Removal of Cd(II) from Aqueous Solutions by Biosorption of *Laurencia Papillosa*

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Abstract: Biosorption properties of *Laurencia papillosa* were investigated as a function of pH, temperature and concentration of algal dosage. Kinetics and equilibrium isotherms were studied to estimate the ability of the biosorbent. The cadmium(II) uptake by the biosorbent was best described by pseudo-second-order rate and Langmuir isotherm curve provide more suitable results with respect to the Freundlich isotherm curve.

Keywords: Biosorption, Cadmium, Freundlich isotherm, Green algae, Laurencia papillosa, Langmuir isotherm

Introduction

The pollution of the environment with toxic heavy metals is spreading through the world along with industrial progress[1]. Toxic metals are metals that form poisonous soluble compounds without biological role[2]. Biosorption employed the natural origin material for removal of heavy metals from environment. The biosorption of toxic heavy metals has received considerable attentions in recent years[3-4].

Among toxic heavy metals, cadmium is one of the most dangerous elements for human health. Cadmium used as corrosion resistant in protective coating for iron, steel and copper[5]. It can enter the human body by eating, drinking, breathing and smoking. By entering the cadmium in the body, it causes serious damage to kidney and bones. It also causes high blood pressure, vomiting, diarrhea, coughs and bronchitis[6].

The major advantages of biosorption include low cost, high efficiency, minimization of chemical and biological sludge, regeneration of biosorbent and the possibility of metal recover[7-10]. Whereas conventional wastewater treatments have several disadvantages including high energy requirements, incomplete metal removal and running costs[11].

Among the various types of biosorbents, algae possess a high metal-binding capacity. This is due to the presence of various functional groups which can act as binding sites for metals[12-13]. In this work, by employing the *Laurencia papillosa* from Persian Gulf as biosorbent, we have studied the possibility of the removal of cadmium from aqueous solutions.

Experimental

Laurencia papillosa was collected from the Persian Gulf on Bushehr Island. Before use, it was washed several times with distilled water to remove dirt. The clean algae was dried in an oven at 60 ºC for 24 h and powdered to maximize the surface of absorption. The various concentrations were prepared by dissolving an accurate quantity of $CdCl_2.2H_2O$ in deionized distilled water.

Two batches of experiments were done to study the effect of parameters and estimate the optimum qualifications for biosorption process. Cadmium solutions with different concentration, such as: 10, 20, 85 and 150 and 170 ppm were used. Also different value of algal dosage such as: 12.5, 25, 112.5, 200 and 320 mg/L were used.

The experiments were performed in conical flasks with distinct values of biomass. The *p*H value was adapted by addition sodium hydroxide or hydrochloric acid. The effect of *p*H on cadmium biosorption was studied by varying the *p*H at 1, 2, 5, 8, 10 and 12.

The effect of temperature was studied on cadmium biosorption by varying the temperatures at 4, 40, 60 and 75 °C. The effect of algal dosage was studied on cadmium biosorption by variation of algal dosage in 12.5, 25, 112.5, 200 and 320 mg/L.

The cadmium solution and biosorbent were in contactand then filtered. The concentration of cadmium(II) in the solution before and after the equilibrium was determined by an atomic absorption spectrometer (Varian SpectrAA.200 model). The metal uptake q_e (milligram of metal adsorbed per gram of adsorbent) was calculated from the mass balance equation as Eq (1)

$$q_e = (C_i - C_e)V / 1000 \ W \qquad (1)$$

Where C_i (mg/L) is the initial concentration, C_e (mg/L) is the metal concentrations at equilibrium, V (mL) is the volume of the solution and W (g) is the mass of sorbent[14].

Results and Discussion

The effect of pH

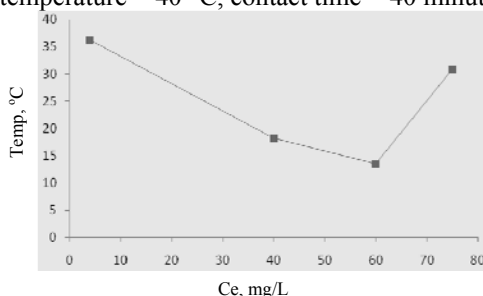Concentration of cadmium(II) after absorbance (mg/L) at various *p*H was shown in Figure 1. In acidic conditions *i.e.* *p*H = 1 and *p*H = 2, the absorbance of cadmium (II) was low because the H_3O^+ compete with the cadmium (II) to occupy the activated sites on biosorbents. In basic conditions, the absorbance decreased again, that can be related to formation of cadmium hydroxide[15-17].

The effect of temperature

Temperature is found to be a critical parameter in the biosorption of cadmium(II) as shown in Figure 2. The maximum cadmium(II) biosorption occurred at 60 ^{0}C which decreased continuously by increasing temperature. For lower temperature, the absorbance of cadmium(II) will be decreased continuously that can be related to the mobility of active cite of alga composition with metal, and for upper temperature, the absorbance of cadmium(II) will be decreased that can be related to the destruction of alga composition[18].
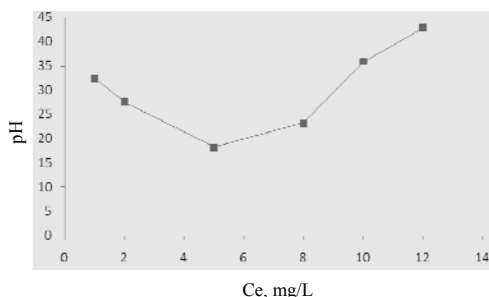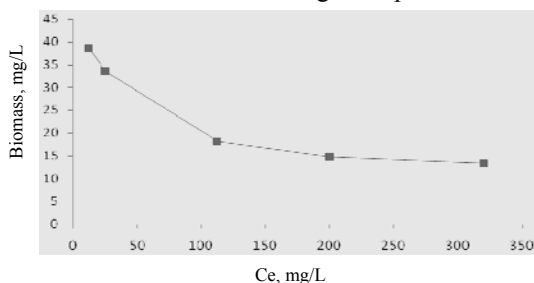
Figure 1. Effect of pH on Cd(II) uptake by *Laurencia papillosa* (initial concentration = 8 ppm, biomass = 200 mg/L, temperature = 40 °C, contact time = 40 minute)

Figure 2. Effect of temperature on Cd(II) uptake by *Laurencia papillosa* (initial concentration = 85 ppm, biomass = 112.5 mg/L, *p*H = 5, contact time = 38 minute)

The effect of algal dosage

The concentration of cadmium(II) after absorbance as a function of adsorbent dosage was shown in Figure 3. It was apparent that the removal of cadmium(II) increased with increasing algal dosage because of the more availability of the biosorbents. In the beginning, the trend of the curve was changed significantly that can be related to the high number of unoccupied active cite of alga composition. At the end, this trend was changed smoothly that can be related to the saturation of active cite of alga composition[19-20].

Figure 3. Effect of biosorbent dose on Cd(II) uptake by *Laurencia papillosa* (initial concentration = 85 ppm, *p*H = 5, temperature = 40 °C, contact time = 38 minute)

The kinetic of biosorption

The kinetics of adsorption describes the rate of cadmium ions uptake on green alga which controls the equilibrium time. The results of kinetic studies employed for identification of the mechanism of solute adsorption onto sorbents.

The sorption data of cadmium(II) uptake by *Laurencia papillosa* was fitted using Lagergren pseudo first order model (Figure 4) and pseudo second order model (Figure 5). The linearized form of first order Lagergren equation is given as Eq. 2.

$$\log(q_e - q_t) = -(k_{1,ads}t)/2.303 + \log q_e \tag{2}$$

and the pseudo second order model is given as Eq. 3.

$$t/q_t = t/q_e + (1/k_{2,ads}q_e^2) \tag{3}$$

Where q_e is the mass of metal adsorbed at equilibrium (mg g^{-1}), q_t the mass of metal at time t (min.), $k_{1,ads}$ the first-order reaction rate of adsorption (min.$^{-1}$), $k_{2,ads}$ the pseudo-second-order rate constant of adsorption (mg g^{-1} min.$^{-1}$)[21-22].

The results of Figures 4 and 5 for both algae concentrations *i.e.* 112.5 and 200 mg/L for two models were found in Table 1. The close agreement between the experimental q_e (mg g^{-1}) values and the estimated q_e (mg g^{-1}) values from pseudo second-order kinetic model suggested kinetic data followed the pseudo-second order. Also the coefficient of correlation (R^2) for the pseudo second-order kinetic model is more suitable than the pseudo-first-order model[23-24].
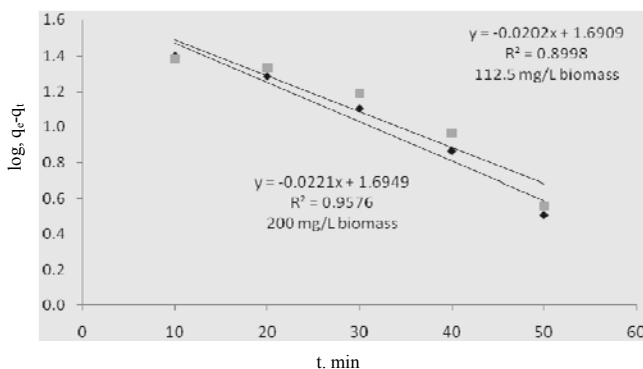
Figure 4. Pseudo-first-order sorption kinetic plots on Cd(II) uptake for 112.5 mg/L and 200 mg/L of *Laurencia papillosa* (initial concentration = 150 ppm, biomass = 25 mg/L, temperature = 25 °C, *p*H = 8)
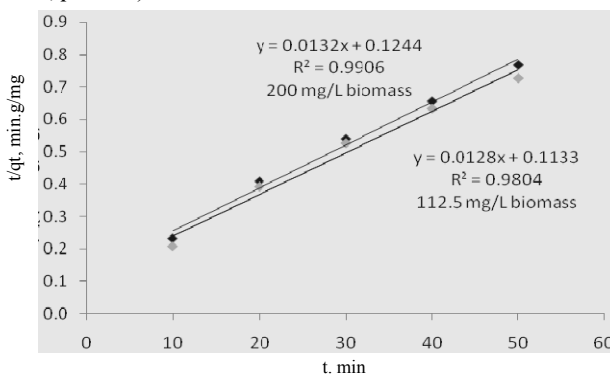
Figure 5. Pseudo-second-order sorption kinetic plots on Cd(II) uptake for 112.5 mg/L and 200 mg/L of *Laurencia papillosa* (initial concentration = 150 ppm, biomass = 25 mg/L, temperature = 25 °C, *p*H = 8)

Table 1. Comparison of the kinetic results for experimental, pseudo-first order and pseudo-second order of Cd(II) uptake by *Laurencia papillosa*

| parameter	Experimental	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Algae concentration mg L^{-1}	q_{eexp} mg g^{-1}	q_{ecal} mg g^{-1}	$K_{2, ads}$ g mg^{-1} min^{-1}	R^2	q_{ecal} mg g^{-1}	$K_{2, ads}$ g mg^{-1} min^{-1}	R^2
112.5	72.4	49.1	0.046	0.900	78.1	1.44×10^{-3}	0.980
200	68.3	49.5	0.051	0.958	75.8	1.40×10^{-3}	0.990

Adsorption isotherms

Equilibrium studies in adsorption give the capacity of adsorbent. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms[25,26]. In order to study the adsorption isotherm, Langmuir and Freundlich isotherm models were used more than the others such as Temkin, Dubinin−Radushkevich and Sips[27-29]. The saturated monolayer Langmuir isotherm is expressed as:

$$q_e = q_{max} bC_e /(1 + bC_e) \qquad (4)$$

Where q_{max} (mg g^{-1}) is the amount of adsorption corresponding to complete monolayer coverage, *i.e.*, the maximum adsorption capacity and b (L mg^{-1}) are the Langmuir constant. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous surface sites within the adsorbent and has found successful application in many sorption processes[30]. On the other hand, Freundlich isotherm is expressed as:

$$q_e = K_f C_e^{1/n} \qquad (5)$$

In this equation, K_f (L g^{-1}) and n are the constants to be determined from this model. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. It assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich constants indicate the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption respectively[31-32]. We plotted corresponding Langmuir and Freundlich curve in Figures 6 and 7. The Langmuir model is better than the Freundlich model, because of the suitable value of regression constant (R^2) as shown in Table 2.
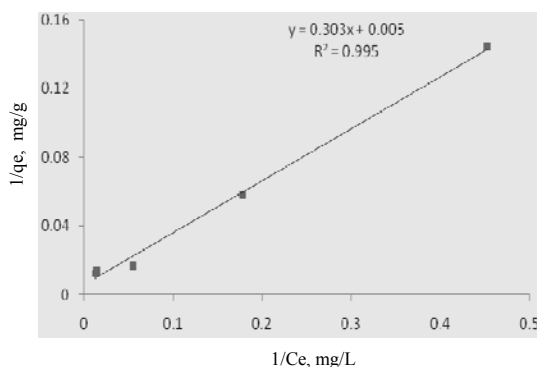
Figure 6. Langmuir adsorption isotherm for Cd(II) uptake on *Laurencia papillosa* (initial concentration = 8 ppm, biomass = 200 mg/L, temperature = 40 °C, contact time = 40 minute)
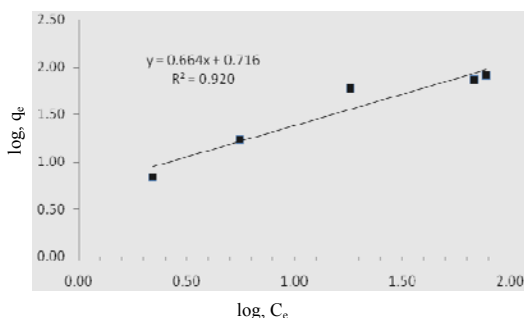
Figure 7. Freundlich adsorption isotherm for Cd(II) on *Laurencia papillosa* (biomass = 112.5 mg/L, temperature = 40 °C, contact time = 40 minute)

Table 2. Comparison of Langmuir and Freundlich isotherm parameters for Cd(II) uptake by *Laurencia papillosa*

Freundlich isotherm		Langmuir isotherm	
K_f mg g^{-1}	5.20	q_{max} mg g^{-1}	172.4
1/n	0.664	b L mg^{-1}	0.019
R^2	0.920	R^2	0.995

Conclusion

Biosorption properties of *Laurencia papillosa* were changed as a function of *p*H, temperature and concentration of algal dosage. The removal of cadmium(II) increased with increasing temperature until 60 °C, after that the biological ability of biomass and absorbance decreased.

We have concluded that the optimum *p*H was 5 and the biosorption increased with increasing algal dosage because of greater availability of biosorbent. Also the biosorption rate of cadmium(II) was relatively rapid in the first 20 min for solutions with high initial concentration of cadmium(II) and then the rate decreased gradually. The kinetic data followed the pseudo-second order. Furthermore adsorption isotherm fit to Langmuir model. So that adsorption takes place with limited levels homogeneous site of *Laurencia papillosa*.

Acknowledgement

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