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## Simultaneous biosorption of $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ and $\text{Cr}^{6+}$ from aqueous solution by *Streptomyces rimosus* biomass

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### Abstract

The  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  biosorption capacity of the *Streptomyces rimosus* biomass pretreated with NaOH was studied in the batch mode. Under optimal experimental conditions, a biosorption capacity of 30 mg  $\text{Cu}^{2+}$  g<sup>-1</sup> biomass, 27.4 mg  $\text{Zn}^{2+}$  g<sup>-1</sup> biomass and 26.7 mg  $\text{Cr}^{6+}$  g<sup>-1</sup> biomass was obtained. The equilibrium data poorly fitted the Langmuir and Freundlich model isotherms over the whole range of initial  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  concentrations tested (0–300 mg L<sup>-1</sup>).

**Keywords:** Copper; Zinc; Chromium; *Streptomyces rimosus*; Biosorption; Wastewater treatment; Batch processing

### 1. Introduction

Many industries such as tannery, coating, car, aeronautic and steel industries generate great quantities of wastewater containing various concentrations of Cu, Zn and Cr. These concentrations are usually too low to be treated by standard methods. The main techniques that are commonly

used for the recovery of metal ions from industrial effluents include precipitation, coagulation–adsorption, ion exchange, membrane processing and solvent extraction. These techniques suffer from diverse drawbacks [1]. For example, precipitation processes cannot guarantee the metal concentration limits required by regulatory standards and produce wastes that are difficult to treat. On the other hand, ion exchange and adsorption processes

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are very effective but require expensive adsorbent materials for the removal of heavy metals from dilute aqueous streams. The use of low-cost and waste materials of biological origins as adsorbents of dissolved metal ions has been shown to provide economic solutions to this global problem.

In the literature, the capability of either living or non-living organisms for fixing metal ions is widely described. Modak et al. [2] showed that non-living *A. niger* biomass attached to wheat bran was selective for the extraction of copper and zinc. Guibal et al. [3] studied the biosorption of uranium by filamentous fungus *Mucor* and Gardea-Torresdey et al. [4] performed batch experiments with inactivated cells of *Mucor rouxii* for  $\text{Cu}^{2+}$  binding. Other studies were performed with different biomaterials as marine [5–9], bacteria [10–18], chitosan [19], humic substances [20] and sewage sludge [21,22]. All these studies were done to remove and recover heavy metals from dilute aqueous streams by biosorption.

In a preceding study, we have shown that a waste *Streptomyces rimosus* biomass obtained from an antibiotic (oxytetracyclin) production plant at Medea (Algeria) was able to accumulate metal ions from dilute aqueous solution [23]. Cadmium biosorption was more particularly investigated. The purpose of the work presented here was to confirm the potentialities of this waste microbial biomass as a cost-effective metal biosorbent by extending the sorption tests to  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions. The effects of the initial pH, stirring speed and initial  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  concentration on the binding capacity of *S. rimosus* biomass for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions were studied. The biosorption equilibrium data were compared to the Langmuir and Freundlich adsorption models.

## 2. Materials and methods

### 2.1. Biomass preparation

The *S. rimosus* biomass collected at the antibiotic production site was washed with distilled

water and dried at  $50^\circ\text{C}$  for 24 h. Biomass samples were then ground manually in a mortar and sieved to select a fraction with particle diameters between 50 and  $160\ \mu\text{m}$ . Five grams of native biomass were maintained for 30 min in 500 ml NaOH (0.1 M) with a stirring speed of 250 rpm and at ambient temperature (around  $25^\circ\text{C}$ ). After decantation and filtration, the NaOH-treated biomass was obtained. This biomass was once again dried and sieved to obtain a 50– $160\ \mu\text{m}$  particle size fraction.

### 2.2. Biosorption tests

The biosorption tests were performed in a closed system at ambient temperature under magnetic stirring. A known amount of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  solution prepared with ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ),  $\text{ZnCl}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  salts was added to the biomass suspended in 500 ml of distilled water until adsorption equilibrium was reached. The initial pH of the test medium was adjusted to defined values with HCl (0.1 M) and NaOH (0.1 M) before addition of the metal ion solution. Standard conditions for biosorption experiments were the following: agitation speed 250 rpm; initial  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  concentration  $100\ \text{mg L}^{-1}$ ; temperature  $c\ 25^\circ\text{C}$ , biomass dry weight concentration  $3\ \text{g L}^{-1}$ ; initial pH 5. Varying agitation speeds, initial  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  concentrations and pH values were also tested as specified.

Residual concentrations of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions in water were monitored using a Unicam 939 atomic absorption spectrophotometer with a wavelength of 324.8 nm, 213.9 nm and 358.9 nm, respectively. All adsorption tests were duplicated.

### 2.3. Sorption isotherms: Langmuir and Freundlich models

The Langmuir model corresponds to the following equation:

$$q_e = q_m \frac{bC_e}{1 + bC_e} \quad (1)$$

where  $C_e$  is the metal concentration in solution at equilibrium ( $\text{mg L}^{-1}$ ),  $q_m$  is the maximum amount of metal adsorbed per unit weight of dry biomass, and  $b$  is a binding stability constant.

The Freundlich model equation is of the form:

$$q_e = kC_e^{1/n} \quad (2)$$

where  $k$  and  $1/n$  are the Freundlich adsorption constant and exponent characterizing the system.

### 3. Results and discussion

#### 3.1. $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ and $\text{Cr}^{6+}$ biosorption kinetics

The kinetics of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  biosorption to the native and NaOH-treated biomasses was very fast (Figs. 1 and 2), suggesting very active phenomena at the biomass surface. For the native biomass, the adsorbed quantity tended towards a value of  $26.6 \text{ mg Cu}^{2+} \text{ g}^{-1}$  biomass,  $23.5 \text{ mg Zn}^{2+} \text{ g}^{-1}$  biomass and  $23 \text{ mg Cr}^{6+} \text{ g}^{-1}$  biomass, respectively (Fig. 1). Equilibrium was reached after about 90 min, 120 min and 150 min, respectively. At the very beginning of the sorption experiment, the pH fell from 4.5 to 4.37, highlighting  $\text{H}^+$  release from the biomass due to ion exchange between protons and  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions. Then the solution pH

stabilized, implying other biosorption mechanisms such as complexation and electrostatic attraction.

The limiting value of adsorbed  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions on the NaOH-treated biomass after 50 min, 75 min and 90 min, respectively, was  $30 \text{ mg Cu}^{2+} \text{ g}^{-1}$  biomass,  $27 \text{ mg Zn}^{2+} \text{ g}^{-1}$  biomass and  $26.5 \text{ mg Cr}^{6+} \text{ g}^{-1}$  biomass (Fig. 2). The contact time of 1 h was considered as the equilibrium time for all following experiments (performed on the treated biomass only). The solution pH remained approximately constant (equal to 5) over the sorption experiment, suggesting that the biosorption mechanism was an ion exchange between  $\text{Na}^+$  and  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions. The improvement of biosorption by NaOH treatment confirms that the ion exchange sites of the biomass, i.e., functional groups of the cell wall such as carboxylic and phosphate groups were more efficient in the sodium form than protonated.

#### 3.2. Effect of initial pH on $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ and $\text{Cr}^{6+}$ biosorption

The efficiency of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions removal by the NaOH-treated *S. rimosus* biomass was strongly affected by the initial pH of the  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  salt solution (Fig. 3). Below or around pH 4, the metal adsorbability was very

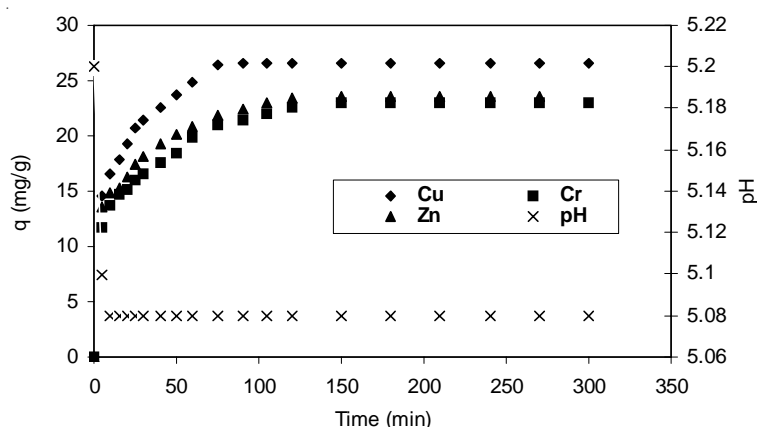


Fig. 1. Time evolution of the biosorption capacity ( $q$ ) of the native biomass. Changes in pH during the biosorption tests are also shown.

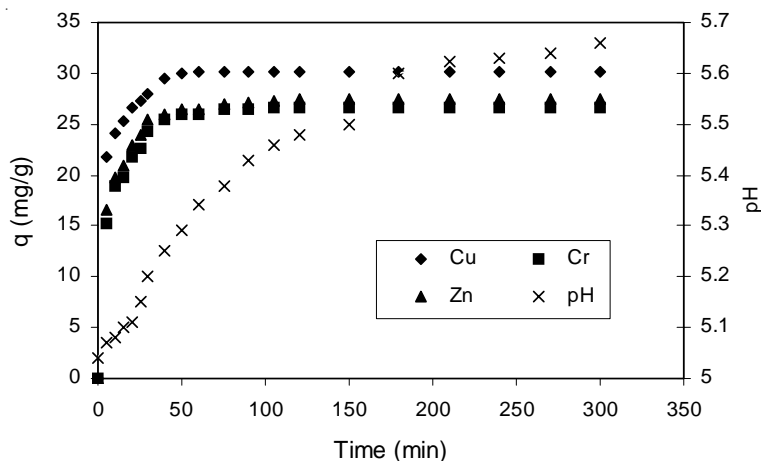


Fig. 2. Time evolution of the biosorption capacity ( $q$ ) of the NaOH-treated biomass. Changes in pH during the biosorption tests are also shown.

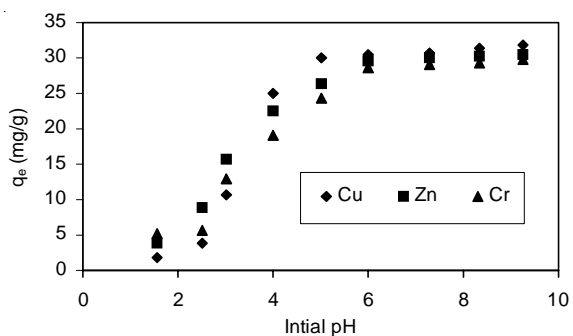


Fig. 3. Effect of initial pH on the  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  biosorption capacity of NaOH-treated *S. rimosus* biomass at equilibrium ( $q_e$ ).

low owing to poor ionisation of functional acidic groups implied in the biosorption process. Following the appearance of negatively charged groups (e.g., carboxylic and phosphate groups) at the biomass surface, there was an increase in  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  biosorption capacity with increasing pH from 4 to 6. At pH 6, the maximum equilibrium uptake value was found as  $30.5 \text{ mg Cu}^{2+} \text{ g}^{-1}$  biomass,  $29.6 \text{ mg Zn}^{2+} \text{ g}^{-1}$  biomass and  $29 \text{ mg Cr}^{6+} \text{ g}^{-1}$  biomass.

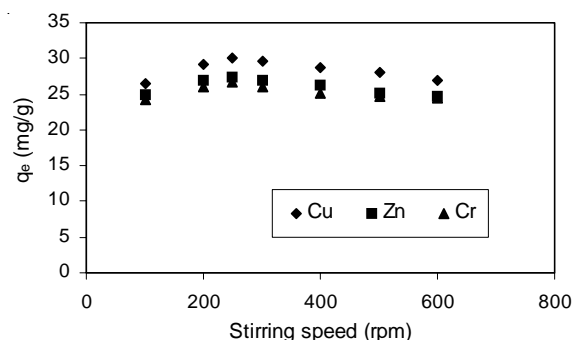


Fig. 4. Effect of stirring speed on  $q_e$ .

### 3.3. Effect of stirring speed on $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ and $\text{Cr}^{6+}$ biosorption

A stirring speed of 250 rpm was optimal for adsorption capacity (Fig. 4). This value represented a compromise between lower speeds, unable to ensure efficient dispersion of biomass particle in the liquid medium and increasing external mass transfer resistance, and higher speeds creating vortex phenomena.

### 3.4. Influence of the initial $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ and $\text{Cr}^{6+}$ concentration

Fig. 5 shows that the amount of adsorbed  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  per unit mass of NaOH-treated biomass increased with the initial concentration of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions  $C_o$ . The values of residual concentrations and percentages in weight of adsorbed  $\text{Ag}^+$  ions are shown in Fig. 5. The maximum  $q_e$  value (i.e.  $30 \text{ mg Cu}^{2+} \text{ g}^{-1}$  biomass,  $27.4 \text{ mg Zn}^{2+} \text{ g}^{-1}$  biomass and  $26.7 \text{ mg Cr}^{6+} \text{ g}^{-1}$  biomass), corresponding to the saturation of active sites on the biomass, was reached at  $C_o = 100 \text{ ppm}$ ,  $C_o = 100 \text{ ppm}$  and  $C_o = 100 \text{ ppm}$  respectively.

### 3.5. Adsorption isotherm analysis

The isotherm curve showed a limiting biosorption capacity attained at an equilibrium concentration of about  $11 \text{ mg.L}^{-1}$  for  $\text{Cu}^{2+}$ ,  $17.7 \text{ mg.L}^{-1}$  for  $\text{Zn}^{2+}$  and  $60 \text{ mg.L}^{-1}$  for  $\text{Cr}^{6+}$  (Fig. 6). The Langmuir and Freundlich equations [Eqs. (1) and (2), respectively] were tested to model this equilibrium curve. None of these two classical models of adsorption isotherms was found to fit correctly the experimental curve over the whole range of tested  $C_o$  values.

### 3.6. Desorption

The *S. rimosus* biomass should be reused several times to decrease material cost.

Desorption of the biosorbed  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions from the *S. rimosus* biomass was studied in a batch system. The  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions adsorbed onto *S. rimosus* biomass were eluted with 500 ml of  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  at  $\text{pH} = 2$ . For one cycle biosorption–desorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions, the biosorption capacity of *S. rimosus* biomass was decreased up to 55%, 11%, 6%, respectively for  $\text{Zn}^{2+}$  ions, and 50%, 36%, 17%, respectively for  $\text{Cu}^{2+}$  ions. No decrease was observed for  $\text{Cr}^{6+}$  ions.

The regeneration of *S. rimosus* biomass should be performed with our tests in order to take the biosorption–desorption process reversible and the

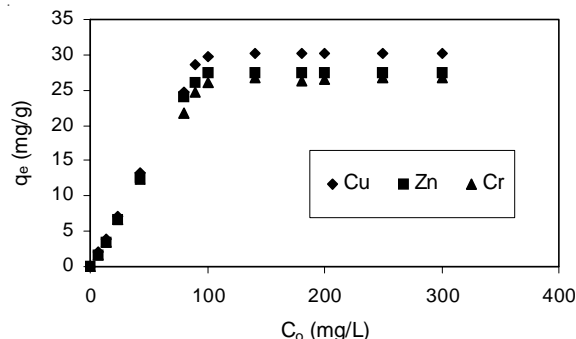


Fig. 5. Influence of initial  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  concentration on  $q_e$ .

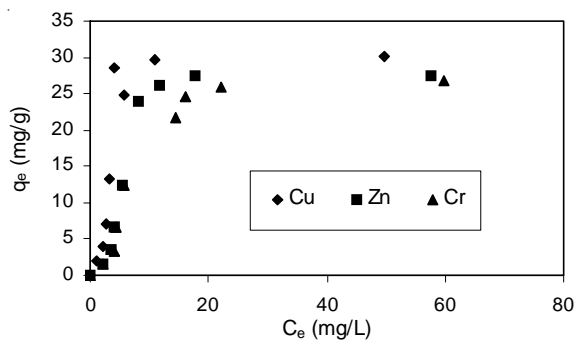


Fig. 6. Adsorption equilibrium data binding of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions on the NaOH-treated *S. rimosus* biomass.

*S. rimosus* biomass can be repeatedly used for the removal of heavy metals ions from wastewater.

## 4. Conclusion

The present results indicate that NaOH-treated *Streptomyces rimosus* biomass may be a suitable material for the removal of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cr}^{6+}$  ions from dilute solutions. However, desorption experiments remain to be performed to assess the reusability of this low-cost biosorbent. Furthermore, in view of the practical application of this waste biomass to the treatment of metal bearing streams, this preliminary study needs obviously to be completed by additional experiments con-

cerning in particular the influence of ionic strength and diverse constituents that are frequently found in actual industrial effluents, such as surfactants, complexing agents and other metal ions. These extensions are under investigation and will be reported later.

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