



Mechanisms of Cr(III) biosorption onto residual brewer's yeast



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INTRODUCTION

The knowledge and understanding of metal-biomass interactions is crucial to develop and maximize biosorption processes potential to the concentration, removal and recovery of heavy metals from dilute solutions, as well as to define strategies to regenerate and reuse biosorbent in multiple cycles (Ahlwalia and Goyal, 2007; Volesky, 2001). It also turns possible biosorption optimization at a molecular level, including biomass genetic modification to induce changes in morphologic and physiologic characteristics in order to increase metal uptake (Srinath *et al.*, 2002; Volesky, 2001). To reach that purpose, and considering that several mechanisms may contribute to the overall metal uptake depending on the metal and the biosorbent used, environmental factors, and the cell metabolic activity (Dhankhar and Hooda, 2011), it is necessary to study in detail the interactions established in each biosorption system.

Heavy metal biosorption involves a combination of several passive accumulation processes, that may include: i) physical adsorption; ii) chemisorption, including ion exchange, coordination, complexation and chelation; iii) and inorganic precipitation (Ahlwalia and Goyal, 2007; Wang and Chen, 2006). According to Gadd (2004), metal-microorganism interactions may be seen as natural strategies to remove, recover or diminish metal toxicity in organic or inorganic forms. Different organisms exhibit different responses to the exposure to toxic ions, varying from transport through cellular membrane, biosorption onto cell walls, entrapment in extracellular structures, precipitation, complexation and redox reactions.

METHODS

Fresh brewer's yeast was collected from UNICER, a Portuguese brewing industry. Biomass was three times washed in distilled water followed by centrifugation (3 min, 3000 rpm) and it was suspended in 100 mL of distilled water.

Batch systems (Figure 1) were prepared mixing yeast suspension with Cr(III) solutions with initial concentration from 25 to 200 mg.L⁻¹, with biomass concentration around 5 g.L⁻¹ (dry weight basis). The assessment of Cr(III)-biosorbent interaction mechanisms involved the analysis of:

- i) changes in medium pH;
- ii) cation and intracellular organic material efflux;
- iii) FTIR analysis for *S. cerevisiae* surface characterization;
- iv) SEM observations; and
- v) cells viability monitoring.



Figure 1 – Experimental set up

RESULTS AND DISCUSSION

From pH and Cr(III) uptake profiles (Figure 2) it is possible to point out the effect of yeast suspension reflected in medium pH raise, delayed in the presence of metal ions. Initial pH drop occurring in solutions with higher initial Cr(III) concentration may be explained by proton release from ion exchange of Cr³⁺ hydrolysis into Cr(OH)²⁺. The pH raise occurs for contact periods longer than 24 h, simultaneously with a second Cr(III) uptake equilibrium phase.

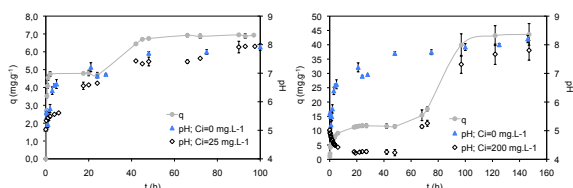


Figure 2 – pH and Cr(III) uptake profiles: comparison with a control essay. a) C_i = 25 mg.L⁻¹; b) C_i = 200 mg.L⁻¹

The presence of Cr(III) in aqueous solutions results in a faster and more intense cation (K⁺, Ca²⁺ and Mg²⁺) efflux (Figure 3).

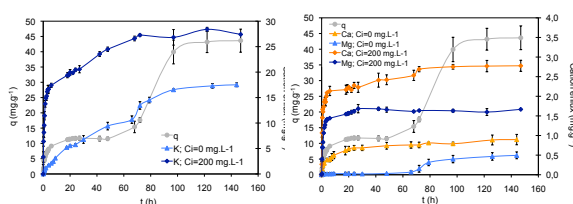


Figure 3 – Cation efflux from *S. cerevisiae* during Cr(III) uptake in solutions with C_i = 200 mg.L⁻¹: a) K⁺; b) Ca²⁺ and Mg²⁺

K⁺ efflux is independent of Cr(III) uptake, but Ca²⁺ and Mg²⁺ efflux profile suggests a stoichiometric relation with Cr(III) uptake during the first equilibrium phase, indicating ionic exchange occurring during the initial sorption phase. Ionic exchange between Ca²⁺ and Cr(OH)²⁺ may be associated to the substitution of the metallic ions necessary to the yeast flocculation.

Concerning intracellular organic compounds efflux, spectra in Figure 4 confirms the leakage of UV-absorbing compounds (Abs₂₆₀) with increasing intensity until 48 h. This behaviour may result from the release of proteins/nucleic acids due to cell permeability, lysis and viability loss, in agreement with the observed cell viability decay in metal solutions.

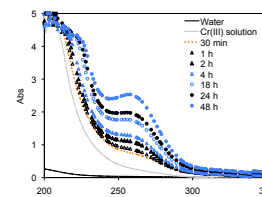


Figure 4 – UV-visible spectra for increasing sorption times (C_i = 200 mg.L⁻¹)

From FTIR spectra (Figure 5) it is possible to confirm that Cr(III) sorption onto *S. cerevisiae* does not involve chemical changes in yeast surface. Therefore, it is possible to assume that chemisorption involves ionic bonding, as suggested by cation efflux data. SEM observations and X-ray analysis of samples collected during the second equilibrium phase shows that Cr(III) sequestration involves the formation of metal precipitates (Figure 6).

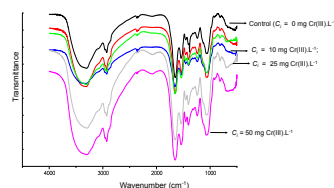


Figure 5 – *S. cerevisiae* FTIR spectra after 24 h contact: control, C_i = 10, 25 and 50 mg Cr(III).L⁻¹

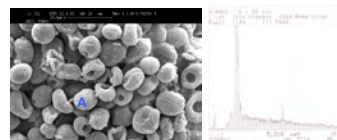


Figure 6 – SEM image of *S. cerevisiae* (C_i = 25 mg.L⁻¹; t = 74 h) and X-ray analysis (cell A)

CONCLUSIONS

From the present study, investigating Cr(III) biosorption onto a low cost biosorbent, *S. cerevisiae* residual from a Portuguese brewing industry, it is possible to assume that metal uptake occurs in two distinct phases:

- i) First phase - identical to other biosorbent systems using viable biomass, where chemisorption plays an important role, with ion exchange being the most probable reaction occurring;
- ii) Second phase - occurring for long contact times, involves metal precipitation onto cells surface.

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