Adsorption of heavy metals using marine algae

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Abstract- The discharge of heavy metals into aquatic ecosystem has become a matter of concern in South Africa over the last few decades. These pollutants are introduced into the aquatic systems significantly as a result of various industrial operations. Conventional methods for metal removal such as ion exchange, reverse osmosis, etc. have proven to be expensive. Due to the increasing awareness of ecological effects of heavy toxic metals, a research on new and cheap technologies involving the removal of heavy toxic metals from wastewater on the principle of adsorption was investigated in this study. The aim of the study was to investigate the adsorption characteristics of marine algae on copper solution as an alternate cheaper option with emphasis on its adsorption efficiency, stability and regeneration. In this study, the rate and extent for removal of copper is subjected to parameters such as pH, initial metal concentration, biosorbent size, contact time, temperature and the ability of the biomass to be regenerated in sorption-desorption experiments. The metal adsorption was found to be rapid within 25 minutes. The maximum copper uptake of 30 mg of copper / g of biomass has been observed, in the following conditions: 100 mg / L, 0.1 g of biomass, pH 4 and at temperature of 25°C. Metal biosorption behaviour of raw seaweed Sargassum in six consecutive sorption-desorption cycles were also investigated in a packed-bed column, during a continuous removal of copper from a 35 mg/l aqueous solution at pH 4. The sorption and desorption was carried out for an average of 85 and 15 hours, respectively, representing more than 40 days of continuous use of the biosorbent. The weight loss of biomass after this time was 13.5%. The column service time decreased from 25 hrs in the first cycle to 10 hrs for the last cycle. From this study, it was found that copper uptake is increasing with increase in pH, with optimum being pH 4. The biomass of the marine algae Sargassum species demonstrated a good capacity of copper biosorption, highlighting its potential for effluent treatment processes.

INTRODUCTION

While pH in lakes and rivers may vary as much as from 4 to 10; in sea water the pH range is between 7.5 and 8.4. Aqueous heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain. The main sources of heavy metals pollution are mining, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives, milling and surface finishing industries, discharging a variety of toxic metals such as cadmium, chromium, copper, zinc, lead, mercury, selenium, arsenic, gold, silver and nickel into an environment. Heavy metals such as zinc, lead and chromium have a number of applications in basic engineering works, paper and pulp industries, leather tanning, organochemicals, petrochemicals fertilizers, etc. Major lead pollution is through automobiles and battery manufacturers. As a result, removal of these toxins from industrial effluents has become an important priority that is reflected in tightening and enforcement of environmental regulations.

Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, especially shellfish, liver, mushroom, nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product, such as food, water or drink. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well.

While the removal of toxic heavy metals from industrial wastewaters has been practiced for several decades, the effectiveness, and particularly the cost effectiveness of the most common physical-chemical processes are limited. Biological materials have shown potential for heavy metal removal, but only low-cost biological materials with sufficiently high metal-binding capacity and selectivity for heavy metals are suitable in a full-scale biosorption process (Kuyucak et al., 1988).
Various bio-materials have been examined for their biosorptive properties and different types of biomass have shown levels of metal uptake high enough (in the order of 1mmol/g) to warrant further research (Crist et al., 1990). Among the most promising types of biosorbents studied is the algal biomass. The abundance of algae can hardly be overestimated. Biosorption in algae has mainly been attributed to the cell wall, composed of the fibrilar skeleton (Figueira et al., 1997).

Conventional methods for removing metals from aqueous solutions before they are disposed of include chemical precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, electrochemical treatment, and evaporation. While the cheaper of these processes are becoming inadequate with progressively more stringent regulatory effluent limits, methods that are more effective are invariably prohibitively costly. Alternative processing methods are considered more seriously as their understanding is developing (Volesky and Holan, 1995). Considering the number of metals and different biosorbent materials of interest, in the absence of theoretical apparatus, experimental testing of these effects requires a large volume of laboratory work (Figueira et al., 1997). Although copper is not considered as a major environmental problem, its ubiquitous presence in the solutions makes it an obvious investigation target as to its effect on biosorbent uptake of any other metals of interest. Among them, cadmium is of a primary interest for its well-recognized acute toxicity (Holan et al., 1993).

Brown seaweeds (Phaeophyceae) constitute an algal group containing the characteristic pigment fucoxantine, responsible for their brown color. Floating masses of Sargassum constitute the Sargasso Sea, being also very common in the Brazilian Coast. All Sargassum species contain floating bubbles, responsible for their decreased density, thus contributing for their presence in the marine environment. Quantitatively, the most abundant polysaccharide in the cell wall of brown seaweeds is alginate. Alginate is a polymer constituted by two uronic acids (β-1,4-D-mannuronic and α-1,4-L-guluronic), with molar ratio between the acids ranging from 0.25 to 2.5. Alginate acid is present in these seaweeds usually as calcium, magnesium, sodium and potassium salts, mainly in the cell wall. It is a structural polysaccharide with strong ion-exchange properties. Beyond its high metal uptake capacity, this algal genus has been selected for study due to their wide distribution in most tropical countries, being available at high quantities as a waste biomaterial. In this work, the use of Sargassum species as a biosorbent for copper ions from aqueous solution was investigated. The influence of different parameters on copper uptake such as sorption time, initial pH, temperature, biomass sizes, biosorption kinetics and initial copper concentration was investigated.

Simple isotherms in this investigation were constructed as a result of studying equilibrium batch sorption behavior of different biosorbent material characteristics, which enable quantitative evaluation of biosorption performance. The aim of this study is to investigate the adsorption characteristics of marine algae on copper with emphasis on its efficiency, stability and regeneration.

**EXPERIMENTAL**

**Sample Preparation**

Sargassum, seaweed biomass was collected during low tide on the North Coast of Kwa-Zulu Natal (Umdhloti Beach). After the seaweed biomass was collected it was sun-dried for two days. The biosorbent was prepared by washing it with 0.1N HCl (to convert alginates to alginic acid) and then rinsing it with distilled water. The sargassum was then dried in an oven for the duration of 24 hours at a temperature of 60°C. The algae were then put in a grinder, to prepare for different sizes of biomass. In order to separate the different sizes, the load was placed in a shaker and collected through differently sized sieve trays.

**Sorption Dynamics Experiments**

In order to determine the contact time required for the sorption equilibrium experiments, the batch sorption dynamics experiments were conducted first. 0.1g of biomass was mixed with 50ml of different concentrations of Cu as CuSO₄·5H₂O solution in a 100 ml Erlenmeyer flasks on a rotary shaker at 3Hz and room temperature. The pH value of the solution was controlled. The 0.1N HCl or 0.1N NaOH solution was added to maintain the pH value of the reacting solution at the level of the designed end-point.
The metal concentration were analysed before and after the experiment using Atomic Absorption Spectrophotometer (AAS). Figure 1 represents the schematic diagram for the experimental procedure for obtaining equilibrium data. A simple preliminary sorption kinetics test established the exposure time necessary for the given sorbent particles to reach the equilibrium state characterized by the unchanging sorbate concentration in the solution. This was determined by time-based analysis. Enough time was allowed for the sorption system to reach equilibrium.

Figure 1: Outline of an experimental procedure for determining equilibrium data

**Sorption and desorption column experiments**

Separation processes based on what is widely labeled as adsorption, followed by desorption are widely utilized (Hines and Maddox, 1985). Due to its inherent effectiveness in adsorption processes the packed-bed reactor is generally preferred (Levenspiel, 1962). Its advantage is the highest possible packing density of the sorbent, yielding a high volumetric productivity. The performance of packed-bed adsorbers is analyzed using the effluent concentration versus time curves. For adsorption the plot is usually referred to as the breakthrough curve, and for desorption it is the elution curve. Both curves are a function of the column flow parameters, sorption equilibrium and mass transport factors (Aldor et al., 1995).

The column experiments were performed in a packed bed column of inner diameter 30 mm and length of 500 mm uniformly packed with 38 g (dry basis) of acid treated biomass operated in a trickle bed regime (see figure 2). During the column sorption operation, an aqueous solution containing 35 mg/l copper (from CuSO\(_4\cdot5\)H\(_2\)O), at pH 4 was pumped through the column at a constant flowrate (15 ml/min) continuously. At pH 4 it was shown that the rate of adsorption was high. Experiments were conducted at different pH. The samples were collected from the outlet of the column at different time intervals and analyzed for the copper effluent concentration by AAS. After the biomass in the column became saturated, the column was washed at the same flowrate by distilled water for several hours, before a subsequent copper elution with 0.1N HCl acid. The reason for washing the column for several hours was to ensure that all solution with Cu ions was removed. This forms first step of biomass regeneration before elution step. The outlet sample collection and analysis was the same as that used in the biosorption uptake run.
Procedure used to obtain the experimental adsorption isotherm.

1. Sorbate in solution at the highest concentration of interest was prepared.
2. Dilutions to cover the entire concentration range (from 0–blank to the maximum) were made.
3. Parameters such as pH were adjusted.
4. The sorbate initial concentrations $C_i$ (mg/l) in all liquid samples were determined.
5. The amount of the (bio) sorbent solids $S$ (g) to be used were accurately weighed for each contact test and recorded. It is helpful to be able to roughly estimate the anticipated sorption uptake so that there is a well detectable sorbate final concentration left in the solution at equilibrium in each sample. If there is too much solids added there may be virtually no sorbate left in the solution for a reliable analysis (Alkan et al., 2001).
6. The sorbent solids were added into each sample solution and gentle mixing was provided over the sufficiently long contact period.
7. Parameter such as pH was controlled at a constant value during the contact period, using appropriate acid. In order to do that, the sorption system was not diluted by adding excessive volume.
8. At the end of the contact period, solids from liquids were separated by decantation or filtration.
9. The liquid portion was analyzed for the residual, final sorbate concentration $C_f$ (mg/l).
10. The sorbate uptake $q$ (mg sorbate/g biomass) was calculated as:

$$ q = V(C_i - C_f)/S $$

where $V$ is a volume of solution (l), and other variables are defined above. The sorption isotherm ($q$ vs. $C_f$) was plotted. In the above procedure, it was the initial sorbate concentration $C_i$ that was varied.
RESULTS AND DISCUSSION

Sorption dynamics and isotherms at different pH values in a batch system

In order to determine the minimum contact time for the equilibrium experiments, the sorption dynamics was examined first. Figure 3 shows the profiles of dimensionless copper concentration against time.

The copper biosorption rate was strongly influenced by the sorption system pH value, the copper solution concentration in the solution decreased with contact time faster at higher pH values. At various pH values, approximately 60-70% of the copper present originally in the solution was sorbed onto biomass in about 25 minutes after the start of biosorption and the equilibrium could be reached within 3 hours. This provided a guide for the biosorption contact time to be used in the equilibrium experiments. Same conditions were also applied to determine the contact time at pH 4 and it was observed that 3 hours is sufficient for the system to reach equilibrium as represented in figure 3. Best adsorption was observed at pH 4 as illustrated in figure 4 by approximately 75% adsorption rate.

![Figure 3: Dimensionless copper concentration against time for determination of the minimum contact time for equilibrium experiments at different pH values and T=25°C](image-url)
Copper biosorption kinetics

The purpose of these experiments was to determine the contact time required to reach the equilibrium between dissolved and solid-bound sorbate. Equilibrium time is a function of many factors, such as type of biomass (number and kind of biosorption sites), size and form of biomass, physiological state of biomass (active or inactive, free or immobilized), as well as the metal involved in the biosorption system. Reported values for equilibrium time are in the range from 15 minutes (Aksu et al., 1991).

Figure 5 presents the results at two different initial concentrations of 92 and 162 mg/l of copper with a contact time of 3 hours was enough for the system to reach equilibrium. So, this time was used to obtain the isotherms in all experiments. Figure 5 clearly indicates that sorption can be divided into two stages: one in which the sorption rate is very high (60% of biomass saturation capacity in a contact time of 25 minutes), followed by a second stage with a much lower sorption rate. This behaviour has often been reported by other researches (Crist et al., 1994), the proton uptake by algal cells consists of two processes, a fast surface reaction and a slow diffusion of protons into the cells. The fast biosorption kinetics observed is typical for biosorption of metals involving no energy-mediated reactions, where metal removal from solution is due to purely physico-chemical interactions between biomass and metal solution (Aksu and Kutsal, 2001).
Influence of biosorbent size on copper biosorption

The influence of biosorbent size on copper biosorption can be evaluated from figure 6. The experimental results indicate that the biosorbent size did not influence the capacity and rate of copper biosorption.

Although this is contrary to expected for an intraparticle diffusion controlled process, it is necessary to point out that the two sizes of biomass are actually of the same thickness (dimension which determines the diffusion distance). This is so because size grading of ground biomass particle by standards sieves works on the length and width dimensions and the particle shape is flake.
This behaviour has been reported by other researchers, although it has been showed that larger biomass particles of *Sargassum fluitans* and *Ascophylum nodosum* had higher metal uptake than smaller particles in the case of Cadmium, nickel, lead and zinc (Volesky *et al*., 1999).

**Effect of pH**

It is now well established that heavy metals are taken up from water predominantly by ion exchange (Volesky *et al*., 1999). Carboxyl and sulphate groups have been identified as the main metal-sequestering sites in seaweed and, as these groups are acids, its availability is pH dependent (Marulanda and Harcum, 1999). At pH in the range 3.5-5.0 these groups generate a negatively charged surface, and electrostatic interactions between cationic species and this surface is responsible for metal uptake (Kratochvil and Volesky, 1998). As the pH increased, the ligands such as carboxylate groups in *Sargassum* sp. would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface.

Figure 7 shows the effect of pH on the biosorption capacity of the marine algae *Sargassum* species. It is shown that as the pH increases, the rate of adsorption also increases with the optimum pH of 4 for copper biosorption. Copper precipitated at pH higher than 4 and no adsorption was observed. The effect of pH on metal biosorption has been studied by many researchers, and the results demonstrated an increase in cation uptake with increasing pH values, both on fungi and algae biomass (Fourest and Roux, 1994). At pH values lower than 2.5, copper (II) removal was inhibited, possibly as a result of the competition between hydrogen and copper ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as a consequence of the repulsive force (Matheickal and Yu, 1999).
Multiple sorption-desorption cycles

After it was established that biomass has a characteristic of adsorbing copper, the activeness of biomass in a multiple sorption-desorption was tested. The main reason was to see if the biomass can be regenerated or it must be used once only. The multiple sorption-desorption cycles were performed in a continuous flow biosorption process with the aim to determine:

- the efficient utilization of biomass,
- checking its performance,
- change in mechanical properties,
- efficiency of biosorption and elution,
- biomass damage and stability over a prolonged operation time

Figure 8 shows six sorption and desorption cycles, which were carried out with the column packed with raw *Sargassum* biomass. The packed bed contained seaweed fragments of approximately 1.77mm diameter and bladders, leaves and complete branches with a length of up to 4 cm. A copper bearing feed solution of 35 mg Cu/l with pH 4 at a flow rate of 15 ml/min was passed through the column. The sorption process was stopped after reaching 35 mg Cu/l in the effluent and the regeneration solution of 0.1N HCl was pumped through the bed. Table 1 shows the results in terms of the breakthrough time ($t_b$) and exhaustion time ($t_e$) for each cycle.

![Figure 7: Effect of pH on the biosorption capacity of marine algae *Sargassum* species (t=3 hours, T=25°C)](image)

![Figure 8: Breakthrough parameters for six sorption-desorption cycles.](image)

<table>
<thead>
<tr>
<th>Breakthrough number</th>
<th>$t_b$ (hr)</th>
<th>$t_e$ (hr)</th>
<th>Time of elution (hr)</th>
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<tr>
<td>1</td>
<td>25</td>
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<td>2</td>
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</table>
The breakthrough point is the time \( t_b \) when the sorbate appeared in the effluent stream at some predetermined concentration, which was 1 mg Cu/l. The time \( t_e \) is the time when the whole column sorption bed became totally saturated by the sorbate, and the bed was no longer effective and the effluent concentration was 35mg Cu/l corresponding to the initial concentration. The time interval between \( t_b \) and \( t_e \) corresponds to the length of the mass-transfer zone of the bed as shown in figure 8.

To determine the weight loss after the 6\(^{th} \) cycle, the biomass was washed with distilled water and dried in the oven at 45\(^\circ\)C overnight. From the initial 38 g of raw Sargassum, 29 g remained, with a weight loss of 23.7%. Process conditions used in this study included use of raw biomass, analytical reagents and distilled/deionised water. While a shortening breakthrough time from cycle to cycle was observed, the uptake capacity exhibited no decreasing trend.

The reason for shortening breakthrough time was apparently not the diminishing equilibrium uptake capacity, but rather a slight change in the column overall adsorption rate. This means that while adsorbing sites were still available, they became less accessible. A loss of sorption performance during the long-term use may have a variety of reasons. It may be caused by changes of the chemistry and of the structure of the biosorbent, as well as by changes of the flow within the column. Deteriorating sorption properties may be due to chemical changes of the cell wall components such as alginate and sulphated polysaccharides, which play a major role in adsorption by marine algae (Aldor \textit{et al.}, 1995).

![Figure 8: Breakthrough curves for six biosorption cycles for a copper solution: \( C_i=35 \) mg/L, \( pH=4 \), \( T=25\)\(^\circ\)C, flowrate=15 ml/min)](image)
CONCLUSIONS

- The biomass of the marine algae *Sargassum* species demonstrated a good capacity of copper biosorption, highlighting its potential for effluent treatment processes. This biosorbent is widely available and easy to find.
- The kinetics of copper biosorption by inactive biomass of marine algae *Sargassum* species was fast, reaching 60% of the total biosorption capacity in twenty-five minutes.
- The biosorbent size had no influence on copper biosorption rate for flake-shaped particles.
- pH had a strong effect on copper biosorption capacity. The capacity of copper biosorption by biomass increased with pH up to pH 4.0.
- From the sorption-desorption experiments, a weight reduction of 24% of the biomass was observed after the 6th cycle.
- The length of the packed bed after the 6th desorption decreased from 38 to 35 cm.
- The high efficiency of biosorption and elution, low biomass damage and stability over a prolonged operation make a new biosorption process an effective alternative for copper pollution control.
- Therefore, marine algae can be used to treat effluents with heavy metals, with an advantage that it can be regenerated and is widely available along the coast of seashores.

RECOMMENDATIONS

Surface characterization of the biomass with scanning electron microscope (SEM) before adsorption, and after adsorption and desorption should be conducted to identify other effects which might have an effect on the adsorption characteristics of marine algae.

REFERENCES


