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Continuous Biotreatment of Copper-Concentrated Solutions by Biosorption With *Sargassum* sp.

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Abstract

Seaweed *Sargassum* sp. biomass proved to be useful for the recovery of ionic copper from highly concentrated solutions simulating effluents from semiconductor production. In the case of solutions containing copper in the form of chloride, sulfate, and nitrate salts, the best pH for the recovery of copper was 4.5. It was observed that copper biosorption from copper nitrate solutions was higher than the recovery of copper from copper chloride or copper sulfate solutions. The continuous system used was constituted of four column reactors filled with the biomass of *Sargassum* sp. and showed high operational stability. The biomass of *Sargassum* sp. in the reactors was gradually saturated from the bottom to the top of each column reactor. The biomass of *Sargassum* sp. in the first column saturated first, followed by a gradual saturation of the remaining columns owing to preconcentration performed by the biomass in the first column. The biomass of *Sargassum* in the bioreactors completely biosorbed the ionic copper contained in 63 L of copper sulfate solution, 72 L of copper chloride solution, and 72 L of copper nitrate solution, all the solutions containing copper at 500 mg/L. Effluents produced after biosorption presented copper concentrations <0.5 mg/L.

Index Entries: Biosorption; semiconductor effluents; *Sargassum*; fixed-bed reactors.

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Introduction

Problems associated with the continuing growth of semiconductor fabrication worldwide are the availability of raw feed water and the degree of regulation governing industrial wastewater. The SIA National Technology Roadmap for Semiconductors has identified the reduction of water use as one of the top challenges in semiconductor environmental safety and health. Thirty thousand semiconductor wafers need more than 45 million gal of raw water every month. Copper, as a recent component of modern semiconductors, can be diluted below regulation limits by the water from the rest of the fabrication process. However, a fivefold increase in concentration can be estimated owing solely to the reduction in water use.

For the production of sub-0.25-μ semiconductor technologies, copper interconnections are needed; as a consequence, the amount of copper in the wastewater will increase substantially *(1)*.

Many techniques can be used to treat process effluents from semiconductor manufacturing, but just a few can be immediately used, owing to water discharge or the possibility of recycling. High copper levels involve the use of electrowinning, pH adjustment, and ion exchange. Membrane techniques cannot be applied, owing to the small size of particles present in those effluents.

Industries have found methods to treat their wastewater, although many are not satisfied that their solutions are cost-effective or adequate for future requirements. The environmental footprint of process tools for chemical mechanical polishing (CMP), wafer cleaning, and copper plating can be significantly reduced by finding solutions for wastewater treatment before the tools are delivered to the fab *(1,2)*.

Microorganisms can remove metals from industrial wastes. However, problems associated with pH, and maintenance of the microbial culture, did not contribute to satisfactory results *(3,4)*. As a substitute or complementary technology, the use of inactivated seaweeds is suggested, in packed-bed reactors. This biosorption presents several advantages compared to conventional treatment methods *(5–10)*.

The main purpose of the present work was to study the behavior of a continuous system composed of fixed-bed bioreactors with the brown seaweed *Sargassum* sp. as adsorbing bed for the treatment of highly concentrated copper solutions simulating wastewater from semiconductor manufacturing.

Materials and Methods

Biomass and Copper Solutions

The seaweed *Sargassum* sp. (*Phaeophyceae*) was selected as the biosorbent material *(8,10)*. The biomass was collected from the northeastern coast of Brazil, washed with distilled water to remove particulate material, and oven dried at 70 ± 1°C (TEMP-THER, Model ES5; London, England).

Synthetic copper solutions used were prepared from the dissolution of $Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2 \cdot 2H_2O$, and $CuSO_4 \cdot 5H_2O$ (Merck, Darmstadt, Germany) in distilled water. Final copper concentrations in each solution were 500 mg/L.

Selection of pH—Batch Tests

To obtain the optimum pH for continuous biosorption experiments with the use of *Sargassum* sp., the pH of 500 mg/L copper solutions from each salt were adjusted in the range of 4.0–6.0. The pH was adjusted using HCl or 0.1 *N* NaOH (Merck). These experiments were performed with and without the addition of *Sargassum* sp. (2.0 g/L) to the solutions. This was necessary to differentiate between chemical copper precipitation and biosorption. In all cases, pH values were monitored before and after equilibrium. Experiments were performed under constant agitation in a temperature-controlled shaker (New Brunswick Scientific, Edison, NJ) at 150 rpm and 30 ± 1°C. After 6 h, each solution was filtered through a 0.47-μm Millipore membrane (Millipore, Bedford, MA), for further quantification of equilibrium copper concentration by atomic absorption spectrometry (Aanalyst, Model 300; Perkin-Elmer, San Francisco, CA). Each individual experiment was performed four times.

Continuous Tests

The continuous system contained four serial fixed-bed column reactors with a 70.0-cm height and a 7.0-cm id, and each was filled with dried *Sargassum* sp. (120 g of biomass/column) as the adsorbing bed. The effluent of each column became the influent solution of the next column reactor in the series, which was fed with the help of a peristaltic pump (Model 220; Milan, Paraná, Brazil) at 50 mL/min and was connected at the bottom of the first column. The influent solution to the first column contained copper at 500 ± 10 mg/L from nitrate, chloride, or sulfate, depending on the experiment, at pH 4.5. Samples were collected from the top of each column at 3-h intervals, filtered, and the filtrate was acidified with 1 *M* concentrated HCl for analytical determination of copper by atomic absorption spectrometry. Analogously, continuous experiments were conducted four times.

Values reported for both batch and continuous experiments constitute average values of copper determinations from each set of experiments. Standard deviations reported were calculated, in order to estimate the dispersion levels of the individual values, in relation to an average calculated value.

Results and Discussion

Selection of pH—Batch Tests

The main group that accumulates heavy metals in *Sargassum* sp. is the carboxyl group, from alginate, an irregular arrangement of 1,4-β-D-mannuronic and α-L-guluronic acids *(11)*.

Table 1
Chemical Precipitation and Biosorption of Copper at pH 4.0, 5.0, and 6.0 From Chloride, Sulfate, and Nitrate Sources

	Equilibrium copper concentration (mg/L)					
	pH 4.0		pH 5.0		pH 6.0	
Source of copper	No biomass	2 g/L *Sargassum*	No biomass	2 g/L *Sargassum*	No biomass	2 g/L *Sargassum*
Copper chloride	500 ± 17	368 ± 15	500 ± 25	290 ± 16	17 ± 1.4	13 ± 2.4
Copper sulfate	490 ± 22	306 ± 8	410 ± 14	302 ± 8	45 ± 6	8.9 ± 2.1
Copper nitrate	410 ± 20	310 ± 12	408 ± 20	306 ± 5	352 ± 17	286 ± 12

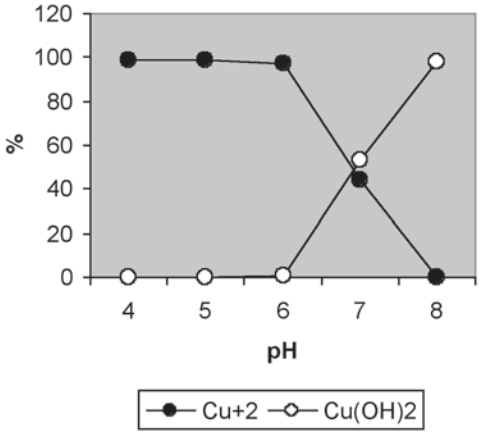

Fig. 1. Percentage of copper ion and copper hydroxides present in solution as function of pH. (Modified from ref. *12*.)

Table 1 presents the results obtained from a copper chloride concentrated solution, as well as chemical precipitation owing to pH change. The results showed that for higher pH values chemical precipitation was observed in both the absence and presence of *Sargassum* sp. biomass, represented by the reduced copper concentration values, in comparison to the concentrated copper solutions (500 mg/L). Thus, copper biosorption is possible from acidic copper solutions, considering the effects of chemical precipitation. Tests with *Sargassum* sp. showed that the seaweed accumulated 70 mg of copper/g of biomass and 110 mg of copper/g of biomass at pH 4.0 and 5.0, respectively. For a pH value of 6.0, this value was 5.8 mg of copper/g of biomass, owing to chemical precipitation of the metal. In that case, the seaweed had a negligible participation in copper removal. Figure 1 presents the percentage of copper ion and copper hydroxide species as a function of pH. The literature reports that the predominating species generated during copper precipitation is copper hydroxide *(12)*.

The results obtained during the biosorption of copper from sulfate by *Sargassum* sp. (*see* Table 1) show that the chemical precipitation of copper occurred at pH 5.0, owing to the decrease in copper concentration from 500 to 410 mg/L after pH adjustment. This was not observed when copper chloride was tested; in that case, both solutions presented the same concentration for both pH 4.0 and 5.0. For pH 6.0, the equilibrium copper concentration was 45 mg/L, corroborating the formation of copper precipitates.

At pH 4.0, *Sargassum* sp. accumulated 80 mg/g of biomass; at pH 5.0, the accumulation was 52.5 mg/g of biomass; and at pH 6.0, it was 15.7 mg/g of biomass. These values indicate that 4.0 is the ideal pH for copper biosorption from copper sulfate. However, to prevent H^+ competition, an optimal pH of 4.5 was selected for future continuous tests. This would be the optimal value for further comparison with other copper salts *(13)*.

Nuhoglu *(5)* also used pH 4.5 to remove copper from aqueous solutions with the green algae *Ulothrix zonata* and observed that pH values

>5.5 precipitated copper. Tien *(14)* also observed that the pH was the most important factor affecting the biosorption of copper, with the optimum values being between 4.0 and 5.0. Sánchez *(15)* investigated the biosorption of copper and zinc by the brown algae *Cymodocea nodosa* and selected similar pH values.

The results obtained for the biosorption of copper from copper nitrate (*see* Table 1) indicated that at pH 4.0 and 5.0 copper equilibrium concentration was 410.0 and 408.0 mg/L, respectively, decreasing to 352.0 mg/L for pH 6.0. The accumulation of copper was 46.8, 57.6, and 32.5 mg of copper/g of biomass for pH 4.0, 5.0, and 6.0, respectively. Again, pH 4.5 was selected for further experiments. Kaesarn *(6)* investigated copper biosorption from a synthetic solution of copper nitrate (127 mg/L) by the brown seaweed *Padina* sp. It was observed that at low pH values, such as 2.0, copper accumulation was very low, owing to the competition of H^+ ions. Hashim et al. *(16)* also investigated the biosorption of copper by *Sargassum baccularia* in several sorption-desorption cycles; the copper nitrate solution used had a pH of 6.0, which indicated that a higher pH value was feasible for copper biosorption.

Based on the overall results, it can be concluded that the best pH value for copper biosorption by *Sargassum* sp. for both chloride and nitrate solutions was 5.0. This value was selected based on the higher loading values observed (110 and 57.6 mg/g). When sulfate solution was used, the best result was observed for pH 4.0 (80 mg/g). To compare the performance of the continuous experiments, a pH of 4.5 was selected for future studies.

Continuous Tests

Table 2 presents the time course of the biosorption of copper for each salt tested. The data show that during the continuous biosorption of ionic copper by *Sargassum* sp. from copper chloride solution at pH 4.5, 9 L (corresponding to 3 h of continuous operation) of the influent solution was treated by the first column reactor according to the Brazilian legislation *(17)*.

The effluent copper solution from the first column was fed to the bottom of the second column. It can also be observed from the results obtained during the biosorption of copper from its chloride salt (Table 2) that 36 L of copper chloride solution was properly treated. Afterward, a gradual increase in the residual copper concentration was observed until complete saturation of the biomass in this reactor.

From the third-column reactor it can be observed that 54 L of copper solution was treated. In the fourth-column reactor, 63 L of copper solution was treated. The good performance observed in the third and fourth columns is related to the pretreatment performed by previous bioreactors, contributing to higher treatment levels. In all cases, it is important to mention that the values reported are cumulative totals that include the volumes effectively treated in the previous columns.

Table 2 also presents the results obtained during the uptake of copper from copper sulfate solution. The first column of the system was able to

Table 2
Continuous Copper Recoveries From Chloride, Sulfate, and Nitrate Sources From 500 mg/L Copper Solutions by *Sargassum* sp.

Time (h)	Copper outlet concentration (mg/L)											
	Copper chloride				Copper sulfate				Copper nitrate			
	Column				Column				Column			
	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th
1	—*	—	—	—	—	—	—	—	—	—	—	—
3	—	—	—	—	—	—	—	—	—	—	—	—
6	200 ± 13	—	—	—	180 ± 12	—	—	—	—	—	—	—
9	248 ± 11	—	—	—	220 ± 21	—	—	—	82 ± 5	—	—	—
12	478 ± 28	—	—	—	480 ± 21	20	—	—	362 ± 21	—	—	—
15	492 ± 21	360 ± 18	—	—	510 ± 32	480 ± 26	—	—	502 ± 34	8.6 ± 3.2	—	—
18	469 ± 7	420 ± 16	—	—	490 ± 15	492 ± 23	9.6 ± 0.8	—	476 ± 32	264 ± 21	—	—
21	458 ± 19	470 ± 32	215 ± 12	—	504 ± 23	496 ± 23	382 ± 17	7.6	509 ± 21	362 ± 28	—	—
24	472 ± 25	468 ± 16	360 ± 19	8.7 ± 0.3	489 ± 20	489 ± 30	504 ± 45	104 ± 12	472 ± 25	349 ± 31	12 ± 4	7.4 ± 0.9

[a]<Detection limit – Copper concentration below the detection limit (0.5 mg/L).

treat 9 L of solution, the second column was able to recover ionic copper from 36 L of solution, the third reactor indicated that the system was able to purify 45 L of solution, and the fourth reactor purified 54 L of solution. Thus, a better biotreatment of the chloride solution was observed, in comparison with the sulfate solution, considering copper biosorption as the main parameter of comparison.

The association between the *Sargassum* sp. seaweed and ionic copper, through the adsorption process, is favored by the fact that copper presents a free *d* orbital in the outer electron chain. This contributes to the instability of the ion, making it able to share electrons. In this case, this chemical element presents a high ability to share electrons with functional groups that are electronically deficient, mainly the carboxyl group. It is expected that covalent or partially covalent bonds will form, indicating the formation of stable complexes named internal sphere complexes *(18)*.

Copper reacts according to the internal sphere mechanism with carboxylate and phosphate, creating stable complexes *(19)*. de Araújo and Sobrinho *(18)* showed that external sphere mechanisms (nonspecific adsorption) are less likely to be involved in the adsorption of copper, the predominating mechanism being internal sphere.

Conversely, chemical links with chloride or sulfate affects the coordination sphere of the metal, thus affecting the total charge of the cation. Chloride ions are known to react through an external sphere mechanism, owing to its high capacity to donate electrons and cause light disturbances in the hydration spheres when present in aqueous medium. However, carboxylate and sulfate anions are known to react through an internal sphere mechanism, although sulfate anion causes a much higher disturbance *(9)*. Water molecules close to halide ions (such as chloride) present a higher mobility compared to pure water, and the residence time of a molecule of water in the internal sphere of a halide is very small. Investigation of the cationic and anionic effect of the homogeneous nucleation of ice in aqueous alkaline halide solutions proved that water molecules close to halide ions face a higher mobility than in pure water, and that the residence time of a molecule of water in the internal sphere of a halide becomes weaker in the order $Cl^- > Br^- > I^-$.

In the present work, when copper chloride was tested, the volume of treated influent was higher in comparison with copper sulfate, indicating that fewer disturbances were caused by this ion, facilitating the interaction between carboxylate groups present in the biomass.

Table 2 also presents the results of copper biosorption by *Sargassum* sp. from copper nitrate. The biomass in the first column treated 18 L of influent solution. From the second bioreactor it was observed that 36 L of copper solution was treated. The results from the third reactor in Table 2 indicated that 63 L of copper solution was treated, although far from saturation (the outlet copper concentration from the fourth reactor was 12 mg/L). The last column of the system also treated 63 L of solution, able to be discharged. It can be easily concluded that the performance of the system was

much better in the recovery of copper from nitrate salt, when compared to chloride and sulfate.

Nitrate is a slightly weak ligand in aqueous solution, in the same manner as chloride ion; consequently, it can cause less disturbance in the hydration sphere when compared to sulfate, thus facilitating interaction with carboxyl groups from the biomass of *Sargassum* sp., as corroborated by the present results. Beyond this fact, the behavior of copper during biosorption by *Sargassum* sp. can also be attributed to a mechanism called metallic nucleation mechanism. It is used to explain the affinity of copper to several adsorbent materials, contributing to an additional deposition of the metal *(20)*.

Hofmeister (2003) classified the ions according to their ability to precipitate some specific proteins as well as to their behavior in water: ions could be classified as cosmothrophics (ions that increase their structure when present in water) and chaothrophics (opposite behavior, thus increasing hydrophobicity of the aqueous medium) (available at www.lsbu.ac.uk/water/hofmeist.html). The ionic series of Hofmeister starts with the stable ions (highly hydrated) citrate, sulfate, phosphate, fluoride, chloride, bromide, iodide, nitrate, and perchlorate, the last one the less stable ion (weakly hydrated). According to the series of Hofmeister, the most hydrated anion, from the ones studied in the present work, is sulfate, followed by chloride and nitrate. The selective order observed in the present work is in close agreement with the hypothesis presented by Hofmeister. This means that nitrate is the less hydrated ion; thus, the metal cation associated with this anion is the most potential one for biosorption, as observed in the present work. Sulfate is the anion that causes marked disturbances in the hydration sphere; thus, sulfate is the one with the least potential for copper biosorption, owing to the disturbances that prevent a better interaction between copper and *Sargassum* sp.

These observations were partially presented by Palmieri et al. *(9)*, who studied the biosorption of lanthanum by *Sargassum* sp. They observed maximum biosorption of lanthanum when lanthanum chloride was used, instead of lanthanum sulfate. They attributed this behavior of lanthanum during biosorption by *Sargassum* sp. to disturbances in the hydration sphere.

In addition, Ahuja et al. *(21)* investigated the biosorption of zinc by *Oscillatoria anguistissima*. An increase in the concentration of nitrate, sulfate, and chloride anion solution (0–10 m*M*) resulted in a decreased biosorption of zinc, from 184 down to 27 mg/g in the presence of sulfate anion, and down to 90 mg/g in the presence of chloride. An increase in nitrate concentration in solution did not have a significant effect on zinc biosorption (from 184 to 167 mg/g). According to the results in the present study, it can be concluded that nitrate favored the uptake of copper by *Sargassum* sp., followed by chloride and sulfate. However, in batch experiments, chloride was better than nitrate regarding copper biosorption.

Conclusion

Copper biosorption under batch conditions indicated a slightly different behavior when compared to the continuous system: under batch conditions, copper biosorption followed the order $SO_4^{2-} < NO_3^- < Cl^-$, whereas under continuous conditions, the order was $SO_4^{2-} < Cl^- < NO_3^-$. This was an indication that the operational regime affected the biosorption of the metal. The removal of copper from the solution made with the sulfate salt indicated that the sulfate anion markedly affected the removal of copper by the biomass of *Sargassum* sp., decreasing its biosorption owing to the hydration sphere formed, causing disturbances that prevented the interaction of the metal ion with the carboxyl groups of the biomass, in accordance with the classification of ions proposed by Hofmeister. The continuous system had a high operational stability during the continuous tests, and the biomass of *Sargassum* sp., highly available in tropical countries as a waste material, can be effectively used for the treatment of industrial wastes produced from the manufacturing of semiconductors. This is especially interesting for tropical countries where the availability and cost of those waste materials brings competitiveness to conventional technologies.

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