Effluent treatment: Copper biosorption on seaweed/chitosan beads

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INTRODUCTION

Concern about **micropollutants** such as pesticides, metal ions, estrogens or PCBs has risen dramatically over the last few years. Although they are present at low levels in many ecosystems, their concentrations have never stopped increasing and affect both plant and animal kingdoms.

Heavy metals such as lead, nickel, chromium, uranium or **copper** are present in many industrial effluents. Due to their low concentration, conventional removal methods such as chemical precipitation, reverse osmosis or electro-deposition are inapplicable or too expensive. **Biosorption** is a valuable alternative since this separation technique is most efficient at low concentrations, due to the form of the isotherms which are generally of the favourable type (Kratochvil, 1998).

Brown seaweeds (*Sargassum sp.*) are known for their ability to remove metal ions from aqueous solutions and are a very popular biosorption matrix (Volesky, 2007). However, dried algae ground into a powder cannot be used in a fixed bed since their rehydration results in a thick, pasty slurry which blocks the adsorption bed.

The purpose of this research was to evaluate the potential of **encapsulation** for the conditioning of dried, ground algae into a **fixed adsorption bed**. **Chitosan**, i.e. de-acetylated chitin, was chosen as the encapsulation matrix since it is a well-known and documented gelling polysaccharide. The primary purpose of chitosan was to provide a matrix that would not hinder adsorption by the seaweed particles while maintaining a suitable rigidity of the bed.

MATERIALS AND METHODS

Materials

Chitosan was purchased from Primex, Island. The brown seaweed (*Sargassum sp.*) came from Vietnam. A 3.929 g/l stock solution of $CuSO_4 \cdot 5H2O$, which corresponds to 1000 mg/l copper, was prepared and appropriately diluted when needed. The pH of the solutions was adjusted to 5.0 with 0.01M HCl and 0.01M NaOH. A Streamline 50 chromatography column from Amersham, Sweden, was used for the fixed bed experiments. All chemicals were of reagent grade.

Production of chitosan beads/encapsulation of seaweed powder

Chitosan beads were prepared as follows: briefly, chitosan (2.0 g) was dissolved in 1% acetic acid (100 mL) and extruded dropwise from a syringe equipped with a hypodermic needle into a gelation bath having one of the three following compositions: 3% w/v NaOH + 1.5% v/v ethyl acetate, 3% w/v NaOH 1.5% v/v ethyl acetate + 1.5% w/v glutaraldehyde (cross-linker) or 1% w/v sodium triphosphate. The beads were then washed with dist. water and stored until use. Smaller beads could be obtained using a coaxial air-flow nozzle (Nisco Engineering, Switzerland). For seaweed/chitosan composite beads, 5g of seaweed powder were mixed with 100g chitosan solution before extrusion.

Adsorption isotherms for the different types of beads were measured at 25°C (pH_0 = 5.0) in conical flasks by contacting 15 ml of Cu(II) solutions at different initial concentrations (1000, 800,

600, 400, 200 and 100 mg/L) with 1.2 g of wet chitosan beads with or without seaweed powder. The residual concentration of Cu(II) was determined by atomic absorption spectrophotometry (Apparatus AAS 220 FS from Varian, Australia) once equilibrium was reached (after ca. 120 min).

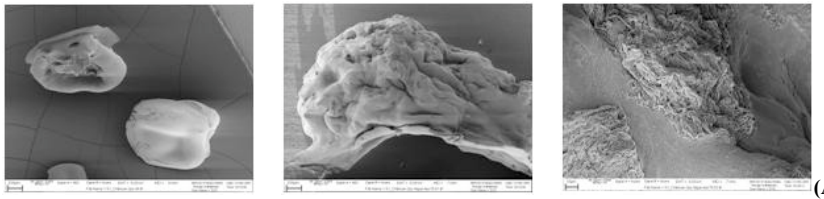
Adsorption kinetics was measured at 25°C (pH_0 = 5.0) in conical flasks by contacting 15 ml of a 1000 mg/l Cu(II) solution with 1.2g of wet chitosan beads (↔ 24 mg dry chitosan). A carrousel-type mixer (SB3 Rotator from Stuart, UK) was used for agitation. The rotating speed was either 20 or 5rpm. Residual Cu(II) concentrations were measured at given time intervals by atomic absorption spectrophotometry (AAS).

The fixed-bed experiments were performed by pumping a 1000 mg/l Cu(II) solution at a flow rate of 0.8 l/h through a 50 mm i.d. chromatography column filled with 1130 g wet, 2% chitosan beads (bed height = 88 cm) using a peristaltic pump. The effluent samples were analyzed by AAS.

RESULTS AND DISCUSSION

Beads morphology

SEM pictures of chitosan and chitosan/seaweed beads gelled in a NaOH + ethyl acetate bath are shown in Fig. 1. The beads display an elongated form, their size distribution is rather broad and cavities can be seen on their surface (Fig. 1A). These features could be linked to the "crude" extrusion technique, to the high surface tension of the gelation bath, to the gelling kinetics and to the agitation. It was not the goal of this work to optimize these aspects, but the use of surface active compounds in order to reduce the surface tension would certainly help improve them.



(A) (B) (C)

Figure 1: SEM pictures of beads. A) chitosan 2% beads. B) chitosan 2% + seaweed 5% beads. C) surface of chitosan 2% + seaweed 5% beads. Bar length = 200 µm for (A) and (B), 10 µm for (C)

Chitosan/seaweed beads (Fig. 1B & 1C) are larger than plain chitosan beads. They are not spherical either, their surface appears pleated (Fig. 1B) and the distribution of seaweed particles in the chitosan matrix can be seen in Fig. 1C.

Adsorption isotherms (T = 25 °C, pH_0 = 5.0)

The adsorption isotherms of seaweed powder, chitosan beads and chitosan/seaweed beads are shown in Fig. 2. Surprisingly, chitosan has a much higher capacity for copper adsorption than seaweed powder (ca. 200 mg/g against 55 mg/g, see Fig. 2). All isotherms could be described using the Langmuir model (solid lines). The isotherm for the chitosan/seaweed beads (intermediate, dotted curve) was calculated from the isotherms of the individual components, and the resulting curve lies close to the experimental data. The types of gelling agents that were used also impact the adsorption capacity of chitosan beads.

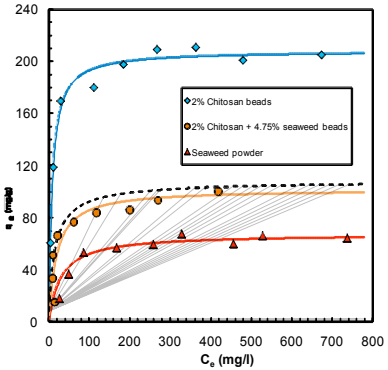


Figure 2: Cu(II) adsorption isotherms on seaweed powder, chitosan and chitosan/seaweed beads

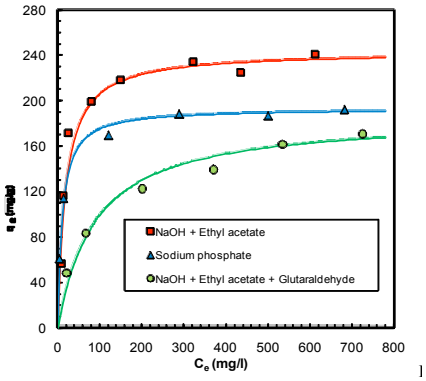


Figure 3: Cu(II) adsorption isotherms on 2% chitosan beads with different agents.

As shown in Figure 3, the highest capacity for Cu(II) was obtained with the NaOH + ethyl acetate bath. Cross-linking the beads with glutaraldehyde results in a reduced capacitiy. Intermediate capacities were measured with sodium polyphosphate. Beads were smaller in this latter case (2.1 mm mean diam.) than when NaOH + ethyl acetate was used (3.4 mm).

Copper adsorption kinetics (T = 25 °C, pH_0 = 5.0, C_0 = 1000 mg/l)

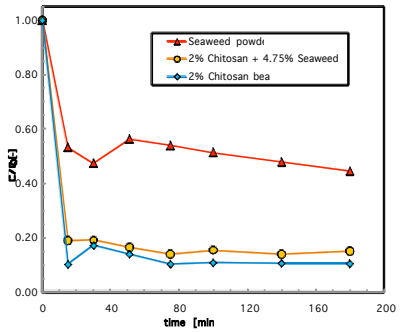


Figure 4: Cu(II) adsorption kinetics on seaweed, chitosan and chitosan/seaweed beads.

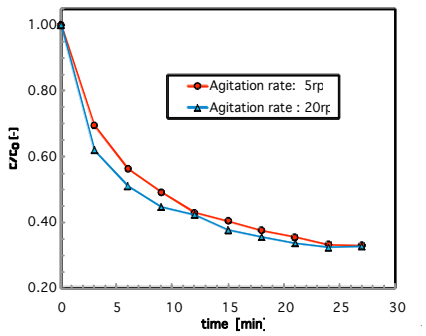


Figure 5: Cu(II) adsorption kinetics on 2% chitosan beads : agitation rates.

Figure 4 shows that adsorption equilibrium is reached in less than 30 min for all three kinds of adsorbents and that, again, seaweed powder has a lower Cu(II) adsorption capacity than chitosan. Fig. 5 shows that the adsorption kinetics of Cu(II) is only slightly accelerated by a higher agitation rate, meaning adsorption is mostly limited by internal mass transfer under these conditions.

The breakthrough curve measured in fixed bed mode and shown in Fig. 6 allowed the determination of the static and dynamic capacities, which amounted to 380 and 85 $mg_{Cu}/g_{adsorbant}$, respectively.

Fixed bed and fluidized bed adsorption

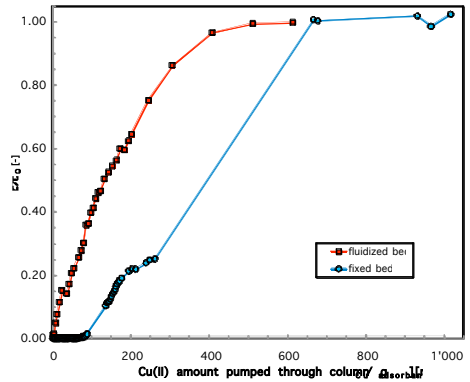


Figure 6: adsorption of copper in fixed bed and fluidized bed. Fixed bed: C_0 1g/L, speed flow 0.8L/h. Fluidized bed: C_0 0.1 g/L, speed flow 1.22 L/h

Figure 7: Bead shrinking and channeling in fixed bed of 2% chitosan beads (50 mm column i.d.) upon adsorption of copper

The dynamic capacity was determined for a breakthrough concentration of 40 mg/l. Significant shrinking of the chitosan beads was observed upon adsorption of Cu(II) which led to channeling in the bed, as shown in Fig. 7. A fluidized bed adsorption was then tried in order to solve this problem, but Fig. 6 shows that breakthrough occurred much earlier than in the fixed bed mode.

CONCLUSION AND PERSPECTIVES

Although more expensive, chitosan has a much higher binding capacity for Cu(II) than seaweed powder. Adsorption kinetics is limited by internal mass transfer, and should be improved upon using smaller beads. The shrinking of chitosan beads and the resulting channeling is however a problem for fixed bed operation. A fluidized bed configuration could help avoid these complications, but the higher flow rates required to suspend the particles severely limits the adsorbed quantities (premature breakthrough). Future investigations shall concentrate on the optimization of the fluidized bed mode of operation with respect to flow rate, as well as bead size and density.

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