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Biosorption of Cadmium from Aqueous Solution using Dead Biomass of Brown Alga *Sargassum* Sp.

Mohamad Hajar*
Master of Science in Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran

The removal of toxic heavy metal ions from wastewaters is of great importance from an environmental viewpoint. Biosorption is an effective technology using non-living biomass to remove heavy metals from aqueous solutions. In this study, the biosorption of cadmium (II) ions onto the dry biomass of *Sargassum glaucescens*, a brown marine alga, was investigated in the batch mode. Langmuir and Freundlich isotherm models were used for the mathematical description of the biosorption equilibrium data and model constants were evaluated. The biosorption capacity was found to be solution pH dependent and the maximum cadmium uptake of 84.7 mg/g was observed at pH 5, according to the Langmuir model.

1. Introduction

The removal and recovery of toxic heavy metal ions from wastewaters is of great importance from an environmental viewpoint. Cadmium is one of the toxic heavy metals with a greatest potential hazard to humans and the environment. It causes kidney damage, bone diseases and cancer. Chronic exposure to elevated levels of cadmium is known to cause renal dysfunction, bone degeneration, liver damage (Iqbal et al., 2007). The major sources of Cd (II) release into the environment through wastewater streams are electroplating, smelting, paint pigments, batteries, fertilizers, mining and alloy industries (Iqbal and Edyvean, 2005).

Conventional techniques for removing heavy metals from industrial effluents include chemical precipitation, chemical reduction, adsorption, ion exchange, evaporation and membrane processes. Compared with conventional methods for the removal of toxic metals from wastewater, the biosorption process offers potential advantages such as low operating cost, minimization of chemical or biological sludge, high efficiency of heavy metal removal from diluted solutions, regeneration of biosorbents, possibility of metal recovery and environmental friendly (Ahluwalia and Goyal, 2007).

Biosorption is an innovative technology using living or dead biomasses to remove toxic heavy metals from aqueous solutions. Various biomasses such as bacteria, yeast, fungi and alga for biosorption of metal ions have been widely used (Vieira and Volesky, 2000). Among the biological materials marine alga have been reported to have high metal binding capacities due to the presence of polysaccharides, proteins or lipid on the cell wall structure containing functional groups such as amino, carboxyl, hydroxyl and

* *E*-mail address: mohamad.hajar@yahoo.com (M. Hajar)

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sulphate, which can act as binding sites for metals (Davis et al., 2003). The main substances of this type in brown alga are alginates, which usually constitute around 20-40% of the total dry weight, and some sulfated polysaccharides. Moreover, the carboxyl groups of alginates are likely to be the main functionalities involved in metal binding reactions because of their higher abundance with regard to both carboxyl and amine groups of the proteins (Lodeiro et al., 2004).

The aim of this work was to study the biosorption of cadmium from aqueous solutions using dead biomass of brown alga *Sargassum* sp. The influence of contact time and solution pH on biosorption of cadmium was studied. Both the Langmuir and Freundlich isotherm models were evaluated to examine biosorption capacity of *Sargassum* sp. for Cd(II) ions.

2. Materials and methods

2.1 Biomass preparation

The brown alga *Sargassum glaucescens* was used as biosorbent for the biosorption of Cd(II) ions. Samples of marine alga were collected from the Oman Sea coast of Chabahar, Iran. The alga was washed several times with tap then deionized water to remove impurities and salts. The biomass sun-dried and then dried in an oven at 60 °C for 48 h. The dried alga biomass was cut, ground in a mortar and subsequently sieved and the particles with an average size of 0.5mm were used for biosorption experiments.

2.2 Cadmium solution preparation

Cadmium (II) solutions were prepared by dissolving a weighed quantity of cadmium chloride monohydrate (Merck, Germany) in deionized distilled water. Before the adsorption study, the pH of the Cd(II) solution was adjusted to required value with 0.1M HCl and 0.1M NaOH solutions using a pH meter.

2.3 Batch biosorption studies

Batch biosorption experiments were carried out in 100 ml conical flasks containing 0.1g of dried alga and 40 ml of cadmium solution at varying pH. The flasks were placed on shaker incubator with constant shaking at 150 rpm and 25 °C. After the separation of used biosorbent by centrifugation, the residual concentration of cadmium in solution was analyzed using atomic absorption spectrophotometer. The amount of adsorbed metal ions per gram of dead alga was obtained using the following equation:

$$q = [(Ci - Ce) \times V] / M$$

where q is the metal uptake (mg/g), C_i is the initial metal concentration (mg/l), C_e is the residual metal concentration (mg/l), V is the volume of metal solution (l) and M is the mass of biosorbent used in the reaction mixture (g) (Hashim and Chu, 2004).

3. Results and discussion

3.1 Effect of contact time

The contact time was evaluated as one of the important parameters affecting the biosorption efficiency. Fig. 1 shows the biosorption efficiency of Cd(II) ions by dead alga *Sargassum* sp. as a function of contact time. The cadmium uptake increases with rise in contact time up to 80 min and after then it is almost constant. The fast initial metal biosorption rate was attributed to the surface binding and the following slower sorption was attributed to the interior penetration (Lodi et al., 1998). Different kinds of functional groups, with different affinities to the metal ions, are usually present on the biomass surface. The active binding groups with higher affinities are firstly occupied (Chojnacka et al., 2005). According to these results, it was set a contact time of 120 min in order to ensure that equilibrium conditions are attained.

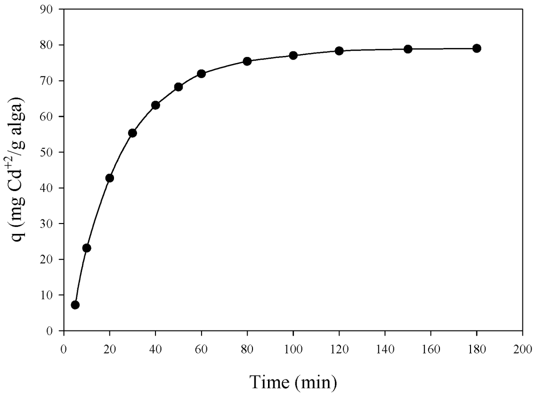

Fig. 1. Effect of contact time on cadmium biosorption using dead biomass of brown alga Sargassum sp. (initial Cd(II) concentration 150 mg/L, temperature 25°C, biomass dosage 2.5 g/L and pH 5)

3.2 Effect of pH

Biosorption of heavy metal ions is depend on the pH of solution as it affects biosorbent surface charge, degree of ionization, and the species of biosorbent (Ahmady-Asbchin et al., 2008). The pH of the solution influence both metal binding sites on the cell surface and the chemistry of metal in solution (Dursun, 2006). In order to demonstrate the effect of pH on biosorption capacity, uptake of Cd(II) ions onto dead alga as a function of pH was studied in the pH ranges of 2 to 8 and showed in Fig. 2.

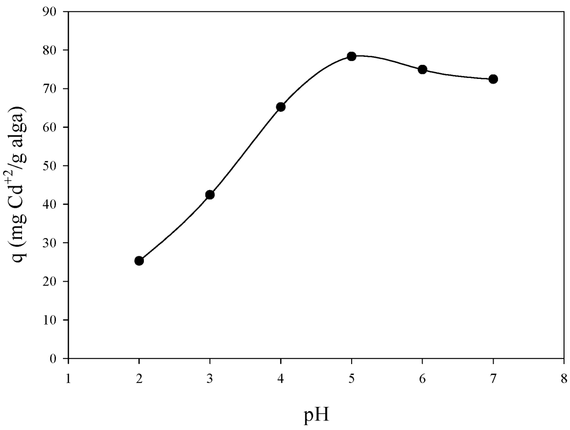

Fig. 2. Effect of pH on cadmium biosorption using dead biomass of brown alga Sargassum sp. (initial Cd(II) concentration 150 mg/L, temperature 25°C and biomass dosage 2.5 g/L)

As the pH of the cadmium solution increased from 2 to 8, the adsorption capacity of Cd(II) increased upto pH 5 and then dramatically decreased. Increased positive charge

(H^+) density on the sites of biomass surface at low pH values (pH 2–4) restricted the approach of metal cations as a result of repulsive force. In contrast, when the pH value increased, biomass surface was more negatively charged and the biosorption of the metal ions with positive charge (Cd^{2+}) was reached maximum around pH 5. The decrease in biosorption at higher pH values (pH> 5) may be attributed to the formation of anionic hydroxide complexes of the metal ions and their competition with the active sites. Similar findings were reported for other types of biosorbents (Sari and Tuzen, 2008). Therefore, all further studies were carried out at pH 5.

3.3 Biosorption isotherm models

The Langmuir and Freundlich isotherm models were used for the mathematical description of Cd(II) ions biosorption and isotherms constants were determined. The Langmuir isotherm model assumes a monolayer adsorption onto a surface containing finite number of identical sites. This isotherm can be defined according to the following equation:

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

where q_e is the amount of adsorbed metal per unit weight biomass at equilibrium (mg/g), C_e is the residual metal concentration in solution at equilibrium (mg/l), q_{max} is the maximum amount of metal per unit of biomass (mg/g) and b is a constant related to the affinity of the binding sites (l/mg) (Langmuir, 1918). Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be described as follows:

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

where K_f and n are the Freundlich constants related to the adsorption capacity and intensity of the sorbent, respectively (Freundlich, 1907).

The plots of non-linearized Langmuir and Freundlich adsorption isotherms were shown in Fig. 3.

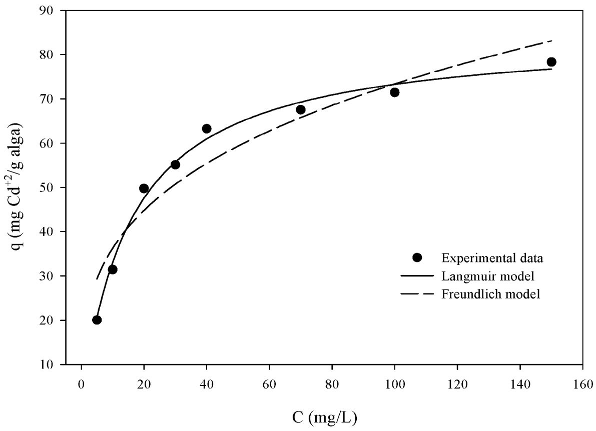

Fig. 3. Non-linearized isotherms for cadmium biosorption by dead biomass of Sargassum sp. The symbols correspond to the experimental points and the lines present the fits to Langmuir and Freundlich equations.

The adsorption isotherm constants were determined by using non-linear regression. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients were also presented in Table 1. The correlation regression coefficients show that the biosorption process is better defined by Langmuir than by Freundlich equation. The Langmuir fit is consistent with strong monolayer sorption onto specific sites.

Table 1. Biosorption isotherm equations for cadmium biosorption

Model	Equation	Isotherm constants	Correlation coefficient
Langmuir	$q_e = \frac{5.424C_e}{1+0.064C_e}$	q_{max}=84.72 b=0.064	0.992
Freundlich	$q_e = 17.89C_e^{0.3065}$	K_f=17.89 n=3.26	0.914

4. Conclusions

The study indicated that the dead biomass of brown alga *Sargassum* sp. could be used as an efficient biosorbent material for the removal of cadmium ions from aqueous solutions. The Langmuir and Freundlich adsorption models were used for the mathematical description of the biosorption equilibrium of cadmium ions to the dead biomass of alga and the obtained results showed that the adsorption equilibrium data fitted very well to the Langmuir model. The biosorption capacities were solution pH dependent and a maximum adsorption capacity was determined to be 84.7 mg/g at a solution pH of 5. The adsorption capacity for cadmium ions onto dead biomass of *Sargassum* sp. was found to be relatively high when compared with those of many other adsorbent materials have been reported for removal of heavy metals.

References

Ahluwalia S.S., Goyal D., 2007, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98, 2243-2257.

Ahmady-Asbchin S., Andres Y., Gerente C., Cloirec P.L., 2008, Biosorption of Cu(II) from aqueous solution by *Fucus serratus*: Surface characterization and sorption mechanisms, Bioresour. Technol. 99, 6150-6155.

Chojnacka, K., Chojnacki, A., Gorecka, H., 2005, Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue-green algae *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process, Chemosphere. 59, 75–84.

Davis T.A., Volesky B., Mucci A., 2003, A review of the biochemistry of heavy metal biosorption by brown algae, Water. Res. 37, 4311-4330.

Dursun A.Y., 2006, A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*, Biochem. Eng. J. 28, 187-195.

Freundlich H., 1907, Ueber die adsorption in loesungen, Z. Phys. Chem. 57, 385–470.

Hashim M.A., Chu K.H., 2004, Biosorption of cadmium by brown, green, and red seaweeds, Chem. Eng. J. 97, 249-255.

Iqbal M., Edyvean R.G.J., 2005, Loofa sponge immobilized fungal biosorbent: A robust system for cadmium and other dissolved metal removal from aqueous solution, Chemosphere. 61, 510-518.

Iqbal M., Saeed A., Zafar S.I., 2007, Hybrid biosorbent: An innovative matrix to enhance the biosorption of Cd(II) from aqueous solution, J. Hazard. Mater. 148, 47-55.

Langmuir I., 1918, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40, 1361–1403.

Lodeiro p., Cordero B., Grille Z., Herrero R., Sastre de Vicente M.E., 2004, Physicochemical studies of cadmium(II) biosorption by the invasive alga in Europe, *Sargassum muticum*, Biotechnol. Bioeng. 88, 237-247.

Lodi A., Solisio C., Converti A., Del Borghi M., 1998, Cadmium, zinc, copper, silver and chromium(III) removal from wastewaters by *Sphaerotilus natans*, Bioproc. Eng. 19, 197–203.

Sari A., Tuzen M., 2008, Biosorption of cadmium(II) from aqueous solution by red algae (*Ceramium virgatum*): Equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 157, 448-454.

Vieira R.H.S.F., Volesky B., 2000, Biosorption: a solution to pollution?, Int. Microbiol. 3, 17-24.