

Multiple sorption-desorption cycles of Cu(II)/Ni(II) ions in a fixed-bed column by *Sargassum* sp. biomass

S. J. Kleinübing¹, E. Guibal², M. G. C. da Silva¹

¹School of Chemical Engineering, State University of Campinas, Caixa Postal 6066, CEP 13081-970, Campinas, SP, Brazil

²Ecole des Mines d'Alès, Laboratoire Génie de l'Environnement Industriel, 6 avenue de Clavière, F-30319 Alès Cedex, France

The objective of this work was to study the biosorption/desorption of copper and nickel ions and their mixture using the acidified seaweed *Sargassum* sp. Biomass as biosorbents. Three sorption-desorption cycles were operated on both monometallic and bimetallic Cu(II) and Ni(II) solutions. For bimetallic bioadsorption, the phenomenon of the sequential change was observed: the more selective cation, Cu(II), remove and replace the other cation, Ni(II) previously sorbed. The breakthrough curves show the same behavior over the three successive sorption/desorption cycles. Ninety percent of elution happened in the first 20 min.

Introduction

Marine algae have been identified as good biosorbents because of their low cost, renewable nature, and high metal biosorption capacity. The capacity of which is normally higher than commercial adsorbents and ion-change resins. The application of biosorption as a viable commercial technique implies the recovery of bound metals and the subsequent recycling of the biosorbents (Schiewer and Volesky, 2000). It is known that a long desorption time could cause the destruction of the biomass structure or, on the contrary, a short elution process could be ineffective. So, it is important to appropriately balance this procedure (Volesky, 2003).

The reusability of the protonated alga *Sargassum muticum* was studied by Lodeiro et al., (2006) using a fixed-bed column for eleven sorption-regeneration cycles, employing 0.1M of HNO₃ solution as the eluant. The maximum metal uptake resulted in a considerable reduction after the first desorption cycle. For other cycles the values of metal uptake remained almost constant. Volesky et al., (2003) studied ten consecutive sorption-desorption cycles for copper removal using raw seaweed *Sargassum filipendula*, and employing a CaCl₂/HCl solution at pH 3.0 as the eluant. The maximum copper uptake remained constant during these cycles.

There is strong evidence that *Sargassum* sp. could be used commercially for wastewater treatment and that the biomass can be fully regenerated, maintaining a good performance after several cycles of sorption/desorption. However, the most part of these studies focused on the recovery of a single metal ion from synthetic solutions. The

removal process of a metal can be affected by the interaction effects, due to the presence of several metals. Monometallic solutions are rarely found in industrial effluents; the presence of various metals or other ionic species may affect the sorption of metals. In this work, the use of *Sargassum* sp. as biosorbent for Cu(II) and Ni(II), mono and bimetallic was studied for three sorption-desorption cycles in a packed-bed column.

Materials and Methods

1.1 Biomass

Samples of the brown marine alga *Sargassum* sp. it was collected on the coast of São Paulo by the Biology Institute of São Paulo University (CebiMar). Algae samples were dried at 60 °C overnight and stored in a dry cabinet. The biomass was ground and sieved to recover from 0.71 to 1.0 mm particle size fraction. This raw biomass was acidified at pH 5.0 (with HCl 1M). The acid treatment on algae was done in order to avoid the leaching of raw algae and metal precipitation due to pH increase. A weight loss of 22 % was observed with the treatment.

1.2 Column experiments

Fixed-bed column is one of the most effective configurations for cyclic sorption-desorption, allowing for a more efficient use of the biosorbents, as a consequence of the enhanced use of the metal concentration difference between solution and biomass.

The column experiments were carried out in a glass column of 12 cm in length and internal diameter of 1.1 cm, initially filled with 3.0 g of dried acidified biomass. The sorption process was operated using a monometallic solution containing 4 mmol L⁻¹ copper (Cu(NO₃)₂·3H₂O) and 4 mmol L⁻¹ nickel (Ni(NO₃)₂·6H₂O), or a bimetallic solution of total concentration of 8 mmol L⁻¹ (equivalent fraction of Ni(II) and Cu(II)), at pH 4.5, adjusted using 1M HNO₃. The flow-rate of 5 mL min⁻¹ was provided by using a peristaltic pump connected at the bottom of the column. Samples were collected periodically by a programmable fraction collector (Varian, Model 701) and the heavy metal ion concentration was measured by inductive coupled plasma-emission spectroscopy (ICP-ES). The column was stopped when the effluent metal concentration reached a constant value. In order to regenerate the biosorbent material, an elution step was carried out after each adsorption cycle, when the column bed was saturated. After each elution operation, the column was washed with deionised water. The desorbing agent was a CaCl₂ (0.5 M) solution acidified to pH 3.0 with 1M HCl, pumped at flow-rate of 5 mL min⁻¹.

1.3 Bioadsorption/desorption curves

The performance of the packed-bed algae biomass was analyzed plotting the breakthrough curves (i.e. the outlet concentration versus time). The curves are function of column flow parameters, sorption equilibrium, and mass transport factors.

The time (t_e , min) corresponds to the time required for full saturation of the column. The computer program ORIGIN was used to calculate (by numerical integration) the area below the curve. The area allowed determining the amount of Cu(II) and Ni(II) retained in the column. Dividing this value by the mass of alga in the bed (m_s), the uptake capacity of the biomass ($Q_{M,ad}$) was obtained, according following equation:

$$Q_{M,ad} = \frac{C_0 F}{1000 m_s} \int_{t=0}^{t=e} \left(1 - \frac{C_{Mad}}{C_0} \right) dt \quad (1)$$

Where: F is the flow rate (mL min^{-1}); C_0 and C_{Mad} are the metal concentrations (mmol L^{-1}) in the feed and at the outlet, respectively.

The elution curves can be described by the elution efficiency (%E). This parameter can be obtained dividing the metal mass desorbed (m_d) by the metal mass bound to the biomass in the previous adsorption step (m_{ad}). Where m_d is calculated from numerical integration of the regeneration curves from $t=0$ to $t=e'$, with the following equation:

$$m_d = F \int_{t=0}^{t=e'} C_{Md} dt \quad (2)$$

The time (e') corresponds to the time required for total elution of heavy metals in column.

Results and discussion

1.4 Comparison between breakthrough curves for mono and bimetallic bioadsorption of Cu(II) and Ni(II) in algae *Sargassum sp*

The majority of industrial effluents contain more than one toxic heavy metal; consequently, biosorption in column involves competitive ion exchange, in which several toxic heavy metals compete for a limited number of binding sites.

Figure 1 a and b compare the breakthrough curves for Cu(II) and Ni(II) removal, respectively. These figures show the breakthrough profiles for mono and bi metallic solutions.

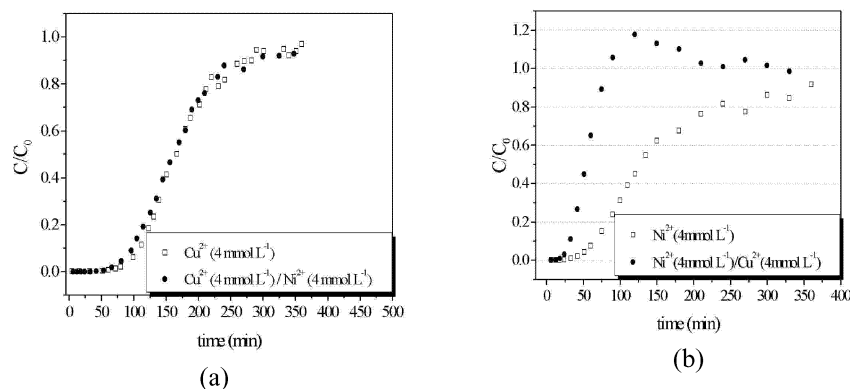


Figure 1 Comparison between the breakthrough curves for: (a) Cu(II) (monometallic) and Cu(II) in presence of Ni(II) (bimetallic); (b) Ni(II) (monometallic) and Ni(II) in presence of Cu(II) (bimetallic), biosorption.

In the case of Cu(II), the breakthrough curves were superposed, for both mono and multi-metallic solution. A completely different behavior is observed for Ni(II)

breakthrough curves: in the case of bi-metallic solution an overshoot is observed with outlet concentration that exceeded the initial concentration. Indeed, Cu(II) ions displace Ni(II) ions previously sorbed resulting in a greater concentration at the outlet compared to inlet concentration.

The uptake capacity and selective binding in brown algae are attributed to the presence of the alginate biopolymer contained within the brown algal thallus (Davis et al., 2003). A reduction of 82 % in the adsorption capacity of Ni(II) was observed when Cu(II) was present; and a reduction of 14% in the adsorption capacity of Cu(II) when Ni(II) was present.

Rupture curves of this type reflect the phenomenon of the sequential change. The more selective cation manages to take over the site of another cation which was previously changed and thereby is liberated. This is a phenomenon of competitive sorption processes.

1.5 Bioadsorption/desorption cycle of mono and bimetallic solution

For a system of continuous operation to work successfully, the desorption process and agents must be effective and should not cause much damage to the biosorbents.

Figures 2 a, c, and e show the breakthrough curves profiles for Cu(II), Ni(II) and binary solution, respectively, for three sorption/desorption cycles. Figures 2 b, d, and f, present the corresponding elution curves.

After three cycles, the biomass was oven dried and weighed. The weight loss reached 4, 3 and 6% for Cu(II), Ni(II), and bi-metallic solutions, respectively.

According to Volesky et al. (2003), a loss of sorption performance during the long-term use may have a variety of reasons. It may be caused by changes in the chemistry and in the structure of the biosorbents, as well as by changes in the flow and mass transport conditions within the column. According to Fourest and Volesky (1996), the deteriorating on sorption properties may be due to chemical changes to the cell wall components such as alginates and sulfated polysaccharides, which play a major role in metal biosorption by marine algae.

According to Table 1 for Cu(II) and Ni(II) mono metallic, elution efficiencies higher than 90% were observed for Ni(II) and higher 96% for Cu(II). In these three cycles, the breakthrough curves followed the same trend. The heavy metal uptake capacity presented a maximum reduction of 8% for Cu(II) and 6% for Ni(II). This result indicates that the biomass did not suffer any damage in the cell structure, maintaining the same metal uptake.

The maximum concentration for Cu(II) and Ni(II) on desorption curves was achieved within 5 min and 6 min, respectively, for monocomponent solutions. The maximum concentration for bi metallic was achieved within 9 min. The necessary total time for column saturation for both metals was of about 360 minutes, elution time in all cases was of about 60 min, and in the first 20 minutes about 90% of the metal previously sorbed was removed.

The competitive effect (bimetallic solution) was observed along the three sorption/desorption cycles. The breakthrough curves showed the same trends. After the first cycle, a reduction in capacity of Cu(II) (maximum 5.6%) and an increase in capacity of Ni(II) (maximum 21%) were observed. The total capacity of both metals, remained constant for each cycle, to 1.28 mmol g⁻¹.

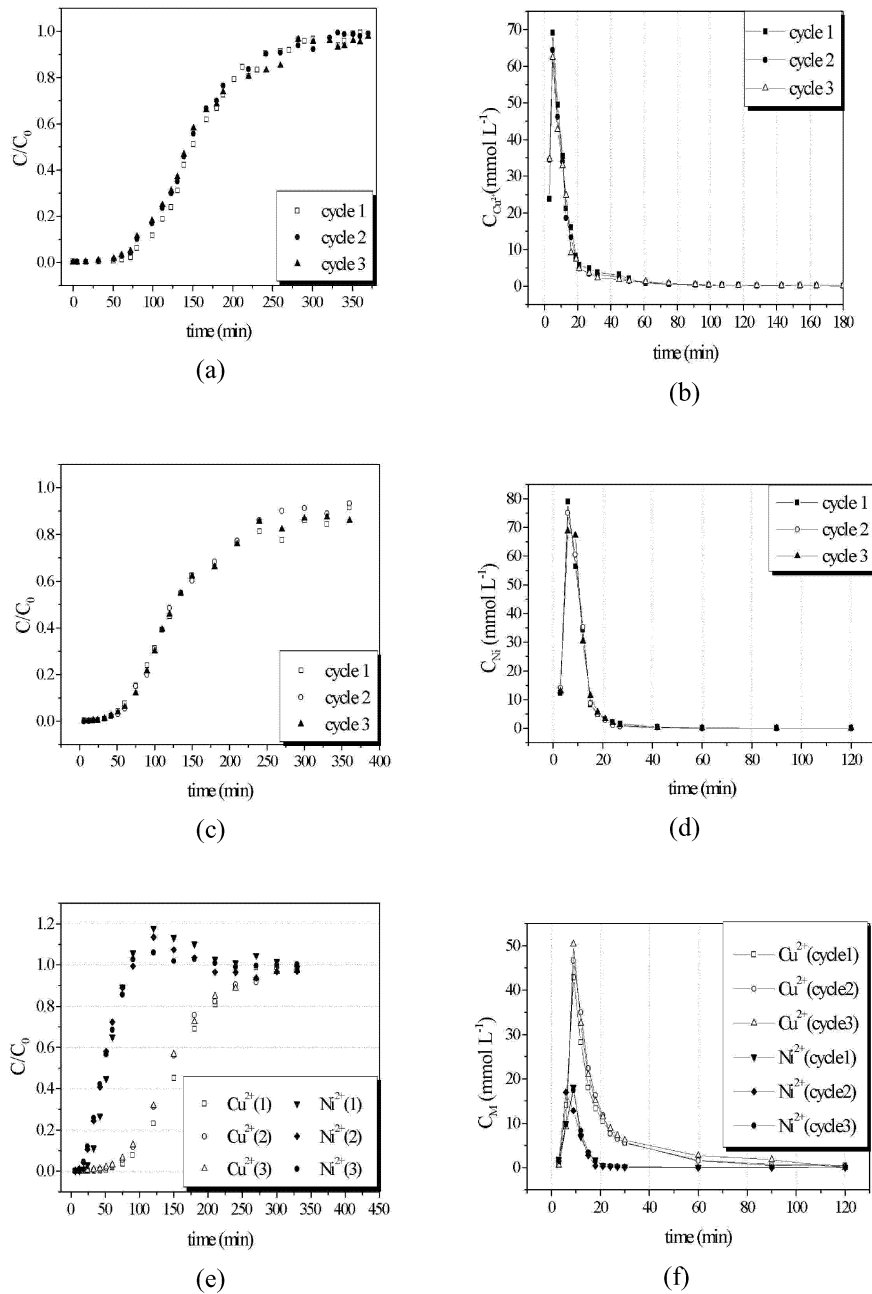


Figure 2 Breakthrough curves for three biosorption cycles: (a) Cu(II) ($C_{0,\text{Cu}} = 4.18 \text{ mmol L}^{-1}$), (c) Ni(II) ($C_{0,\text{Ni}} = 4.2 \text{ mmol L}^{-1}$), and (e) of Cu(II) (4.1 mmol L^{-1}) + Ni(II) (4.17 mmol L^{-1}); Elution curves for three desorption cycles, employing CaCl_2 (0.5 M)/ HCl -solution at pH 3: (b) Cu(II) , (d) Ni(II) , and Cu(II)+Ni(II)

The elution efficiency provides information about the entire desorption curves, based on a previous adsorption step. Therefore, one must be aware of its significance and possible errors in its calculation. The narrow desorption peak make difficult to exactly determine the area below the curve. For this reason, some uncertainty can be found in the metal mass desorbed calculations, which is reflected in the elution efficiency values (Lodeiro et al., 2006).

Table 1 Sorption-desorption parameters for 3 cycles for the removal of Cu(II), Ni(II) and Cu(II)+Ni(II) by acidified *Sargassum* sp. biomass

Cycle	Cu(II) monometallic		Ni(II) monometallic		Cu(II)/Ni(II) bimetallic			
	$Q_{Cu,ad}$ (mmol g ⁻¹)	%E	$Q_{Ni,ad}$ (mmol g ⁻¹)	%E	$Q_{Cu,ad}$ (mmol g ⁻¹)	%E	$Q_{Ni,ad}$ (mmol g ⁻¹)	%E
1	1.24	96	1.11	91	1.06	93	0.22	95
2	1.17	97	1.05	94	1.00	103	0.28	85
3	1.14	97	1.1	90	1.01	110	0.26	90

Conclusion

Biosorption performance of brown alga *Sargassum* sp. biomass was investigated for three sorption/desorption cycles for copper and nickel. The results show good efficiencies in metal removal.

The algae *Sargassum* sp. presents larger affinity for Cu(II) compared to Ni(II). At the concentration of 4 mmol L⁻¹, the uptake capacity reached 1.24 mmol/L and 1.11 mmol/g for Cu(II) and Ni(II), respectively. The biggest affinity of the biomass for copper was confirmed by the displacement of nickel ions in binary solutions overshoot on the breakthrough curve.

As a result of competitive ion exchange species Ni(II) overshoots the acceptable limit in the column effluent well before the breakthrough point of Cu(II), thereby reducing the service time of the column considerably.

The metal uptake property remained practically unaltered during three successive cycles of sorption/desorption, showed favorable regeneration conditions. In all the cycles, the elution curves exhibited a similar trend; a sharp increase in the beginning followed by a gradual decrease.

References

- Aldor I., Fourest E. and Volesky B., 1995, Can. J. Chem. Eng. 73, 516-522.
 Davis, T.A., et al., 2003, Applied Biochemistry and Biotechnology, 110, 75-90.
 Fourest E., Volesky B., 1996, Environ. Sci. Technol. 20, 277-282.
 Lodeiro P., Herrero R., Sastre de Vicente M.E., 2006, J. Hazard. Mater. B137, 1649-1655.
 Schiewer S., Volesly, B., 2000, ASM Press, Washington, DC, pp. 329-362.
 Volesky B., Weber J., Park J.M., 2003, Water Res. 37, 297-306.