}C)$ and the volume of chromium solution was fixed as 50 ml. The equilibrium data and biosorption capacity of chromium can be determined by varying the pH, dosage of adsorbent, contact time and initial metal ion concentration.

To determine the optimum contact time and equilibrium concentration, adsorption studies were conducted at room temperature for different chromium concentrations of 20–500 mg/L and the shaking duration was varied between 15 to 150 minutes. The effect of pH for a fixed concentration was studied for pH ranging from 1 to 4 at room temperature and to study the influence of dosage of biosorbent on adsorption efficiency, dosage varied from 0.25g to 3.5g. The isotherm studies were carried out for different concentrations ranging from 20 to 500 mg/L chromium for equilibrium time of 120 minutes at room temperature. The biosorption isotherms were determined using Langmuir and Freundlich models.

The agitation speed of the shaker is maintained to be 120 rpm throughout the experiment. After agitation the resulting solution was filtered using Whatman filter paper (No. 41) and filtrate was analyzed by UV- Vis Spectrophotometer. All the studies were carried out at an equilibrium concentration of 20 mg/L. The optimum pH of the solution and dosage of the biosorbent was maintained to be 2 and 1.5 g respectively.

The unadsorbed chromium ion was estimated by UV-VIS spectrophotometer and the equilibrium adsorption capacity of the adsorbent was determined according to the following equation:

$$q_e = \frac{(C_o - C_e)V}{m}$$

 C_{o} _ Initial metal ion concentration (mg/L), Ce_ equilibrium metal ion concentration (mg/L), q_e - adsorption capacity (mg/g), m- mass of the bio-sorbent (g), V – volume of the aqueous solution (L) The percentage removal of chromium is found using equation:

Removal (%) = $\frac{Co-Ce}{Co}X$ 100

Results & Discussion

Effect of initial metal ion concentration

The experimental data obtained from the effect of different initial chromium ion concentration (20-500 mg/L) is given in figure 1. It shows that the efficiency decreased from 71% to 25% and hence the optimum concentration for further studies was fixed to be 20 mg/L. At lower concentrations all the metal ions present in the solution could easily participate in the adsorption process and hence the efficiency is higher, but at higher concentrations more and more ions are present and all of them have to compete for the available binding sites. Hence in the later stages even after occupying all the available sites some more chromium ions are left unadsorbed and hence reaches saturation. At low concentrations of sorbate, the ratio of the initial number of moles of metal ions to the available surface area is larger and subsequently the fractional biosorption becomes independent of initial concentrations¹¹. However, at higher concentrations the available sites for biosorption becomes fewer, and hence the percentage removal of metal ions depends upon the initial concentration of Cr (VI) ions.



Figure 1: Effect of initial metal ion concentration on adsorption efficiency





Figure 2: Effect of contact time and concentration on adsorption efficiency

The figure 2 illustrates the influence of contact time and its effect on the capacity of biosorption of chromium. This study is performed at an optimum pH 2 and the metal ion concentration varied from 20 - 500 mg/L at room temperature. The experimental result reveals that the adsorption efficiency gradually increases and then reaches equilibrium around 120 minutes. This is due to the fact that large numbers of vacant sites were available in the beginning and later on most of the biosorption sites were occupied, and adsorption attains equilibrium. The increase in rate of adsorption at the initial stage is due to the availability of positively charged surface of the biosorbent and the anionic Cr (VI) species present in the solution. The later slow adsorption rate in the curve may be due to the electrostatic hindrance caused by already adsorbed negatively charged adsorbate species and the slow pore diffusion of the ions^{12, 13}. The result suggests that an equilibrium time of 120 minutes could be chosen to study the effect of other parameters for the adsorption of chromium.

Effect of biosorbent dosage

The biosorbent dosage was gradually varied from 0.25 - 3.5 g with an optimum concentration of 20 mg/L at a desirable pH of 2. The relationship between the sorption efficiency and the adsorbent dosage is as shown in figure 3. It is a well-known fact that the adsorption efficiency increases with increase in biomass dosage and attains saturation at some point of time, irrespective of whatever the adsorbent is. This increase in sorption is due to the presence of more surface area at higher biomass loading rates. Saturation stage is attained because of the aggregation of solid particles at higher dosage levels of biomass which further reduces the surface area of the biosorbent¹⁴. However the uptake capacity decreases with increase in biosorbent dosage as shown in figure 4. This could be attributed to the fact that at high biosorbent dosage the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting into low metal uptake ^{15, 16, 17}. Hence these studies suggest that lowest biomass dose result in high metal uptake capacity. Both metal uptake capacity and removal efficiency has to be given considerable importance in adsorption studies. Based on the results, the optimum level of 1.5g dosage was selected for further studies, as it has exhibited highest removal efficiency.



Figure 3: Effect of adsorbent dosage on biosorption efficiency



Figure 4: Effect of adsorbent dosage on biosorption capacity

Effect of pH of solution

The effect of pH plays a vital role in favoring or limiting the extent of biosorption, hence the influence of pH on adsorption is an important parameter to determine. Figure 5 shows the performance of biosorbent under the pH range of 1 to 4. This study was performed at the optimal concentration of 20 mg/L for 1.5g biomass dosage. Maximum adsorptive capacity is found to be 4.1 mg/g at a pH of 2 and hence further studies were done at this optimum pH. The sorption efficiency decreases with increase in pH and increases with decrease in pH. A sharp decrease in biosorption with increase in pH may be due to occupation of the biosorption sites by anionic species like HCrO^{4–}, Cr₂O₇^{2–}, CrO₄^{2–}, which retards the approach of such ions further toward the biosorbent surface¹⁸.



Figure 5: Effect of pH of solution on adsorption efficiency

Adsorption Isotherm models

Langmuir and Freundlich models are used to determine the relation between the equilibrium concentrations of the adsorbate in liquid phase and in the solid phase.

The Langmuir isotherm model

The Langmuir isotherm model¹⁹ is valid for monolayer adsorption onto surface containing finite number of identical sorption sites which is given by the following equation

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

 q_e represents the amount of metal adsorbed per specific amount of adsorbent (mg/g), Ce is equilibrium concentration of the solution (mg/L), and q_m is the maximum amount of metal ions required to form a monolayer (mg/g). The Langmuir equation can be rearranged to linear form as shown in equation for the convenience of plotting and determining the Langmuir constants (K_L) and maximum monolayer adsorption capacity of biosorbent (q_m). The values of q_m and K_L can be determined from the linear plot of 1/q_e versus 1/C_e as shown in figure 6:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e}$$

The Freundlich isotherm model

The Freundlich equation¹⁹ is purely empirical based on sorption on heterogeneous surface, which is explained by the given equation:

$$q_e = K_f C_e^{1/n}$$

Where, K_f and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity. The Freundlich equation can be linearized in logarithmic form for the determination of the Freundlich constants as given below:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Based on the experimental data the Freundlich isotherm models for chromium sorption on seaweeds were presented in figure 7. From the plot the Freundlich equilibrium constants were calculated from the intercept and the slope, respectively.

The affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, " R_L ", is as shown in the following equation²⁰:

$$R_L = \frac{1}{1 + K_L C_o}$$

Where K_L is the Langmuir constant and C_o is the initial concentration of chromium ion. The value of R_L (separation parameter) provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible (R_L =0), favourable ($0 < R_L < 1$), linear (R_L =1) or unfavourable (R_L >1).



Figure 6: Langmuir isotherm for Cr (VI) biosorption



Figure 7: Freundlich isotherm for Cr (VI) biosorption

The results of Langmuir and Freundlich isotherms are presented in table 1. The R_L value of 0.735 for 20 mg/L chromium solution suggests that the biomass chosen for the study is favourable for adsorption of chromium. Based on the correlation coefficient value it was found that the data fits well both to Langmuir ($R^2 = 0.99$) and Freundlich adsorption isotherm ($R^2 = 0.98$) representing monolayer adsorption as well as adsorption on heterogeneous surfaces. This result is in good agreement with the biosorption of chromium (VI) by Padina tetrastromatica (Brown algae), Gracilaria edulis (Red algae) and Ulvar eticulate (Green algae) sea weeds ²¹. The monolayer adsorption capacity values calculated from Langmuir isotherm were found to be 4.85 mg/g closer to the experimental values. The adsorption intensity (1/n) based on Freundlich isotherm calculated to be 0.636 represents beneficial adsorption and lower Langmuir constant (K_L =0.018) attributes to higher affinity of chromium ions towards the biosorbent.

	Т	able	1:	Langmuir	and	Freun	dlich	isotherm	parameters
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Parameters of Langmuir Isotherm	Parameters of Freundlich Isotherm
$q_{m} = 4.85$	$K_{F=}5.86$
$K_{L} = 0.018$	n= 1.57
$R^2 = 0.99$	$R^2 = 0.98$
$R_{L} = 0.735$	

Adsorption kinetics

Pseudo-first-order and pseudo-second order models were used to check the validity of the experimental values. These models were tested at different concentrations and at various intervals of time. The uptake of heavy metal ions by seaweeds has often been observed to occur in two stages; an initial rapid uptake due to surface adsorption on cell walls and a subsequent slow uptake due to membrane transport of the metal ions on the cytoplasm of the cells²².

The rate constant, k_{ad} and correlation coefficients of the Cr (VI) under different concentrations were calculated from the linear plots of log (q_e-q_t) versus time (figure 8). The following equation was used to check the validity of the pseudo-first-order model.

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303}t$$

where q_t is the adsorption capacity at time t (mg/g) and k_{ad} (min⁻¹) is the rate constant of the pseudo-first order adsorption



Figure 8: Pseudo first-order kinetics at different Cr (VI) concentrations

The kinetic data were also analyzed using pseudo-second order kinetic model. This model is based on the assumption that the adsorption is assumed to follow second order chemisorption. According to chemical adsorption the metal ions adhere to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination with the surface²³ and it assumes that the biosorption process occurs in two reactions, the first one is fast and reaches equilibrium quickly and the second is slow and keeps going for a long time period²⁴. The model also supposes that that rate of occupation of adsorption sites is proportional to the squares of number of unoccupied sites²⁵. The basic equation and the modified equation to obtain linearity is as given below which checks the applicability of the pseudo-second-order model.

$$\left(\frac{1}{q_e - q_t}\right) = \frac{1}{q_e} + kt$$

k is the rate constant of pseudo-second-order adsorption (g $mg^{-1} min^{-1}$).

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t$$

where $h=kq_e^2 (mg g^{-1} min^{-1})$ can be regarded as the initial adsorption rate as t $\rightarrow 0$. The plot of t/q_t versus time (figure 9) should give a straight line if pseudo-second-order kinetics is applicable and q_e, k and h can be determined from the slope and intercept of the plot, respectively²⁶.



Figure 9: Pseudo second-order kinetics at different Cr (VI) concentrations

Kinetic model	Parameters	Concentration of adsorbate					
Pseudo-	1	20 (mg/L)	50 (mg/L)	100	200 (mg/L)	300 (mg /L)	
first-order				(mg/L)			
equation	$k_{ad} (min^{-1})$	0.028	0.029	0.030	0.026	0.021	
	q _e ,exp	1.18	1.08	2	3.46	4	
	(mg/g)						
	q _e ,cal (mg/g)	1.24	1.41	2.41	4.39	4.79	
	\mathbb{R}^2	0.95	0.96	0.96	0.94	0.96	
Pseudo-	k $(g mg^{-1})$	0.0192	0.0088	0.0087	0.0028	0.0011	
second-	\min^{-1})						
order	q_e , cal (mg/g)	1.48	1.65	2.66	5.2	7.5	
equation	R ²	0.99	0.97	0.99	0.98	0.97	

Table 2: Kinetic and experimental values for pseudo first order model and second order model

The kinetic and experimental values for pseudo first order model and second order model were calculated and presented in table 2. Based on the correlation coefficients obtained pseudo second order model seems to show a better fit for the entire range of concentrations studied. Similar results were also reported in²⁷ and the fitness of experimental data to pseudo second order model implies that adsorption is likely controlled by chemisorption, including the sharing or exchanging of electrons between metal ion and adsorbent.

Conclusions

The experimental results evidence that, the studied biosorbent even without any chemical modification and thermal activation shows the potential to bind the hexavalent chromium from aqueous solution. Optimum pH for biosorption and the maximum adsorption capacity was determined to be 2 and 4.1 mg/g respectively. Maximum efficiency is obtained at a concentration of 20 mg/L and the contact time required to attain equilibrium was found to be 120 minutes. Biosorption data best fitted with both Langmuir and Freundlich isotherms, indicating the likelihood of monolayer sorption, and physical adsorption. The kinetics was found to follow pseudo-second-order rate expression than the pseudo first order model which states the involvement of chemical bonding in the binding mechanism of chromium. Further work is planned to be carried on enhancing the biosorption capacity by carrying out necessary chemical modification on the biosorbent.

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