Removal of nickel as toxic heavy metal using *Entromorpha* as green alga

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ABSTRACT

The biosorption of Ni(II) from aqueous solution by using *Enteromorpha* as cheap green alga were considered. The effects of pH, temperature, contact time, initial concentration of Ni(II) and biosorbent dose were studied. This study shows that *Enteromorpha* can be used for removal of Ni(II) from aqueous solution wastewater. A second-order equation designated for kinetic of the biosorption and Langmuir isotherm model are fitted for equilibrium of the adsorption data. © 2014 Trade Science Inc. - INDIA

INTRODUCTION

The presence of the heavy metals due to industrial activities is of serious challenges for environment. Metal finishing, electroplating, painting, dying, photography, surface treatment and printed circuit board manufacture are involved in these industrial activities[1]. Heavy metals released into the environment by technological activities tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, becoming a serious threat to the environment[2].

These metals are non-biodegradable and maintained indefinitely in bulk of humans, animals and plants. These metals can be toxic to microbial population at sufficiently high concentration. However, some metals such as silver, mercury, cadmium and copper are markedly more toxic even at very low levels[3-6].

The uptake and accumulation of Ni(II) in plants poses a serious health threat to humans via the food chain. The presence of excessive amounts of Ni(II) in soil commonly produces many stress symptoms in plants, such as reduction of root growth, disturbances in mineral nutrition and carbohydrate metabolism[7]. Ni(II) is an oxidizing agent for plant and animal tissues even in small quantities.

It diffuses rapidly through soil and aquatic environments as readily passing through skin[8].

Chemical precipitation, redox reactions, 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[9]. In the biosorption, a solids of natural origin i.e. biosorbent, are employed for removal of heavy metals. It is a promising alternative method to treat industrial effluents, mainly because of its low cost and high metal binding capacity[10].

We were investigated the effect of different experimental parameters such as pH, temperature, contact time, initial concentration of Ni(II) and biosorbent dose on sorption process. Moreover, the equilibrium isotherm and the uptake kinetics were studied.

MATERIALS AND METHODS

Biomass preparation

Enteromorpha was collected from the Persian Gulf

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on Bushehr Island. Before use, it was washed several times with distilled water to remove dirt. The clean alga was dried in an oven at 60 ºC for 24 h and powdered to maximize the surface of absorption. 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 $Ni(NO_3)_2.6H2O$ (Merck) in 500 mL of deionized water. Different concentrations of nickel solutions (20, 50, 75, 100, 125 and 150 ppm) were prepared by dilution of the stock solution with deionized water. The initial pH is adjusted with 0.1N HCl and 0.1N NaOH.

Experimental procedure

The samples of biomass were filtered and analyzed for heavy metals by atomic absorption (Specter AA-200). The experiments were done at *p*H 1, 2, 3, 4, 5, 6, 7 and 8 and contact time of 60 minute 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 ^0C).

Metal uptake

The metal uptake q_e (milligram of metal adsorbed per gram of adsorbent) was calculated from the mass balance equation as following eq.

$$q_e = \frac{C_i - C_e}{1000w} \tag{1}$$

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.

Equilibrium isotherm

Modeling of equilibrium data was done using most widely used Langmuir and Freundlich isotherm models[11,12].

In the Langmuir isotherm, maximum monolayer adsorption capacity, q_{max} (mg/g) was determined from Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_{max}K_L}\frac{1}{C_e} + \frac{1}{q_{max}} \tag{2}$$

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[13].

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

$$\log q_e = \frac{1}{n}\log c_e + \log k_f \tag{3}$$

Where both k_f 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[14,15].

RESULTS AND DISCUSSION

Effect of pH on biosorption

The uptake of Ni(II) in verse of pH showed in Figure 1. An increase in pH=2, followed by a decrease in PH=3 and smooth increase until pH=7 were observed and finally decrease in pH=8.
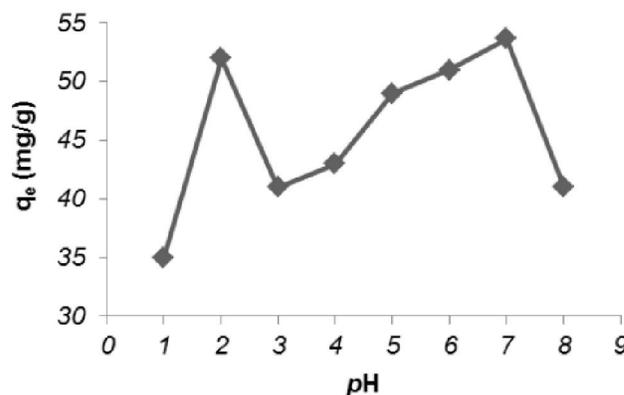

Figure 1 : The effect of pH on the biosorption of Ni (II)

Most biosorption studies have observed large variations in the biosorption capacities with different solution pH values[16-18]. The pH of the aqueous solution is an important controlling parameter in the adsorption process. Marine algae contain ionizable carboxyl groups from mannuronic and guluronic acids on the cell wall polysaccharides, which could be affected by changes in the pH[19].

At high solution pH values, the metal speciation in

solution may become an important factor. The increase in heavy metal uptake has been attributed to reduced solubility and metal precipitation[20,21] reported that the zero-point for alga cell (Sargassum) was at pH 3.0, above which the algal cells could develop a net negative charge.

At very low solution pH, the concentration of the hydrogen ion is high, and it can directly compete with the heavy metal ions. The protonation of the binding sites or the ionized functional groups on the cell wall make the binding site inaccessible to heavy metal cations[21]. As a result, the trend in variations may be mechanism or medium effects[22]. The metal speciation in solution, changes of ionic forms of the functional groups and the competition effects of hydrogen ions are amongst these mechanisms[21].

Effect of temperature

The effect of the solution temperature on the adsorption capacity for Ni(II) ions solution showed in Figure 2. Five different temperatures of 25, 35, 45, 55 and 65°C were considered. It can be observed the removal percent was slightly increased for Ni(II) uptake at 35°C and 45°C. Maximum Ni(II) uptake was observed in 45°C. By increasing temperature from 45°C to 65°C the amount of Ni(II) uptake were decreased. This variation is not be interpreted by empirical Arrehnius or theoretical Eyring equation[22]. Hence we may be concluded that a number of mechanisms are included for Ni(II) uptake.
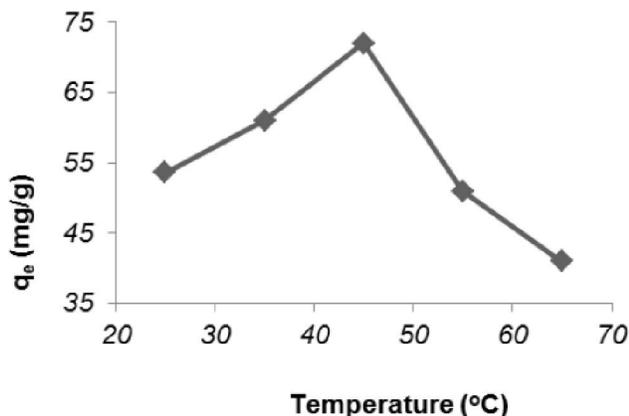

Figure 2 : The effect of temperature on the biosorption of Ni(II)

The effect of contact time

The effect of the contact time on the adsorption capacity for Ni(II) ions solution showed in Figure 3. In this study, with increasing time, the uptake for Ni(II) was increased. 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).
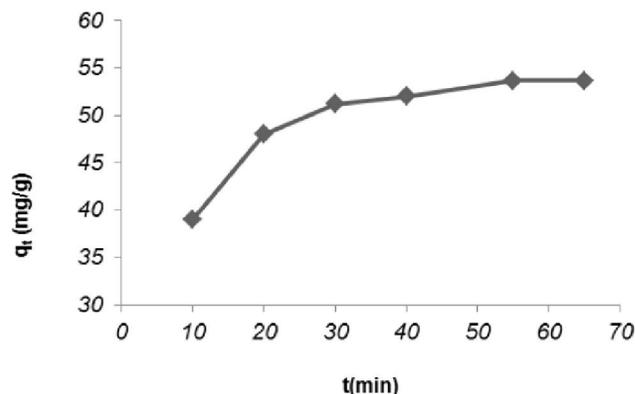

Figure 3 : The effect of contact time on q_e of Ni(II)

Adsorption kinetics studies

Two kinetics models, pseudo first order and pseudo second-order models are used to analyze the sorption data and to identify the mechanism of solute adsorption onto sorbents[23,24].

The linearized form of first order Lagergren equation is given as Eq. 4.

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

and the pseudo second order model is given as Eq. 5.

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

where q_e (mg/g) is the mass of metal adsorbed at equilibrium, q_t (mg/g) is the mass of metal at time t(min.), $k_{1,ads}$ (1/min) is the first-order reaction rate of adsorption, $k_{2,ads}$ (g/mg.min) the pseudo-second-order rate constant of adsorption. A comparison between two kinetic models in TABLE 1 suggested that (1) the coefficient of correlation (R^2) for the pseudo-second-order kinetic model is 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.

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

Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order kinetic model		
q_e (mg/g)	$K_{1,ads}$ (min^{-1})	R^2	q_e (mg/g)	q_e (mg/g)	$K_{2,ads}$ (g mg min^{-1})	R^2
15.82	0.5481	.9702	53.65	55.86	0.0058	.9998

Effect of the initial metal concentration

The uptake of Ni(II) using Entromorpha corresponding to different initial metal (20, 50, 75, 100, 125 and 150(mg/L)) is shown in Figure 4. The increase in initial metal concentration, results in the increased uptake capacity, because of the higher the initial concentrations, the higher number of moles of Ni(II) available to the surface area. This sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations[25].
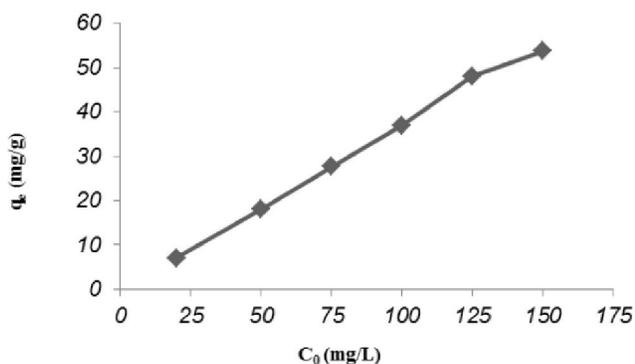

Figure 4 : The effect of initial metal concentration on Ni(II) by entromorpha

Equilibrium isotherm

Modeling of equilibrium data was done using most widely used Langmuir and Freundlich isotherm models[26,27].

In TABLE 2, comparison between Langmuir and Freundlich isotherm data is tabulated. The isotherm experimental results showed that the data could be well modeled according to the Langmuir adsorption isotherm.

Mechanism of adsorption

The prediction of the rate-limiting step is an important factor to be considered in the adsorption process. In the solid–liquid sorption process, the solute transfer is usually characterized by external mass transfer [boundary layer diffusion), or intra-particle diffusion, or both.

The external mass transfer coefficient, β_L (cm/s) of Ni(II) in the liquid film boundary can be evaluated by fallowing equation:

$$\ln\left(\frac{C_t}{C_i} + \frac{1}{1+mk_L}\right) = \ln\left(\frac{mk_L}{1+mk_L}\right) - \left(\frac{1+mk_L}{mk_L}\right)\beta_L S_g t \qquad (6)$$

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

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	161.3	0.007153	.9969	1.067	1.083	.9822

where C_t (mg/ L) and C_0 (mg/ L) are the concentrations of the sorbent at time t and time zero, respectively, K_a (L/g) is a constant defined as the product of the Langmuir constants. The m (g /L) and Ss (cm²) are the adsorbent mass and surface area, respectively[28]. The coefficient β_L can be calculated from the slope of the regression line of the plot of $\ln[(C_t/C_0)-(1/(1+mK_L))]$ versus t. As shown in Figure 5, no linear relation is observed and the regression coefficient was low. This result clearly indicates that the uptake rate is not controlled by mass transfer through a liquid film boundary such as convective mass transfer.

The possibility of intra-particular diffusion is explored by fallowing equation:

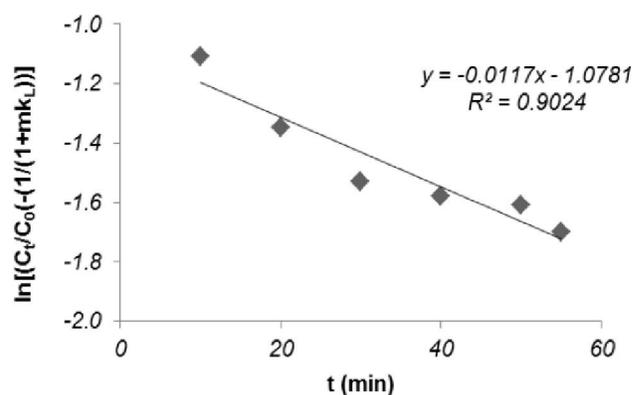$$q_t = k_{dif}t^{\frac{1}{2}} + C \qquad (7)$$

Figure 5 : The plot for evaluating the mass transfer through the boundary film

where C(mg/g) is the intercept and K_{dif} (L/mg) is the intra-particle diffusion rate constant. The values of q_t (mg/g) correlated linearly with values of $t^{1/2}$ (min$^{1/2}$) and the rate constant K_{dif} (L/mg) directly evaluated from the slope of the regression line[29]. The larger the intercept is the higher the thickness of the boundary layer against to the external mass transfer. As shown in Figure 6, no linear relation is observed and the regression coefficient was low. This result clearly indicates that the uptake rate is not only intra-particle diffusion for solute transfer.
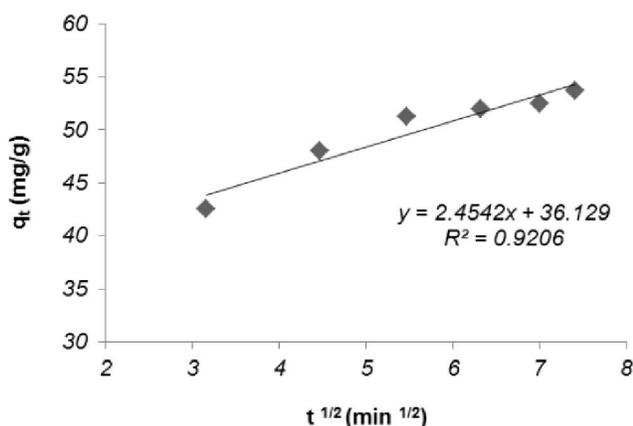

Figure 6 : The plots for evaluating intra-particle diffusion rate constant

Thus, the uptake of nickel ions can be controlled by both the mass transfer through the boundary film and the intra-particular mass transfer.

CONCLUSION

The uptake of Ni (II) showed an maximum in pH=7. The strong pH dependence of Ni(II) biosorption observed in this study could be attributed to more pronounced electrostatic attraction taking place between the biosorbents and the metal ions. Increase uptake of Ni(II) with the increase of algae quantity could be due to the formation of biosorbent aggregates at higher biomass concentration, which in turn could reduce the effective surface area available for the biosorption. The biosorbent showed a different adsorption capacity, which might presumably be due to the presence of the different number of cell surface binding sites. The adsorption kinetic data can be described by the pseudo second-order kinetic models. Also, the equilibrium data of adsorption are in good agreement with the Langmuir's

model. Moreover, both the mass transfer through the boundary film and the intra-particular mass transfer are important for solute transfer.

ACKNOWLEDGMENT

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