

Biosorption of Cu²⁺ and Zn²⁺ by immobilized biosorbents: Study of the biosorbent stability and capacity

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Abstract

The utilization of biosorbent immobilized in polymer matrix is studied to widen the biosorption application in the recent practice. These biosorbents have the right size, mechanical strength, rigidity and porosity. In this work the algae immobilized in calcium alginate were used as biosorbent. The stability of immobilized biosorbents in acidic solutions (pH 1; 2.5 and 5) was observed. Three differently prepared groups of immobilized beads (gel, dry and dry dipped in water for 12 hours before the experiment) were used. All groups of beads were stable in the weak pH solutions but low pH (pH = 1) caused disintegration of beads. Apparently low pH is not suitable for application of biosorbents immobilized in calcium alginate. Biosorption of copper and zinc from the single and binary metals was also studied. Higher capacity of biosorption (36.7 mg · g⁻¹) was found for copper ions in comparison with the zinc ions where the maximum observed biosorption capacity was 27 mg · g⁻¹. The presence of another ion decreased the biosorption capacity of both studied metals. The maximum biosorption capacity from two-ion solution was 32.6 and 10.5 mg · g⁻¹ for Cu and Zn, respectively.

Key words: immobilization, pH, stability, swelling, biosorption, *Chlorella kessleri*

Introduction

The removal of toxic metals from wastewater is a matter of great interest in the field of water pollution (Fiol et al., 2006). In the past decades, one has been looking for inexpensive technologies to control metal pollution. As a cost-effective mean, biosorption has been extensively studied for removing a wide variety of soluble heavy metals (Liu and Liu, 2008). Biosorption can be defined as a passive sequestering of metal ions by metabolically inactive biomass (Kaduková and Štofko, 2006; Wang and Chen, 2009). Biomass immobilization is an essential step for an industrial scale-up of biosorption. Unlike biomass in its native state, immobilization provides biosorbent particles with the adequate size, density and mechanical strength required by continuous systems (Volesky, 2003). Besides, immobilization can save the cost of separating the biomass from the treated solution which can represent up to 60 % of the total cost. This process also enables biomass regeneration in various adsorption-desorption cycles. Natural polysaccharide gel matrixes, such as alginate, are widely used and represent a cost effective alternative to synthetic polymers (Lagoa and Rodrigues, 2007). Alginate is a component of the outer cell wall of the brown algae and it is responsible for the high metal uptakes of algae. Additionally, alginate itself has biosorption capacity, favouring a possible synergic effect with the immobilized biomass (Mata et al., 2009). The knowledge of biosorbents stability in various

environments is one of the main requirements for their usage in the columns. It was found that calcium alginate is very little stable in alkaline conditions and the presence of Na⁺ and K⁺ ions (Ivánová et al., 2009).

The aim of this study was to investigate the swelling behaviour and stability of algae immobilized in the calcium alginate in acidic solutions. Additionally the capacity of immobilized biosorbents to remove copper and zinc ions from the single and binary metal aqueous solutions was studied.

Materials and methods

Biosorbent

Chlorella kessleri, an unicellular green alga, obtained from the Institute of Botany of Slovak Academy of Science was used in this study. It was grown at 25 °C in aerated and lighted liquid medium Milieu Bristol (Kaduková and Virčíková, 2003). In the Log phase of growth, *Ch. kessleri* cells were cooled, centrifuged at 3 000 rpm for 5 min, washed twice with distilled water and then dried at 100 °C for 3 h. Dried powdered biomass was used for immobilization.

Preparation of immobilized algae in calcium alginate beads

Powder prepared from dried algae *Chlorella kessleri* was mixed with 3 % sodium alginate solution in the ratio

1 : 9. The solution was then dropped from a height of 20 cm into gelling medium of 0.2 M calcium chloride solution using a syringe with a needle. On the principle of simple ion exchange water soluble sodium alginate was converted to water insoluble and stable calcium alginate salt. The formed beads were cured in the gelling medium for 2 hours. Prepared beads were consequently divided into three groups:

A. Gel immobilized beads (stored in distilled water). The average size of the bead was found to be 2.6 mm.

B. Dry immobilized beads dipped in distilled water for 12 hours before using. The average size of the bead was (after dipping) 1.7 mm.

C. Dry immobilized beads, with the size 1.3 mm.

Swelling and stability study

The pH values of sulphuric acid solutions used in experiments were 1, 2.5 and 5. Exactly 10 beads from each fraction were immersed in the tubs with 10 ml of acidic solutions and stored at laboratory temperature. Changes of weight and diameter of beads were observed.

The % weight change of the beads with respect to time was calculated according to the formula

$$m_c = \frac{m_f - m_i}{m_i} \cdot 100 \quad (1)$$

where m_c – weight change [%]

m_f – weight of the beads in the swollen state [g]

m_i – initial weight of the beads [g]

Biosorption study

Immobilized algae were used for biosorption of copper and zinc ions from the single and binary metal solutions with initial concentration $135 \text{ mg} \cdot \text{dm}^{-3}$ and $150 \text{ mg} \cdot \text{dm}^{-3}$ for Cu^{2+} and Zn^{2+} , respectively. pH value of used solutions was 4.5. This pH value was chosen according to previous experimental studies (Horváthová et al., 2008). Fraction A (gel beads) were used for biosorption study. Concentration of dry biosorbent added into the solutions was $2 \text{ g} \cdot \text{dm}^{-3}$ (it represents 250 beads). These solutions were stirred during 24 hours. At selected time intervals, solution samples were withdrawn for metal analysis. The concentration of Cu^{2+} and Zn^{2+} ions was measured by atomic absorption spectroscopy (Varian AA20+).

The metal uptake q_t at the time t was calculated from the mass balance equation as follows:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (2)$$

where q_t – the quantity of metal uptake by biomass [$\text{mg} \cdot \text{g}^{-1}$] at time t

C_0 – the initial metal concentration [$\text{mg} \cdot \text{dm}^{-3}$]

C_t – metal concentration at time t [$\text{mg} \cdot \text{dm}^{-3}$]

V – the volume of solution [dm^3]

m – dry weight of the biomass added [g]

Results and discussion

Swelling studies

Wastewater is the heterogeneous mixture of different ions with various pH values so knowing the behaviour of biosorbents in various environments before their application is crucial. Three different pH values (1; 2.5; 5) were chosen for the study of the influence of acidic conditions to the stability of calcium alginate beads. The beads were exposed to the influence of sulphuric acid until their degradation was so large that there was no possibility to handle them. The effect of sulphuric acid to three studied fractions of calcium alginate beads is visible in the Fig. 1.

Fraction A (gel beads) swelled during the first day irrespectively on the pH value of solutions. At pH 1 the beads weight increased only by 3 % but then started to decrease, at day 4 beads had original weight and then the weight of beads was lowering but they kept their shape. The beads at pH 2.5 and 5 have swelled greatly during the first day. The weight of them has grown by 50 %. During next day the weight of these beads did not change significantly. After 29 days beads in solution with pH 1 and 2.5 were degraded in such great extent that they were not able to keep their shape and have disintegrated.

Beads from fraction B (dry beads immersed in water before usage) swelled by 20 % at pH 1 and 5 and by 100 % at pH 2.5 during the first day. After the first day the weight of beads at pH 2.5 and 5 did not change considerably until the end of the experiment. In contrary, the beads from solution with pH 1 started to shrink after first day and continuously loosed their weight. Beads from all studied pH values softened till the end of the experiment but still kept their shape.

Dry beads from the fraction C changed their weight in the greatest extent in comparison with previous two fractions. They swelled by 100 % during the first day. Beads from solution with pH 1 loosed about 25 % of their weight between day 4 and 8 but later their weight did not change significantly. At pH 2.5 the weight of beads started to change after 29 days but then beads shrunken fast and loosed majority of their weight but still did not fall under their original weight. They disintegrated after 44 days of the experiment. The changes in weight of beads in pH 5 were not significant during the experiment. Beads from solutions with pH 1 and 5 kept their shape but after 44 days were difficult for handling.

Changes in bead diameters were also measured but they corresponded with weight changes.

All beads swelled during the first day. It was probably caused because of acid solution penetration into the bead and filling of free space among polymer chains. According to Hoffman (2002) the main reason of hydrogel swelling is the hydration of hydrophilic groups of alginate. Shrinking was observed only at pH 1 at all fractions and at pH 2.5 at fraction C. It was not observed at solutions with pH 5. At low pH probably carboxylic groups of alginate were protonated and hence electrostatic repulsion among these groups lessened and shrinkage was favoured (Hoffman, 2002). Shrinking of beads from fraction C (dry beads) could be

caused by a little content of water in their bodies so higher amount of acid solution could enter inside in comparison with bead from fraction A and B which all contained some amount of water before the experiment. Penetration of weak acidic solution caused probably mostly swelling while penetration of strong acidic solution (because of protonation and consequent chain repulsion) caused shrinking.

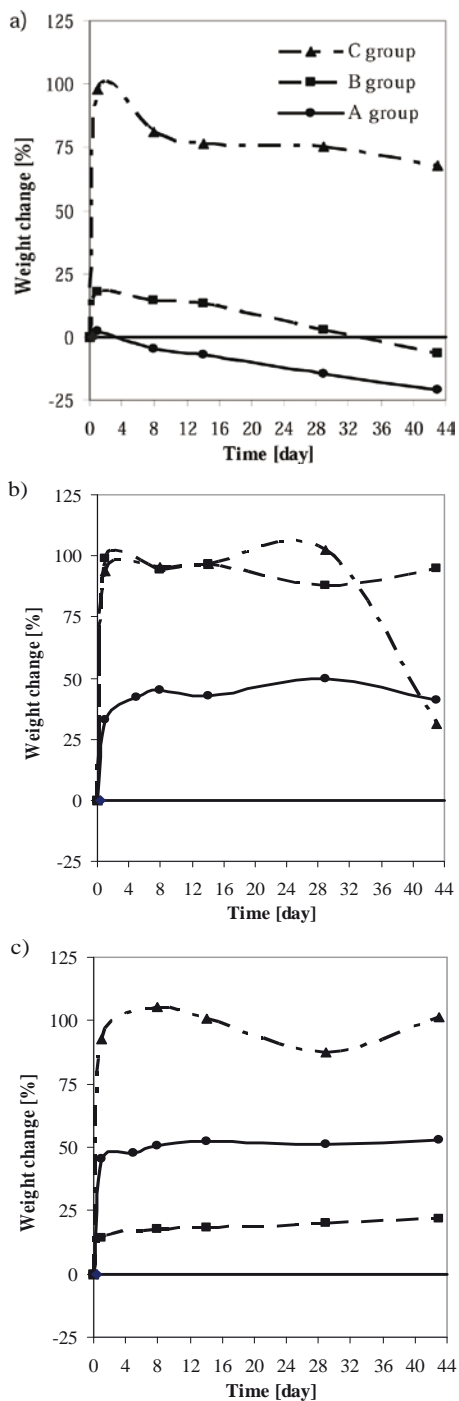


Fig. 1. Swelling profiles of gel (A) and dry (B, C) immobilized beads in solutions of sulphuric acid with: a) pH = 1; b) pH = 2.5 and c) pH = 5.

Application of immobilized algae for the removal of Cu^{2+} and Zn^{2+} ions from the single and binary metal aqueous solutions

Biosorption of Cu^{2+} ion from the single and binary solutions is visible from the Figs. 2A and 2C. Previous experiments (Horváthová, 2008) confirmed that optimal pH for the copper biosorption is in the range 4 – 5 so values from this interval were used for experiments. During the first 30 minutes the biosorption was fast and later continued slowly until equilibrium was reached. Six and four hours were necessary to reach the equilibrium in the single and binary solutions, respectively. The two-step-process of biosorption can be connected with the nature of used biosorbent. During the first fast step metal ions were probably adsorbed onto the surface of beads and then in the second step they diffused inside the beads. Maximum biosorption capacity of immobilized biosorbent for Cu^{2+} ions was 36.7 and 32.6 $\text{mg} \cdot \text{g}^{-1}$ from the single and binary solutions, respectively.

Biosorption of Zn^{2+} ions from the single and binary solutions is shown in the Figs. 2B and 2C. The two step behaviour was observed also in the case of Zn biosorption by immobilized biosorbent. Maximum values of biosorption capacity for Zn were 27 and 10.5 $\text{mg} \cdot \text{g}^{-1}$ of biosorbent from the single and binary metal solutions, respectively. Time necessary for equilibrium was 6 hours in the case of single metal solution. But in the case of two-ion solutions the concentration of Cu^{2+} ions did not change after 4 hours but concentration of Zn^{2+} ion slightly changed during the whole experiment. Although, changes in Zn^{2+} concentration did not exceed 6 %.

Presence of Cu^{2+} ions in solution significantly decreased the Zn^{2+} biosorption. Zn^{2+} ions did not have so significant influence on Cu^{2+} biosorption although also in this case very slight decrease of biosorption capacity was observed.

For both studied metal ions visible decrease of the biosorption capacity after its steep increase was observed (although the decrease of Cu^{2+} biosorption capacity in two-ion solution was neglectable). Kaduková and Virčíková (2005) found similar phenomenon during the study of Cu bioaccumulation by living cells of *Ch. kessleri*. Authors proposed that cell wall damage followed by the cell death could be responsible for it. But they did not observe it when non-living cells (biosorption) were used. But Melčáková and Horváthová (2010), studying biosorption of Zn with plant debris (*Reynoutria japonica*), and Štofko et al. (2007), studying biosorption of Cu and Zn by saw dust, observed similarly the decrease of biosorption capacity after its initial steep increase. In both cases authors suggested that water content in used materials could cause the behaviour. As in our experiment biosorbent was used in the form of gel beads presence of water inside the beads could influence the biosorption capacity and caused the release of ions previously adsorbed on the biosorbent surface. Further studies are necessary to explain this behaviour.

Conclusions

Knowledge of the behaviour of biosorbents immobilized in polymer matrix is one of the key factors for their application in practice.

Weakly acidic pH value of solutions caused significant increase of weight of calcium alginate beads. Probably higher volume of water had to enter into the bead to protonate all available sites in the calcium alginate chains. But in spite of bead weight increase beads were usable. The protonation was probably not enough strong to cause the disintegration

of beads. To eliminate the weight increase is better to use gel beads (they already contain specific amount of the water) or to dip dry beads into water before the use. The utilization of alginate immobilized biosorbents in solution with low pH values (around 1) is not suitable because of strong damage of their structure which results in beads disintegration.

Immobilized biosorbents show satisfactory copper and zinc biosorption capacity but in the process kinetics there is possible to observe phenomena similar with metal ion biosorption by plant debris (saw-dust, dry leaves ...) which are probably connected with the water content in biosorbent particles. Further study is necessary to elucidate this behaviour.

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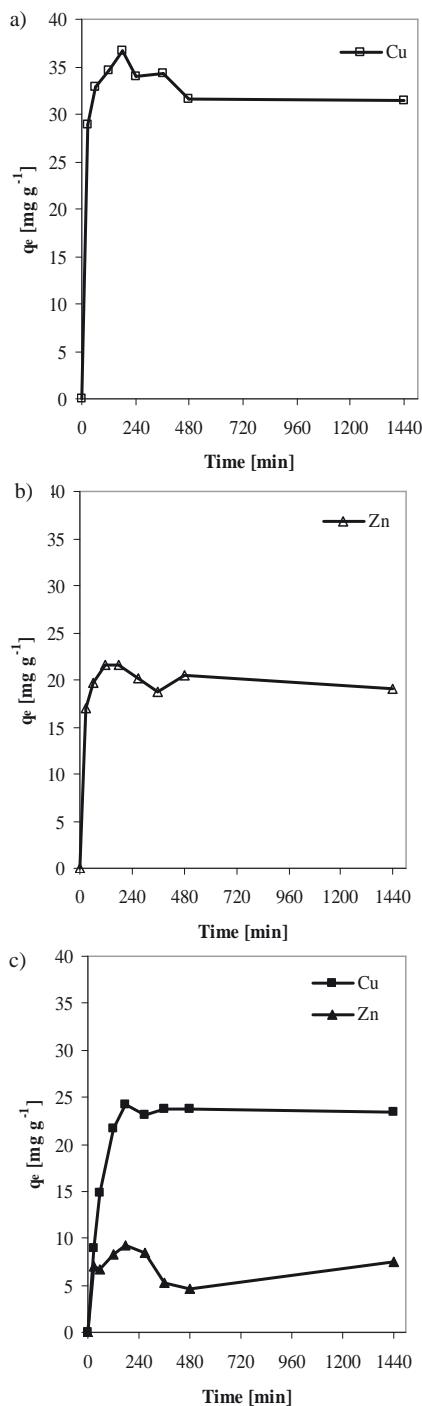


Fig. 2. Changes in metal concentrations in solutions after addition of biosorbents a) in single solution of Cu^{2+} ($\text{pH}_{\text{initial}} = 5$; $C_{\text{Cu, initial}} = 135 \text{ mg} \cdot \text{l}^{-1}$) or b) Zn^{2+} ($\text{pH}_{\text{initial}} = 4.15$; $C_{\text{Zn, initial}} = 150 \text{ mg} \cdot \text{l}^{-1}$) and c) in binary solution of Cu^{2+} and Zn^{2+} ($\text{pH}_{\text{initial}} = 5$; $C_{\text{Cu, initial}} = 135 \text{ mg} \cdot \text{l}^{-1}$; $C_{\text{Zn, initial}} = 150 \text{ mg} \cdot \text{l}^{-1}$).

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