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Removal of nickel from wastewater by using *Colpomenia* as brown algae biomass

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ABSTRACT

The effects of *pH*, temperature, biosorption time and metal ion concentration were considered for removal of nickel from wastewater. The kinetic of biosorption of Ni(II) from aqueous solution by using *Colpomenia* were studied. The isotherm models for equilibrium adsorption data were investigated.

KEYWORDS

Biomass;
Colpomenia;
Isotherm;
Nickel;
Wastewater.

INTRODUCTION

The contamination of water by toxic heavy metals is a worldwide problem[1]. The heavy metals tend to persist indefinitely, circulating and eventually accumulating throughout the food chain. These metals can be toxic to microbial population at sufficiently high concentration[2-4]. Heavy metal solutions are widely used in industrial activities such as metal finishing, electroplating, painting, dying, photography, surface treatment, printed circuit board manufacture[5]. Mining activities, agricultural runoff, industrial and domestic effluents are mainly responsible for the increase of metallic species released into the environment[6].

Ni(II) is a non-essential element that can be highly phytotoxic. This element has deleterious impacts on soil quality and mineral nutrition cycle. Ni(II) ranks the highest in terms of damage to plant growth and human health within the toxic heavy metals. Moreover, its uptake and accumulation in plants poses a serious health threat to humans via the food chain. The presence of excessive amounts of Ni(II) in soil commonly elicits many stress symptoms in plants, such as reduction of growth, especially root growth, disturbances in mineral nutrition and carbohydrate metabolism and may thus strongly reduce biomass production[7]. Ni(II) is carcinogenic, mutagenic and strong oxidizing agent which irritates plant and animal tissues even in small quantities. It diffuses rapidly through soil and aquatic environments as readily passing through skin[8].

Different effective methods have been reported for removing or reducing Ni(II) toxicity by some researchers. Chemical precipitation, oxidation/reducation, mechanical filtration, ion exchange, membrane separation and carbon adsorption are among the variety of treatment processes widely used for the removal of toxic heavy metals from the waste streams. In recent years biosorption has been recognized as an effective method of deduction of metal contamination in surface water and in industrial effluents[5]. Biosorption process are employed the natural origin solids for binding the heavy metals. Biosorption method used for treat industrial effluents, because of its low cost and high metal binding capacity[9].

The present study is undertaken to investigate the effect of different experimental parameters such as *p*H, temperature, contact time, initial concentration of Ni(II) and biomass dose on sorption process. Additionally, the equilibrium isotherm and the uptake kinetics are studied

EXPERIMENTAL

Study area and biomass preparation

The *Colpomenia* were sampled from northwestern (near the Bushehr Province coastline) part of the Persian Gulf. *Colpomenia* was collected from Persian Gulf coast of Boushehr. After harvesting from the sea, this was washed several times using deionized water to remove the sand particles and salts, then dried in an oven at 60^0C until constant weight. Dry biomass was chopped and sieved for biosorption experiments.

Nickel solutions

Stock nickel solution (150 mg/L) was prepared by dissolving 171.135 mg of $Ni(NO_3)_2.6H_2O$ (Merck) in 500 mL of deionized water. Different concentrations of nickel solutions (20, 50, 75, 100, 125 and 150 ppm) were prepared by adequate dilution of the stock solution with deionized water. The initial *p*H was adjusted with 0.1N HCl and 0.1N NaOH.

Analytical methods

The nickel solution and *Colpomenia* as biomass were in contact in specific time and then filtered. The concentration of nickel was determined by Varian SpectrAA.200 atomic absorption spectrometer.

Experimental procedure

The experiments were done at *p*H 1, 2, 3, 4, 5, 6, 7, 8 and 9 and 60 min contact time with different initial concentrations (20, 50, 75, 100, 125 and 150 ppm) for Ni(II) and 200 mg/L of biomass at different temperatures intervals (25, 35, 45, 55 and 65 ^{0}C).

Equilibrium isotherm

Modeling of equilibrium data was done using most widely used Langmuir and Freundlich isotherm models[10,11]. In the Langmuir model, maximum monolayer adsorption capacity, q_{max} (mg/g) and Langmuir adsorption constant, K_L (L/mg) were determined from equation 1.

$$\frac{1}{q_e} = \frac{1}{q_{max}k_L}\frac{1}{c_e} + \frac{1}{q_{max}} \tag{1}$$

Where q_e (mg/g) was the metal ion sorbed and C_e (mg/L) was the equilibrium concentration of metal ions solution. The heterogeneous adsorption capacity, q_e (mg/g) of *Colpomenia* for Ni(II) was determined by Freundlich isotherm that have shown in following equation 2.

$$log\, q_e = \frac{1}{n} log\, c_e + log\, k_F \tag{2}$$

Where k_F (mg/L) and n were Freundlich constants.

Metal uptake

The metal uptake, q_e (mg/g), milligram of metal adsorbed per gram of adsorbent was determined according to equation 3.

$$q_e = \frac{(C_i - C_e)\,V}{1000w} \tag{3}$$

where C_i (mg/L) was the initial metal concentration, C_e (mg/L) was the metal concentrations at various time intervals, V (mL) was the volume of the solution and w (g) was the mass of sorbent.

RESULTS AND DISCUSSION

Effect of *p*H on biosorption

Many parameters can be influenced on the uptake of heavy metals in biosorption, such as the biomass type, pretreatrnent methods, ionic strength, and solution *p*H. Most biosorption studies have observed large variations in the biosorption capacities with different solution *p*H values[12-14]. The *p*H of the aqueous solution was an important controlling parameter in the adsorption process[15].

Maximum uptake was observed at *p*H=2 as shown in Figure 1. The strong *p*H dependence of Ni(II) biosorption could be attributed to more pronounced electrostatic attraction taking place between the biomass and the metal ions. Marine algae contain high content of ionizable groups on the cell wall polysaccharides, which responsible for depending upon the biosorption process with the *p*H[16].

The effect of *p*H on biosorption, can be related to competition of several mechanisms involved in biosorption such as metal speciation in solution, changes of ionic forms of the functional groups involved in biosorption, the protonation of the binding sites and metal precipitation[18].

Effect of temperature on biosorption

Five different temperatures, i.e. 25, 35, 45, 55 and

65 ^{0}C were considered for the effect of the temperature on the adsorption capacity. From Figure 2, it can be observed that the maximum Ni(II) uptake was observed in 55 ^{0}C. By increasing temperature from 55 to 65 ^{0}C the amount of Ni(II) uptake were decreased that can be related to the destruction of ionizable groups on the cell wall polysaccharides in high temperature.

The effect of contact time on biosorption

In this study, with increasing time, the uptake was increased as shown in Figure 3. The maximum uptake for Ni(II) was observed at 10 minutes initial. After 55 minutes, Ni(II) uptake rate was steady and equable. This was due to the saturation of the sorption sites on adsorbent with Ni(II).

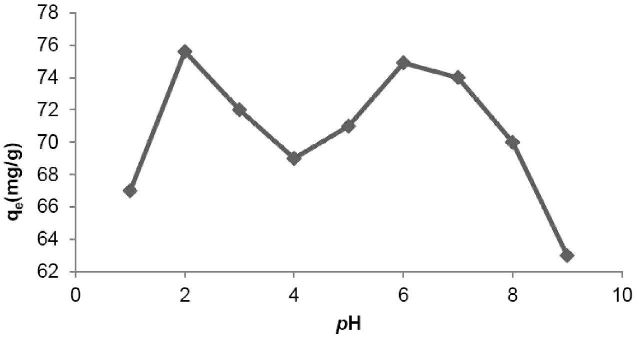

Figure 1 : Effect of *p*H on the biosorption of Ni(II)

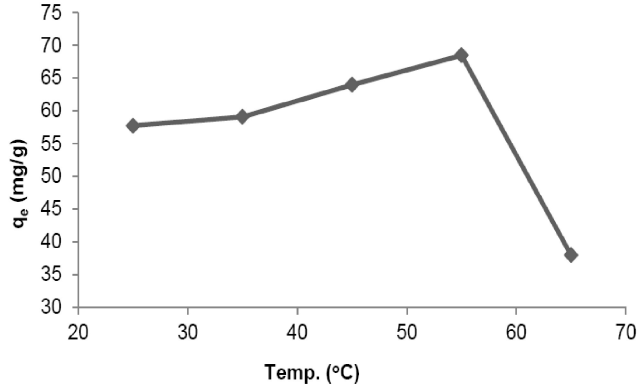

Figure 2 : Effect of temperature on the biosorption of Ni(II)

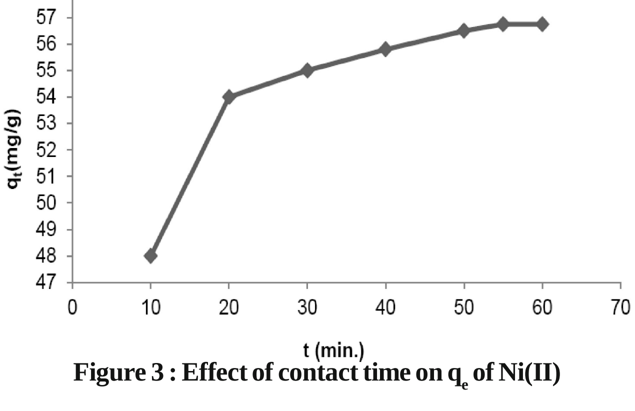

Figure 3 : Effect of contact time on q_e of Ni(II)

Adsorption kinetics studies

The kinetics of adsorption describes the rate of nickel ions uptake on alga which controls the equilibrium time. Two kinetics models, pseudo first order in equation 4 and pseudo second-order models in equation 5 were used to analyze the sorption data and to identify the mechanism of solute adsorption onto sorbents[19,20].

$$log(q_e - q_t) = log\, q_e - \frac{k_{1,ads}t}{2.303} \quad \textbf{(4)}$$

$$\frac{t}{q_t} = \frac{1}{k_{2,ads}q_e^2} + \frac{t}{q_e} \quad \textbf{(5)}$$

where q_e (mg/g) was the mass of metal adsorbed at equilibrium, q_t (mg/g) was the mass of metal at time t (min.), $k_{1,ads}$ (1/min.) was the pseudo-first-order rate constant of adsorption, $k_{2,ads}$ (g/mg min.) was the pseudo-second-order rate constant of adsorption.

Both pseudo first-order sorption kinetics as shown in Figure 4 and pseudo second-order sorption kinetics as shown in Figure 5 were plotted for adsorption kinetics studies of Ni(II) on *Colpomenia* biomass.

A comparison between two kinetic models in TABLE 1 suggested that: (1) the coefficient of correla-

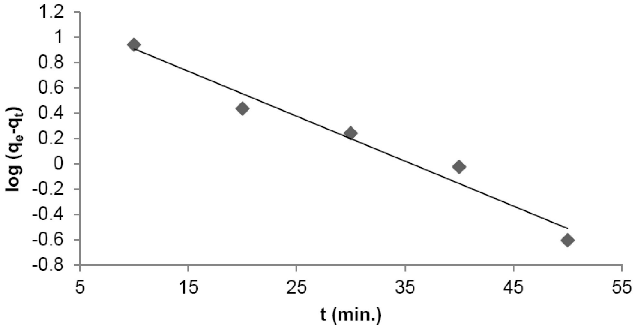

Figure 4 : Pseudo first-order sorption kinetics plot of Ni(II) on *Colpomenia*

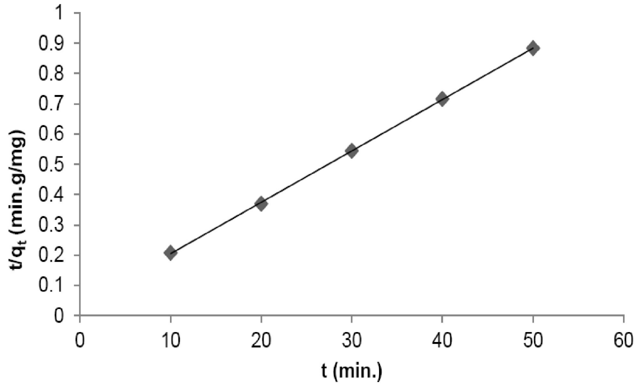

Figure 5 : Pseudo-second-order sorption kinetics plot of Ni(II) on *Colpomenia*

tion (R^2) for the pseudo-second-order kinetic model was much higher in comparison to pseudo-first-order model (2) the close agreement between the experimental q_e (mg/g) values and the estimated q_e (mg/g) values from pseudo-second-order kinetic model. These facts suggest that obtained Ni(II) kinetic data followed the pseudo-second order kinetic model which describes the biosorption as the rate limiting step.

Effect of initial metal concentration

The metal removal using *Colpomenia* corresponding to different initial metal concentrations (20, 50, 75, 100, 125 and 150 mg/L was shown in Figure 6. The increase in initial concentration of Ni(II), results in the increase uptake capacity of Ni(II). The increase in initial metal concentration, results in the increased uptake capacity, because of the higher initial concentrations, the higher number of moles of Ni (II) is available to the surface area. This sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations[21].

TABLE 1 : Comparison between pseudo-first-order and pseudo-second-order kinetic models for Ni(II) sorption by *Colpomenia*

Experimental value for q_e = 56.75 (mg/g)					
Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
q_e (mg/g)	$K_{1,\,ads}$ (1/min)	R^2	q_e (mg/g)	$K_{2,\,ads}$ (g/mg min.)	R^2
18.4	0.0817	0.9674	58.8	0.0082	0.9999

Equilibrium isotherm

Modeling of equilibrium data was done using most widely used Langmuir and Freundlich isotherm models[22,23]. In the Langmuir isotherm, maximum monolayer adsorption capacity, q_{max} (mg/g) was determined from Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_{max}K_L}\frac{1}{C_e} + \frac{1}{q_{max}} \tag{6}$$

Where q_e (mg/g) is the absorbed metal ion, C_e (mg/L) is the equilibrium concentration of metal ions solution and K_L (L/mg) is the Langmuir adsorption 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[24].

In the Freundlich isotherm, the heterogeneous adsorption capacity, q_e (mg/g) was determined from Freundlich equation:

$$\log q_e = \frac{1}{n}\log c_e + \log k_F \tag{7}$$

Where both k_F(mg/g) and n are the Freundlich constants. 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[25,26].

The linearized regression plot of Langmuir isotherm is presented in Figure 7 and the linearized regression plot of Freundlich isotherm is presented in Figure 8,

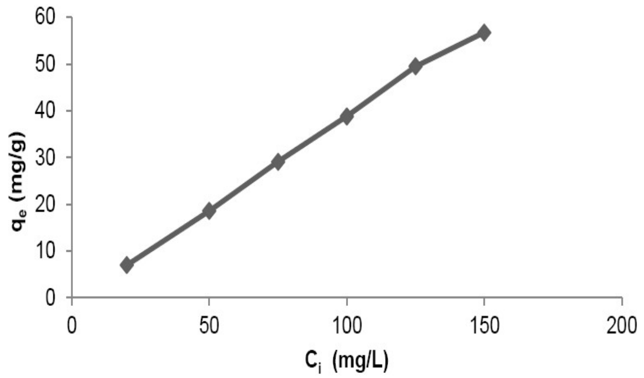

Figure 6 : Effect of initial metal concentration on Ni(II) by *Colpomenia*

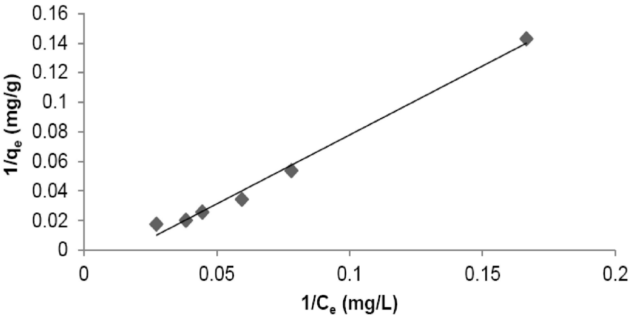

Figure 7 : Langmuir adsorption isotherm for Ni(II)

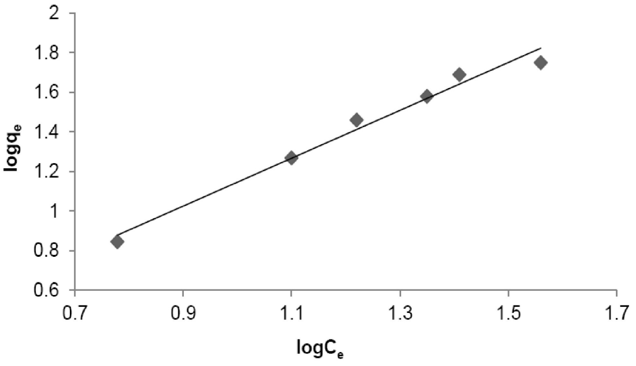

Figure 8 : Frendulich adsorption isotherm for Ni(II)

TABLE 2 : Comparison of Langmuir and Freundlich isotherm parameters for Ni(II) uptake by *Colpomenia*

Condition	Langmuir isotherm parameters			Freundlich isotherm parameters		
C_0 (mg/L)	q_{max} (mg/g)	K_L (l/mg)	R^2	K_F (mg/g)	1/n	R^2
150	65.00	0.0165	0.9901	0.8667	1.208	0.9801

respectively.

A comparison between two isotherm models in TABLE 2 suggested that the data could be well modeled according to the Langmuir adsorption isotherm.

CONCLUSION

The uptake of Ni(II) showed with an increase in *p*H from 1 to 2. The strong *p*H dependence of Ni(II) biosorption observed in this study could be attributed to more pronounced electrostatic attraction taking place between the biomass and the metal ions. The optimum temperature for absorption was find in 55 ^{0}C. The adsorption kinetic data can be described by the pseudo second-order kinetic models. Also, the equilibrium data of adsorption were in good agreement with the Langmuir's model.

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