J. BIOL. ENVIRON. SCI.,
2012, 6(18), 271-279

Original Research Article

Biosorption of Cu (Ii) and Ni (Ii) Ions from Aqueous Solution by Marine Brown Algae *Sargassum angustifolium*

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Received: 14.09.2012; Accepted: 06.12.2012; Available Online: 25.01.2013

ABSTRACT

This study focused on the batch removal of Cu^{2+} and Ni^{2+} ions from an aqueous solution and wastewater using marine brown algae *Sargassum angustifolium*. With high capacities of metal biosorption and desorption, the biomass of *S. angustifolium* is promising as a cost-effective biosorbent for the removal of Cu^{2+} and Ni^{2+} from aqueous solution. According to X-ray photoelectron spectroscopic (XPS); the possible organic functional groups in the metal binding include carboxyl, amino, sulfhydryl and sulfonate groups. Langmuir, isotherm model were applied to describe the biosorption of the Cu^{2+} and Ni^{2+}onto *S. angustifolium* biomass. The maximum uptake of Cu^{2+} and Ni^{2+} ions by the *S. angustifolium* biomass under the optimal conditions was approximately 0.94 and 0.78 mmol/g dry alga respectively. According to result biomass of *S. angustifolium* could be used as an effective biosorbent for the treatment of Cu^{2+} containing aqueous solution.

Key Words: *Sargassum angustifolium,* nickel, copper, biosorbent

INTRODUCTION

As today`s technology progresses and increment in industrial activities, a high volume of wastewater containing heavy metal is released to the natural environment. Heavy metal poses a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature (Paul Chen and Yang, 2006). Copper ions are recognized to be one of the most widespread heavy metal contaminants in the environment (Ho and McKay, 2003). Nickel, like the majority of heavy metals, is toxic but it has been widely used in metallurgical and tanning industries. Nickel at trace amount may be beneficial as an activator of some enzyme systems but if the nickel ion intake over the permissible levels results in different types of diseases such as pulmonary fibrosis, lung cancer, renal edema, skin dermatitis and gastrointestinal disorder such as nausea, vomiting, diarrhea. In cases, governments may consider it necessary to remove some pollutants from the ecosystem; however, the economic cost of treatment may be very high, based on volume, concentration of metals, and salinity of wastewaters, making it impossible to use conventional technologies, such as precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, electrochemical treatment, and evaporation (Patron-Prado *et al.*, 2010). These processes may be ineffective or extremely expensive especially when the metals in solution are in the range of 1-100 mg l^{-1}. In this context, biosorption can be considered as an alternative technology for industrial wastewater treatment when the concentration of transition metals is low. Biosorption is based on the ability of biological materials to accumulate heavy metals from wastewater by physico-chemical pathways of uptake. It is a property of both living and dead organisms and their components. The biomass of brown algae of Sargassum genus is reported to possess a metal binding capacity superior to other organic and inorganic sorbents. Although actual wastewater treatment systems often have to deal with a mixture of heavy metals, most biosorption studies involving Sargassum and other biomasses only focus on the removal of heavy metal cations from metal solution(Davis *et al*.,2004; Vieira *et al*., 2007; Martins *et al*.,2006). Biosorption of metals involves several mechanisms that differ qualitatively and quantitatively, according to the species used, the origin of the biomass, and its processing procedure (Holan and Volesky, 1995). There are several chemical groups in biomass that can attract and sequester the metals: acetamido, amino, amido, sulfhydryl, sulfate, and carboxyl (Volesky, 1991; Schiewer and Volesky, 2000).

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Solution pH plays an important role. It can change the nature of metal speciation and thus affect the sorption. With a higher pH, cationic metal ion uptake is generally enhanced. Among the biosorbents are some species of the brown algae *Sargassum* that have proved to be a highly effective biosorbent because of their capacity to remove high metals at a relatively rapid rate (Davis *et al*., 2000). In the Persian Gulf of Iran, the genus *Sargassum* is an untapped resource that could be used for treating effluents from mining activity (Esmaeili *et al.*, 2007). This brown macroalgae showed a tendency to incorporate higher concentrations of elements from marine environments than red and green algae present in the region Bushehr near of Persian Gulf. To develop a biosorption process by using the *Sargassum* for industrial applications, it is desirable to better understand the metal uptake process (Taboada-Serrano *et al.*, 2005, Dambies *et al.*, 2001). Advanced instruments such as X-ray, photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) can provide good tools to achieve the goal because they can provide insight into environmental process at the molecular level. XPS and FT-IR have been adopted to identify the major functional groups in a biopolymer and coordination types between the metal ions and the surface ligands (Figueria *et al*., 1999; Buschman and Sigg, 2004; Dambies *et al*., 2001). For example, the involvement of ion exchange, sorption and reduction was determined in the biosorption of Cu^{2+} on chitosan according to XPS analysis. An ion exchange model was developed and used to illustrate the metal biosorption onto the protonated *Sargassum* (Schiewer and Volesky, 1996).

Therefore, in the present work, the adsorption of Cu^{2+} and Ni^{2+} ions by *S. angustifolium* was studied by investigating the influence of different experimental parameters on metals uptake, such as sorption time, initial pH and metals concentration.

MATERIALS AND METHODS

Seaweed

The biosorbent of brown macroalgae, *S. angustifolium* used in this study was collected during January 2011 from the city of Chabahar, in southeast of Iran (Lat. 25°16′ 30″ N, Long 60°40′ 32″ W) located close to the Oman Sea. Raw material was washed twice with tap water, then twice with deionised water. After a drying at 60°C, the algae were crushed, sieved, and the 0.355–0.5 mm particle size fraction was kept for the experiments. Copper and nickel solutions with different initial concentrations (0.01 - 0.44 mmol l^{-1}) were prepared by dissolving $CuCl_2.6H_2O$, $NiCl_2$.6H2O in company Merck in deionized water.

Batch biosorption experiments

In this present work the *S. angustifolium* was used to remove $Cu^{2+,}$ Ni^{2+} from aqueous solution. A series of Cu^{2+} and Ni^{2+} biosorption experiments was conducted; the factors in the investigation included pH, adsorption capacity, and the pH effect experiment. The desired solution pH was first adjusted by HNO_3 and NaOH. The sargassum was added to the solutions while being shaken at 150 rpm in the orbital shaker. The experiment was performed at room temperature of 25 ± 1°C. After the experiments, the supernatants were taken from each flask, acidified, and filtered.

In the isotherm experiments were carried out in bottle flasks filled with 1000 ml of water thoroughly mixed with 0.1 g of *S. angustifolium* at 25°C and pH initial close to 5. The initial concentrations of metal ions were ranged from 0.01 - 0.44 mmol l^{-1}. Single-metal concentrations in the relevant samples were determined by an atomic absorption spectrophotometer (Chem. Tech. Analytical CTA 2000). The liquid phase was separated from the adsorbent by a filtration system using 0.45 μm membranes.

The metal uptake at equilibrium was calculated by the following equation:

$$q_e = \frac{V\left(C_i - C_e\right)}{W} \qquad \text{(Eq.1)}$$

Where q_e is the metal uptake (mmol Cu^{2+} and Ni^{2+} adsorbed per g adsorbent), V (l) is the solution volume, W (g) is the amount of sorbent, C_i (mmol l^{-1}) and C_e (mmol l^{-1}) are the initial and equilibrium metal concentration in solution, respectively.

X-ray Photoelectron Spectroscopy Analysis (XPS)

Instrument analysis by XPS was performed to obtain the chemistry in the metal ions and functional groups of biosorbent were involved. The changes in the sorption chemistry were then compared. An equilibrium model capable of identifying the important sorption chemistry was developed, which was subsequently used to predict the biosorption process as a function operation parameters. Dry *S. angustifolium* dehydrated before and after copper biosorption was examined in high and low resolution with the Perkin-Elmer PHI 5600Multi-Technique AES/XPS System. The samples were prepared by attaching a very thin layer to an adhesive tape placed on sample holder. A description of this technique and its interpretation were reported by Briggs (1999).

RESULTS AND DISCUSSION

Potentiometric Titration

As shown in Figure1, protonated *S. angustifolium* has a weak acid property. Some hydrogen ions are released from the biosorbent to neutralize the hydroxide when the NaOH is added. Before the sodium hydroxide was added, the pH values were 2.9 for the solution containing the *Sargassum*. It can be found that the biosorbent feature several *pk* values.

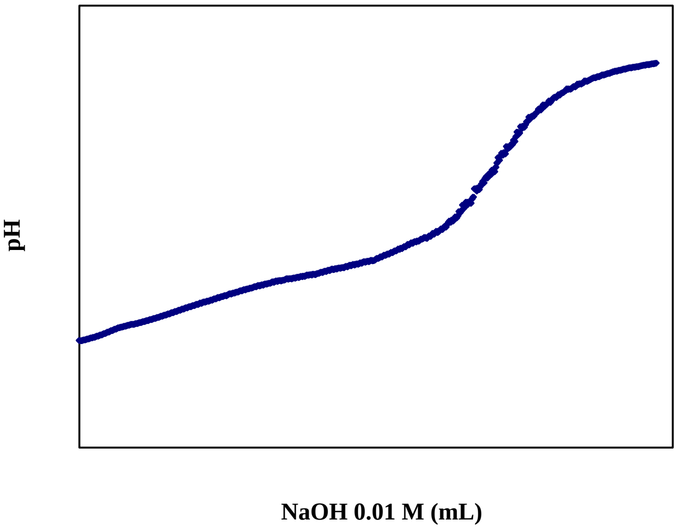

Figure 1. Potentiometric titration of protonated *S. angustifolium* biomass (biosorbent 0.1 g, NaOH 10^{-2}, pH=2.9-10.25).

Biosorption Isotherms

Figure 2 shows the Cu^{2+} and Ni^{2+} uptake isotherms at pH 5.0. The experimental results were corrected with the Langmuir isotherm model. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The Langmuir adsorption isotherm is probably one of the most widely applied adsorption isotherm. This model which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent.

$$q_e = \frac{b q_m C_e}{1 + b C_e} \qquad \text{Eq. (2)}$$

Where q_e is the amount of metal ions adsorbed (mmol g^{-1}), C_e is the equilibrium concentration (mmol l^{-1}), q_m (mmol g^{-1}) is the maximum adsorption capacity and b (l $mmol^{-1}$) is an affinity constant. For determining the equilibrium parameters, Equation (2) can be altered into a linear from as follows (Equation 3):

$$\frac{1}{q_e} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \qquad \text{Eq. (3)}$$

The values of q_m (mmol g^{-1}) and b (l $mmol^{-1}$) were obtained from Eq.3. The linear correlation coefficient was 0.996, and 0.991 and q_m was 0.94, 0.78 mmol $g^{-1}$from calculation using the Langmuir equation for Cu^{2+} and Ni^{2+} respectively. (Table 1, Figure 3). The correlation coefficient was 0.976 and 0.941 from calculation using Freundlich equation (data not presented).

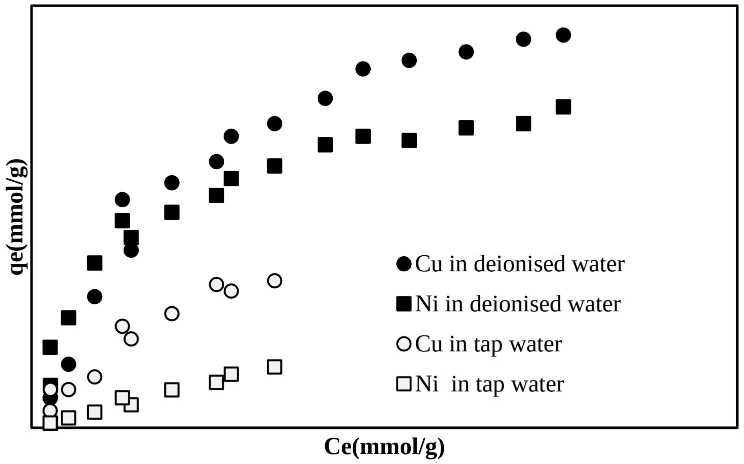

Figure 2. Sorption isotherm of a Cu^{2+} (●, ○) and Ni^{2+} (■, □) in deionized water and in tap water (initial concentration metal 0.01-0.44; pH 5.5;Temperature 25° C)

Table 1. Calculation parameters from Langmuir equation in deionized water.

parameter / metal	**q_m** (mmol g^{-1})	**b_L** (l $mmol^{-1}$)	**r^2**
Cu^{2+}	0.949	22.63	0.996
Ni^{2+}	0.788	55.74	0.991

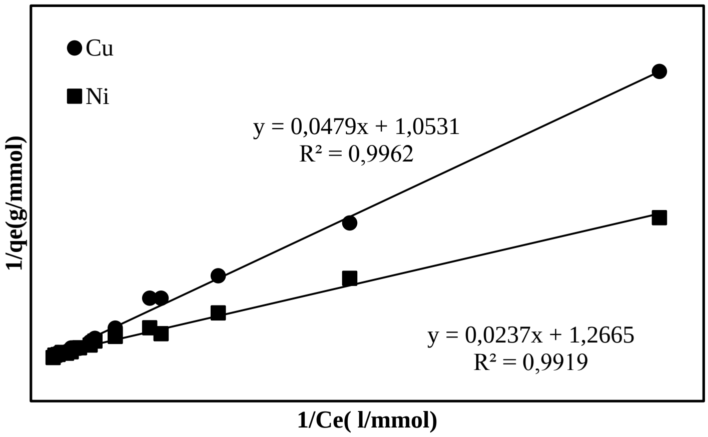

Figure 3. Sorption isotherm of Cu^{2+} and Ni^{2+} ions in deionized water by Langmuir linear form.

Experimental fixation capacities obtained in tap water are much less described by the tested models and show a decrease in comparison with deionised water. The difference could be attributed to a competition mechanism between ions naturally present in tap water and Cu^{2+} and Ni^{2+}, for the binding moieties present onto *Sargassum* surface. This indicates that, in addition to the ion exchange mechanism, there are other reactions contributing to the heavy metal binding (Paul Chen and Yang, 2006). The comparison of various literature studies of Cu^{2+}, Ni^{2+} removal by biosorption showed in Table 2. The adsorption study has highlighted an ion exchange mechanism responsible for metal uptake. The release of calcium, initially fixed onto the *Sargassum*, has been followed in the same time of Cu^{2+} and Ni^{2+} adsorption. This release depends on the initial Cu^{2+} and Ni^{2+} concentration of the solution, which could lead to a fixation mechanism by ion exchange for 600 min. Because the isotherms of Cu^{2+} and Ni^{2+} adsorption and Ca^{2+}, Mg^{2+}desorption were practically similar, Cu^{2+} and Ni^{2+} ions seemed to be exclusively adsorbed by an ion exchange mechanism. Ion-exchange is an important in biosorption, because it explains many of the observations made during heavy metal uptake experiments. Under certain conditions, the ions attracted to a solid surface may be exchanged with other ions in an aqueous solution. Both cations and anions exchange can occur, but in some natural material, cations exchange is the dominant process (Ahmady *et al.*, 2008).

Table 2. Comparison of various literature studies of Cu^{2+}, Ni^{2+} removal by biosorption.

Species	**pH**	**Ion**	**Capacities (mmol/g)**	**References**
Fucus serratus	5.5	Cu^{2+}	1.73	Ahmady *et al,* 2009
Fucus serratus	5.5	Ni^{2+}	0.95	Ahmady *et al,* 2009
Sargassum vulgare	4.5	Cu^{2+}	0. 93	Davis *et al,* 2003
Gracillaria sp.	3.5	Ni^{2+}	0.27	Sheng et al,2004
Sargassum fluitans	4.5	Cu^{2+}	0.80	Davis *et al,* 2000
Codium vermilara	6.0	Cu^{2+}	0.27	Romera *et al,* 2007
Spirogyra insignis	6.0	Cu^{2+}	0.30	Romera *et al,* 2007
Chondrus crispus	6.0	Cu^{2+}	0.64	Romera *et al,* 2007
Palmaria palmata	6.5-7	Cu^{2+}	0.10	Prasher *et al,* 2004
Palmaria palmata	6.5-7	Ni^{2+}	0.5	Prasher *et al,* 2004
Chondria armata	6.0	Cu^{2+}	0.33	Romera *et al,* 2007
Aspergillus niger	5.0	Cu^{2+}	0.24	Dursun *et al,* 2003
Gelidium	5.3	Cu^{2+}	0.21	Vilar *et al,* 2008
Aspergillus armata	6.0	Ni^{2+}	0.29	Romera *et al,* 2007
Aspergillus terreus	4-6	Cu^{2+}	0.24	Cerino *et al,* 2011
Acinetobacter baumannii	4.5	Ni^{2+}	0.14	Rodriguez, et al,2006
Sargassum angustifolium	5.5	Cu^{2+}	0.94	This work
Sargassum angustifolium	5.5	Ni^{2+}	0.78	This work

Effect of pH on biosorption

The metal ion binding in biosorption could be attributed to several mechanisms such as ion exchange, complexation, electrostatic attraction and micro precipitation. For algae biomass, ion exchange has been considered as a main mechanism responsible for metal sequestering (Cris *et al.*, 1988). The effect of pH on Cu^{2+} and Ni^{2+} biosorption on *Sargassum* biomass is studied at room temperature by varying the pH of metals solution. In our experimental results indicate that in the present of the biomass a chemical precipitation occurred since the Cu^{2+} and Ni^{2+} began to precipitate after pH 5.5 and 7.5 respectively (Figure 5). At pH lower than3.0, Cu^{2+} and Ni^{2+} removal was inhibited possibility as result of a competition between hydrogen and metal ions (Cu^{2+}, Ni^{2+}) on the sorption sites. The pH is one of the most important parameters of biosorption (Kapoor *et al.*, 1999; Aksu, 2001) and, regarding *Sargassum* sp., its high content of ionizable groups (carboxyl groups), makes it very liable to be influenced by the pH of the medium. For *Sargassum* sp., carboxyl groups are chiefly responsible for binding metallic ions. However other functional groups may contribute to the process, such as the sulfonate and amine groups.

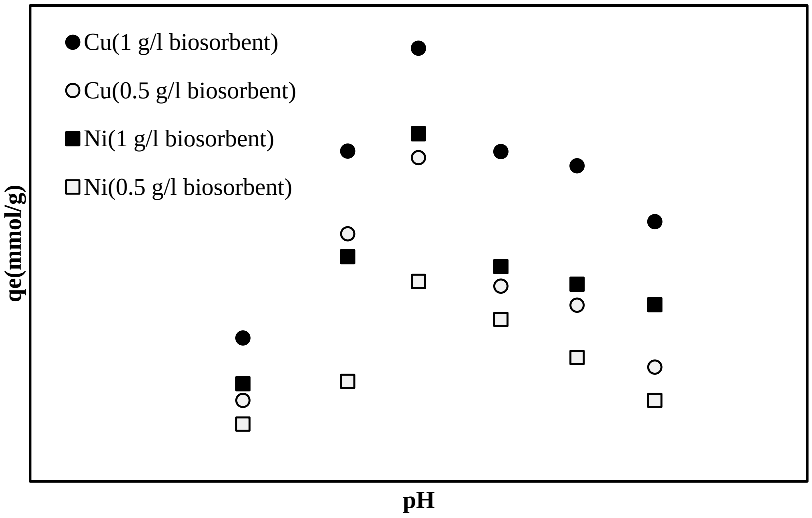

Figure 5. Effect of pH on the Cu^{2+} and Ni^{2+}biosorption by *Sargassum angustofolium*. (Temperature 25°C, Cu and Ni initial concentration 4 mg l^{-1}).

X-ray Photoelectron Spectroscopy Analysis

Table 3 shows the atomic concentrations of Cu^{2+} in the metal-laden *S. angustifolium* samples, according to the XPS spectra analysis. It's also shows changes in the atomic concentration in the functional groups after the metal binding process (values in brackets).

Table 3. XPS atomic concentration (in percentage) of relevant chemical elements in *S. angustifolium* sample before and after heavy metal uptake

Atom	**No metal uptake**[1]	**Cu(II)** [2]
C	47.44	59.24 (+24.89)
O	38.4	24.18 (-37)
N	3.52	1.2 (-65.9)
Ca	4.99	_ (-100)
Mg	4.53	1.4 (-69.1)
S	1.12	3.98 (+249)
Cu	-	10

[1]Raw *S. angustifolium* sample, [2]Values in brackets represent changes in XPS atomic concentrations after metal uptake by *S. angustifolium* biomass.

The changes in algal biomass observed after metal uptake included increases in carbon and sulfur atomic concentrations and decreases in nitrogen, oxygen, and calcium and magnesium atomic concentrations. After Cu^{2+} uptake, there were significant changes in the atomic concentration of oxygen, carbon and nitrogen and almost no change in sulfur atomic concentrations. These findings indicate that heavy metal uptake is accompanied by changes in sulfur, nitrogen, oxygen and carbon binding.

CONCLUSIONS

This study indicates that brown marine algae *S. angustifolium*, which is widely available at a low cost, can be used as an efficient biosorbent material for the treatment of Cu^{2+} and Ni^{2+} in aqueous solution. The adsorption isotherm of Cu^{2+} and $Ni^{2+}$by dried *S. angustifolium* pieces could be adequately described by the Langmuir isotherm model. The maximum adsorption capacity of Cu^{2+} and Ni^{2+} was 0.94 and 0.78 mmol/g respectively.

The pH value that was selected for the experiments on the biosorption of Cu^{2+} and Ni^{2+} by *S. angustifolium* was pH 5 since it combined the best characteristics for the lowest chemical precipitation and the highest biosorption. A large number of acidic functional groups at the surface lead to a high value of total proton exchange capacity and a Cu^{2+} and Ni^{2+} uptake by cationic exchange mechanism. During this process, algal cell wall matrix cations were replaced by the tested Cu^{2+}, Ni^{2+} ions. With advantages of high metal biosorption and desorption capacities, the biomass of *S. angustifolium* is a promising application as a cost-effective biosorbent material for the removal of Cu^{2+} and Ni^{2+} from aqueous solution.

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