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## Biosorption of Copper, Cobalt and Nickel by Marine Brown Alga *Sargassum sp.* in Fixed-Bed Column

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**Abstract:** The biosorption of copper, cobalt and nickel by marine brown alga *Sargassum sp.* were investigated in a fixed-bed column (temperature=30°C; different pH). Langmuir and Freundlich sorption models were used to represent the equilibrium data. The maximum Cu<sup>2+</sup> uptake was obtained at pH 4 and the optimum Co<sup>2+</sup> and Ni<sup>2+</sup> uptake were at pH 7. Different dosage of biosorbent did not have an effect on the results, but the 3.5 and 5 g of biosorbent were shown higher uptake. The metal removal rates were rapid, with about 80% of the total adsorption taking place within 40 min.

**Key words:** Biosorption, copper, cobalt, nickel, bed column, *Sargassum sp.*

### INTRODUCTION

Protection of the environment is a major concern of human communities. Development and various related activities release lots of poisonous materials into the environment and heavy metals are the most dangerous of all (Alloway and Ayres, 1997). Biosorption is a proven technology for the removal of heavy metal ions from synthetic and real industrial effluents. Several researchers investigated numerous biomass types and proposed excellent metal biosorbents including bacteria, fungi, seaweed. Among the most promising biomaterials studied, seaweed are found to be very efficient and bind variety of metals (Volesky and Holan, 1995).

The biosorption capability of algae has been attributed mainly to the cell wall. Some successfully used and best performed seaweed for cobalt and nickel biosorption include *Ascophyllum nodosum* for cobalt removal and *Sargassum fluitans* for nickel removal. Volesky *et al.* (2003) employed a simple polyacrylic tube packed with raw *Sargassum filipendula* biomass to study its copper biosorption behavior in ten consecutive sorption-desorption cycles.

Modeling of biosorption isotherm data is important for predicting and comparing biosorption performance. The

two widely accepted for single solute systems are the Langmuir and Freundlich isotherms (Vijayaraghavan *et al.*, 2005).

The objective of the present study was to assess the potential of *Sargassum sp.* (brown macroalgae) for the biosorption of copper, cobalt and nickel. The equilibrium isotherm, the uptake kinetics and the effect of pH, retention time, initial concentrations and dosage of biosorbent were studied.

### MATERIALS AND METHODS

**Biomass:** *Sargassum SP.* a brown macroalgae collected from the Persian Gulf on Queshm Island, was used as the biomass. The algae was dried in the sun, transferred to the lab. Cut in pieces (d=2-5 mm), washed with double distilled water to wash out any mineral contaminants and then dried at 60°C to the fixed weight. A part of this biomass was examined for a sign of the metals in question to be used as blank. The tests were carried out at the chemical laboratory of the Islamic Azad University, North Tehran Branch since May to October 2006.

**Preparation of ions solutions:** Solutions of Cu(II), Co(II) and Ni(II) in CuCl<sub>2</sub>·2H<sub>2</sub>O (99%), distilled water were prepared using:

Co (NO<sub>3</sub>)<sub>2</sub> (97%), NiCl<sub>2</sub> · 6H<sub>2</sub>O (97%)

**Column:** Sorption experiments were conducted in a glass column with an internal diameter of 2 cm and 35 cm in length.

**Experimental procedure:** These experiments were done at pH 2, 4, 6, 7, 8, 10 and 15, 40 min retention time with different initial concentrations (50, 100 and 150 mg L<sup>-1</sup>) for copper and cobalt, (25, 50 and 75 mg L<sup>-1</sup>) for nickel and 2.5, 3.5, 5 g of biomass at a constant temperature. Samples (1 mL) were removed at different times intervals (15 and 40 min) and analyzed for heavy metals concentration by atomic absorption spectrometer (GBC-932).

The equilibrium concentration of metal ions in the solid phase (q<sub>e</sub>) was calculated from initial concentration (C<sub>0</sub>) and the equilibrium concentration (C<sub>e</sub>) in each column using the following equation:

$$q_e = (C_0 - C_e) V/M \quad (1)$$

Where V the solution volume (mL) (using 25, 30 and 50 mL of metal solution for 2.5, 3.5 and 5 g of biomass at constant pH and temperature) and M the mass of biosorbent (g).

**Equilibrium studies:** In order to optimize the design of a sorption system for the removal of metals from effluents, it is important to establish the most appropriate correlation for equilibrium curves. Experimental isotherm data acquired at different pH conditions were fitted to 10 different models of sorption isotherms: Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Flory-Huggins, Redlich-Peterson, Sips, Khan, Radke-Prausnitz and Toth isotherm models (Vijayaraghavan *et al.*, 2006).

**Langmuir isotherm:** The Langmuir adsorption model was used to correlate the isotherm data obtained at constant solution pH value

$$q_e = b \cdot q_{max} \cdot C_e / (1 + b \cdot C_e) \quad (2)$$

Where q<sub>e</sub> is the amount of ions adsorbed at equilibrium (mg g<sup>-1</sup>), C<sub>e</sub> is the ion concentration in solution at equilibrium (mgL<sup>-1</sup>), q<sub>max</sub> is the maximum adsorption capacity and b is an affinity constant.

**Freundlich isotherm:** The Freundlich adsorption model was used as follow :

$$q_e = K_f \cdot C_e^{1/n} \quad (3)$$

Where K<sub>f</sub> and n are the Freundlich constants (Sheng *et al.*, 2004).

**Adsorption Kinetics:** In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. These kinetic models included the first-order equation and second-order equation .

**First-order equation:** First- order equation of Lagergren is generally expressed as follows :

$$dq_t/dt = k_1 (q_e - q_t) \quad (4)$$

Where q<sub>e</sub> and q<sub>t</sub> are the sorption capacity at equilibrium at time t , respectively (mg g<sup>-1</sup>) and K<sub>1</sub> is the rate constant of first-order sorption (min<sup>-1</sup>)

The integrated form of Eq. (4) becomes :

$$\text{Log} (q_e - q_t) = \text{Log} (q_e) - (k_1/2.303) t \quad (5)$$

A plot of Log (q<sub>e</sub> - q<sub>t</sub>) versus (t) indicate a straight line of slope (k<sub>1</sub>/2.303) and an intercept of Log (q<sub>e</sub>)

**Second-order equation:** Second-order chemisorption kinetic rate equation is expressed as :

$$dq_t/dt = k_2 (q_e - q_t)^2 \quad (6)$$

Where q<sub>e</sub> and q<sub>t</sub> are the sorption capacity at equilibrium at time t , respectively (mg g<sup>-1</sup>) and K<sub>2</sub> is the rate constant of second-order sorption (g mg<sup>-1</sup> min)

The integrated form of Eq. (6) becomes :

$$1/(q_e - q_t) = 1/(q_e) + k_2 t \quad (7)$$

which has a linear form:

$$t/q_t = 1/k_2 \cdot q_e^2 + (1/q_e) t \quad (8)$$

A plot of t/q<sub>t</sub> versus t indicate a straight line of slope (1/ q<sub>e</sub>) and an intercept of (1/k<sub>2</sub> · q<sub>e</sub><sup>2</sup>) (Ag and Aktay *et al.*, 2002).

## RESULTS

**Effects of pH:** The pH of the metal solution usually plays an important role in the biosorption of metals. Preliminary

Table 1: Freundlich isotherm constants for Cu<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> adsorption

Metal	m (g)	pH	K <sub>f</sub>	n	R <sup>2</sup>
Cu	2.5	4.0	4.0 E-2	1.14	0.48
Cu	3.5	4.0	1.8 E-1	1.43	0.99
Cu	5.0	4.0	1.1E-4	0.34	0.89
Co	2.5	7.0	1.4 E-1	1.68	0.97
Co	3.5	7.0	1.3 E-1	1.54	0.99
Co	5.0	7.0	1.4 E-1	1.45	0.94
Ni	2.5	7.0	4.0 E-2	1.08	0.55
Ni	3.5	7.0	3.6 E-2	1.03	0.94
Ni	5.0	7.0	9.0 E-2	1.60	0.94

examination of *Sargassum SP.* on the basis of nickel, cobalt and copper biosorption potential revealed that highest nickel and cobalt uptake were observed at pH 7 and at pH 4 for copper. Further increase in pH resulted in decreased nickel, cobalt and copper uptake. This may be due to nature of binding sites in *Sargassum SP.* biomass. Also, hydrogen ion competition at low pH and solution chemistry of metals are other important factors responsible for variation of metal uptake at different pH values (Davis *et al.*, 2000).

**Effects of retention time and initial concentration:** The results of the different experiments showed that by increasing retention time, the remained concentration of heavy metals in the solution was reduced. Fifteen minutes retention time for removing the metal was enough. However, increase in retention time from 15 to 40 min resulted in decreased the remained concentration of heavy metals. Kinetic studies (at pH 4 for copper and at pH 7 for nickel and cobalt) showed that about 80 % of the total metal ions adsorption occurred within 40 min.

Also, by increasing initial concentration, uptake was increased. The maximum uptake for copper with initial concentrations 50, 100, 150 mg L<sup>-1</sup> at pH 4 were obtained 69, 81.2 and 91.14 % , for nickel with initial concentrations 25, 50 and 75 mg L<sup>-1</sup> at pH 7 were obtained 79.9, 88.0 and 84.1%, for cobalt with initial concentrations 50, 100 and 150 mg L<sup>-1</sup> at pH 7 were obtained 89.3, 88.0 and 83.0% .

**Adsorption equilibrium:** The isotherm experimental results showed that the data could be well modeled according to the Langmuir and Freundlich adsorption isotherm. The Langmuir constant (q<sub>max</sub>) is dependent on experimental conditions such as solution pH. Another important factor in evaluating sorbent performance is the initial gradient of the adsorption isotherm, since it indicates the sorbent affinity at low metal concentrations. In the Langmuir equation, this initial gradient corresponds to the affinity constant (b). A high value of the adsorption capacity (q<sub>max</sub>) and the affinity constant (b) under the

experimental conditions i.e., pH 7 for cobalt and nickel, pH 4 for copper were observed. The maximum capacities for copper, cobalt and nickel uptake ranged from 0.14 to 5.0 mg g<sup>-1</sup>, 1.99 to 3.12 and 2.0 to 5.0 mg g<sup>-1</sup>, respectively.

The Freundlich isotherm constants in Eq. (3) were then obtained and are presented in Table 1.

## CONCLUSION

The study indicated that the treated biomass of the *Sargassum SP.* could be used as an efficient biosorbent material for the treatment of Cu<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> is pH dependent and the optimum Cu<sup>2+</sup> uptake was obtained at pH 4 and the optimum Co<sup>2+</sup> and Ni<sup>2+</sup> uptake was at pH 7.

Different dosage of biosorbent did not have an effect on the results, but the 3.5 and 5 g of biosorbent were shown higher uptake. Sorption rate would be increased by increasing retention

Time from 15 to 40 min. Kinetic studies showed that about 80% of the total metal ions adsorption occurred within 40 min. Also, by increasing the initial concentration of the solution, uptake was increased.

The maximum uptake for copper with initial concentrations 50, 100 and 150 mgL<sup>-1</sup> at pH 4 were obtained 69, 81.2 and 91.14% , for nickel with initial concentrations 25, 50 and 75 mg L<sup>-1</sup> at pH 7 were obtained 79.9, 88.0 and 84.1% , for cobalt with initial concentrations 50 ,100 and 150 mgL<sup>-1</sup> at pH 7 were obtained 89.3, 88.0 and 83.0% .

The results showed that biosorption stages of Cu<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> follow from second-order kinetic model. Equilibrium data follow from Langmuir and Freundlich isotherms well. The high correlation coefficient showed that this method has been very suitable.

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