

## **Cr (III) recovery from *Saccharomyces cerevisiae* by elution - a preliminary study**

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### **Abstract**

To recover adsorbed metals from biosorbents, in order to recycle metal and reuse biomass in several adsorption/desorption cycles, elution conditions need to be optimized. The present work aimed to study the following elution parameters: eluant type and concentration ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{CH}_3\text{COOH}$  and  $\text{Na}_2\text{CO}_3$  0.1, 0.5 and 1.0 M, and EDTA 0.01, 0.05 and 0.1 M); biosorbent contact time with Cr (III) solution (15 min, 2 and 24 h), and S/L ratio (4 and 8 g/L). Experimental data show a decrease in Cr recovery efficiency with increasing sorption time, probably due to metal bioaccumulation. Concerning the S/L ratio, it was possible to observe, in most essays, that best recoveries were achieved using biosorbent concentration of 8 g/L. Comparing the eluants tested according to their metal recovery efficiencies, it can be concluded that  $\text{Na}_2\text{CO}_3$  is not a good eluant (maximum recovery of 21 %). All the others showed equivalent behaviours, being necessary more assays to determine eluant treatment effect in Cr uptake capacity in subsequent sorption cycles.

### **INTRODUCTION**

The use of biosorbents, from industrial or natural sources, to remove metal ions from contaminated wastewaters may provide an efficient and competitive technology, particularly for treatment of high volumes of low polluted solutions (Wilhelmi and Duncan, 1995; Yang and Volesky, 1996).

The economical and ecological feasibility of biosorption processes, concerning industrial applications, depends both on the biosorbent metal uptake capacity (to reduce metal concentration to legal limits) and the ease of metal recovery from the biosorbent (Aldor *et al.*, 1995; Bux *et al.*, 1995, 1996). Metal recovery allows metal recycling, leading to energy savings and materials conservation (Tsezos *et al.*, 1995), and biosorbent regeneration for use in multiple adsorption/desorption cycles (Bux *et al.*, 1996).

To achieve efficient metal recovery, various elution agents, with different desorption mechanisms, may be used (Aldor *et al.*, 1995). Lowering pH, using acids, cause metal desorption (Tam *et al.*, 1998), resulting from competition between protons and metal ions for binding sites (Aldor *et al.*, 1995; Bux *et al.*, 1995). EDTA is a strong chelating agent (Aldor *et al.*, 1995) and carbonate ions form complexes with metals. Elution solution should be non-toxic, cause no damage to biosorbent, to allow reuse after regeneration, and achieve maximum recovery using minimal quantities at the lowest possible concentration (Wilhelmi and Duncan, 1996). This last characteristic can be express by the solid to liquid ratio - S/L (mass of loaded biosorbent/eluant volume), an important parameter to optimize (Aldor *et al.*, 1995).

In this research work several eluants were tested according to their ability to recover Cr (III) from *Saccharomyces cerevisiae* residual from a brewing industry. These preliminary assays were performed in batch reactors, aiming at the selection of the best desorption conditions to use in future studies.

## **MATERIALS AND METHODS**

### **Yeast biomass:**

*S. cerevisiae* was obtained from a Portuguese brewing industry - UNICER. Biomass was three times washed in distilled water, followed by centrifugation (3 minutes, 3000 rpm). Washed biomass (about 50 g of wet yeast) was suspended in 100 mL of distilled water. This suspension was mixed with Cr (III) solutions in the following proportion: 10 mL yeast suspension/100 mL of metal solution, in order to achieve a biomass concentration around 4 g/L (dry weight basis).

### **Metal solutions:**

Metal solutions were prepared dissolving  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in distilled water. For sorption experiments solution pH was adjusted to 5.0 with NaOH 0.1 M, prior to mixing with yeast suspension.

### **Eluants:**

$\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , HCl,  $\text{CH}_3\text{COOH}$  and  $\text{Na}_2\text{CO}_3$ : 0.1, 0.5 and 1.0 M; EDTA: 0.01, 0.05 and 0.1 M were used.

**Desorption experiments:**

Metal solutions (250 mL) were prepared in 500 mL flasks, with initial concentration of 10, 25, and 50 mg Cr (III)/L. After inoculation with yeast suspension (25 mL), solutions were incubated at 30 °C with orbital shaking (150 rpm). Chromium uptake was followed for 24 hours, with 5 mL sample collection at different periods. For desorption assays, 20 mL samples were taken after 15 minutes, 2 and 24 hours. These samples were centrifuged for biomass separation and resulting pellet was mixed with eluant solution. Two different eluant volumes were tested: 20 mL (same volume as Cr solution sample, also referred as 1:1 volume proportion), corresponding to a solid to liquid ratio (S/L) of 4 g/L; and 10 mL (half the metal solution volume, also referred as 2:1 volume proportion), corresponding to a S/L ratio of 8 g/L. After 1 hour incubation at 30 °C with orbital shaking, solution was again centrifuged for supernatant Cr analysis.

**Analytical methods:**

Cr (III) concentration was determined by Atomic Absorption Spectroscopy after biomass removal by centrifugation. Samples were preserved by acidification at pH 2 with concentrated HNO<sub>3</sub> and kept at 4 °C.

**RESULTS AND DISCUSSION**

Biosorption is a reversible mechanism (Aldor *et al.*, 1995), thus allowing metal recovery. However, from Fig.1 it is possible to notice that Cr (III) recovery efficiency decreases with increasing sorption time, behaviour that suggests intracellular uptake occurring for long contact time with metal solution, turning metals unavailable for recovery. After 15 minutes contact time, recovery efficiency is high for most eluants tested, although Cr uptake isn't very significant (Fig.2). However after 2 hours of contact (86, 95 and 100 % of total uptake for Ci = 50, 25 and 10 mg/L respectively), recovery efficiency dropped significantly. These results indicate that sorption time plays a crucial role in sorption/desorption process.

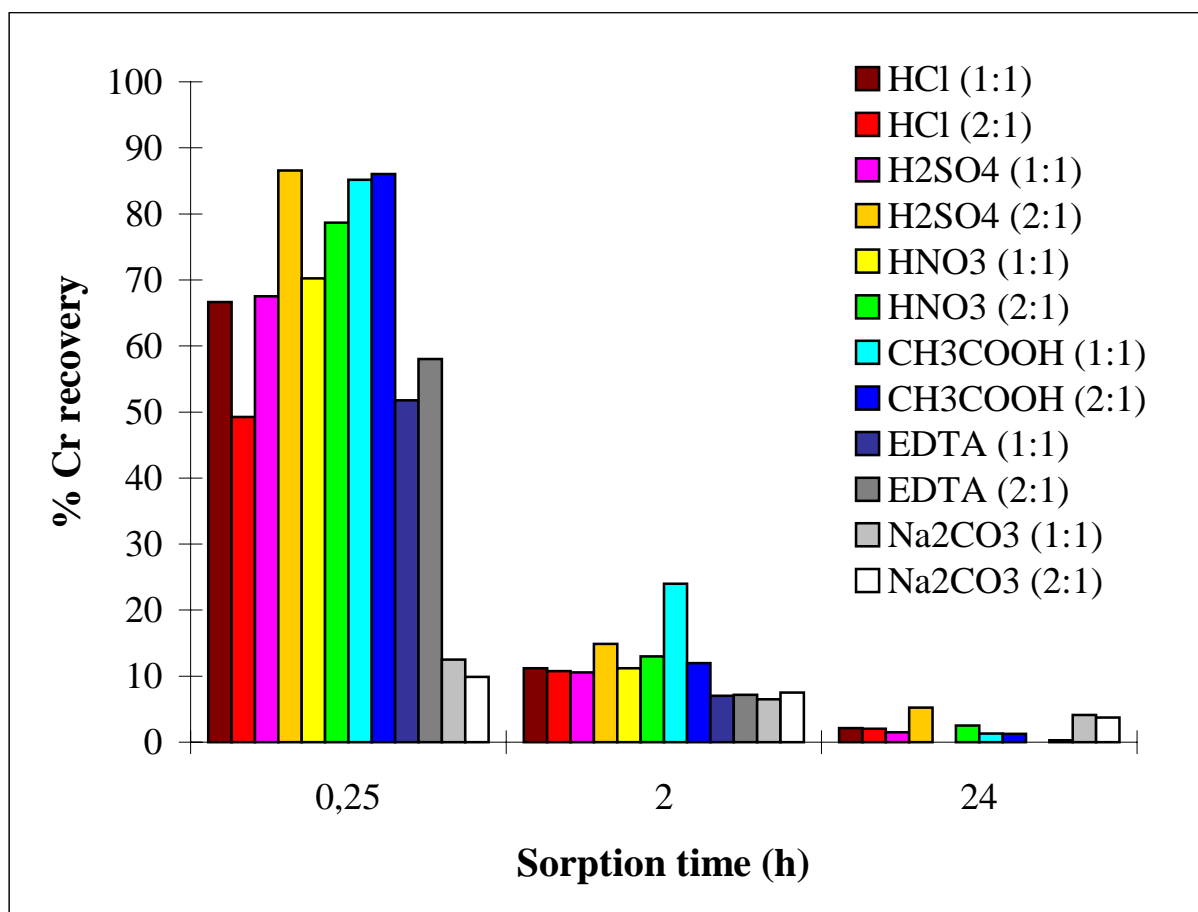


Figure 1 – Cr (III) recovery efficiency for different sorption times ( $C_i = 25 \text{ mg Cr (III)/L}$ ; eluant concentration = 0.1 M, 0.01 M for EDTA).

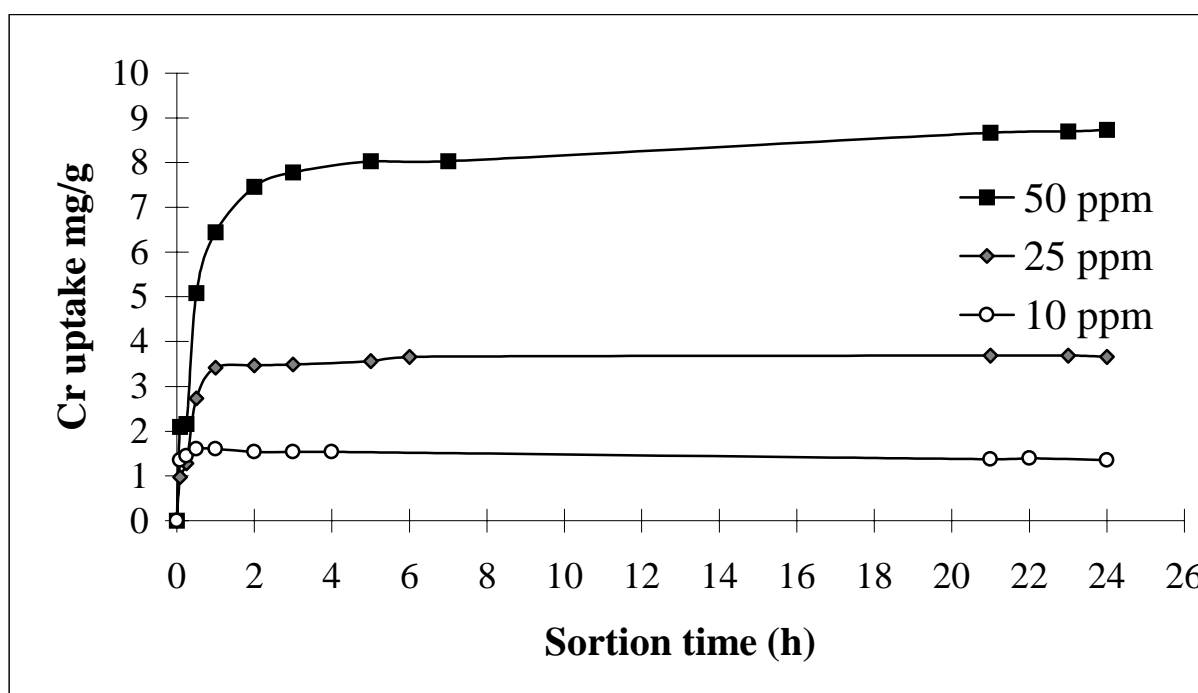


Figure 2 – Cr (III) uptake

Analysing Cr desorption at different metal concentrations (Fig. 3), the trend observed is to a higher recovery with increasing Cr concentration. This may be explained by multilayer sorption onto biomass surface, making easier to desorb external metal layers and to recover the metal at higher metal concentrations (Bux *et al.*, 1995).

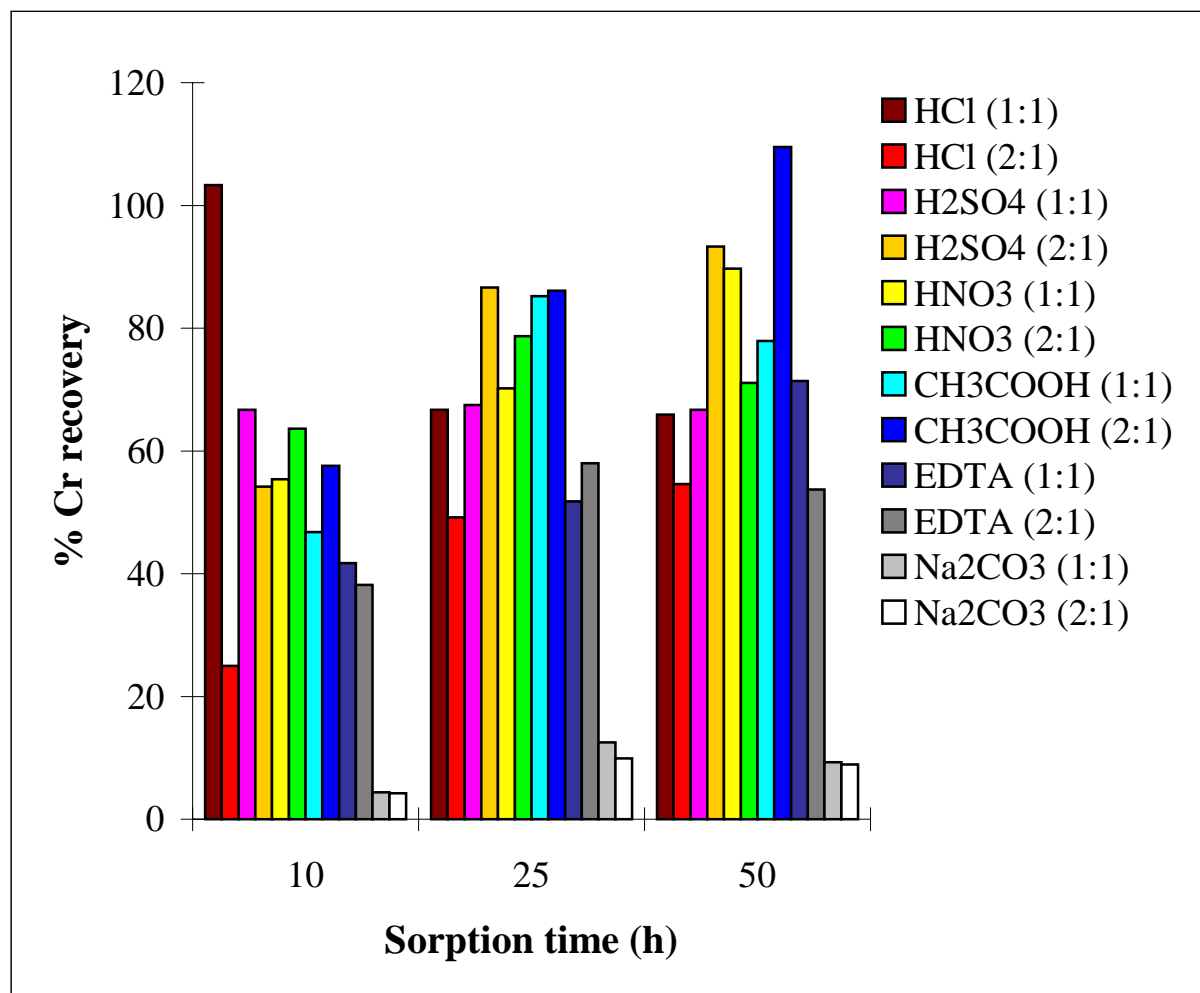


Figure 3 – Cr (III) recovery efficiency for different metal concentrations (Sorption time = 15 min; eluant concentration = 0.1 M, 0.01 M for EDTA).

Concerning the solid to liquid ratio (S/L), analytical data from most assays shows higher recoveries for S/L = 8 g/L (corresponding to 2:1 metal solution/eluant volume proportion). Moreover, this situation allows for eluant economy and a resulting recovery solution more concentrate in metal.

Comparing the 6 eluants tested according to their recovery efficiency, it is possible to consider  $\text{Na}_2\text{CO}_3$  as having a limited desorption capacity (maximum recovery of 21 %, reached with  $\text{Na}_2\text{CO}_3$  1.0 M, for a sorption period of 15 minutes and a volume proportion of 2:1).

The fact that protons play a major role in desorption (Aldor *et al.*, 1995) was confirmed by the higher recoveries attained with the acids tested. From Fig. 4 to 9 it is possible to see that Cr recovery dropped using dilute acids. Since acids may cause damage to biomass, limiting its reuse in subsequent sorption cycles (Bux *et al.*, 1996), more assays are needed to test biosorbent sorption capacity after regeneration.

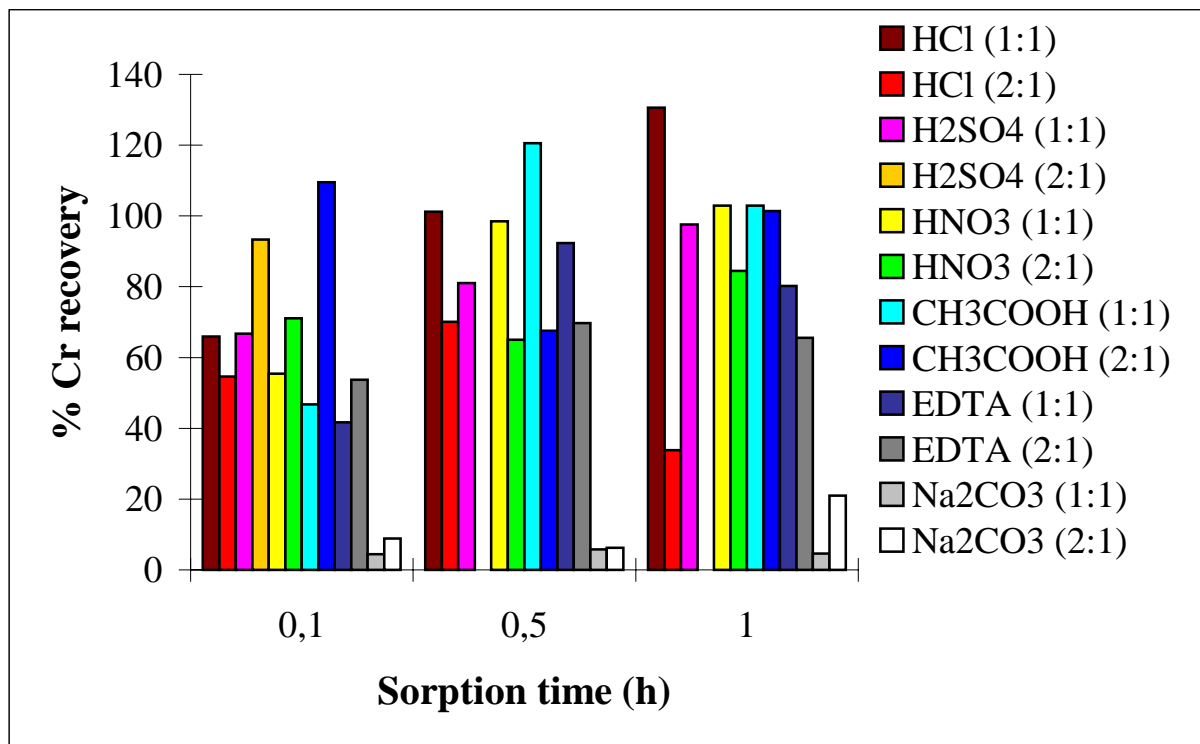


Figure 4 – Cr (III) recovery (15 min;  $C_i = 50$  mg/L)

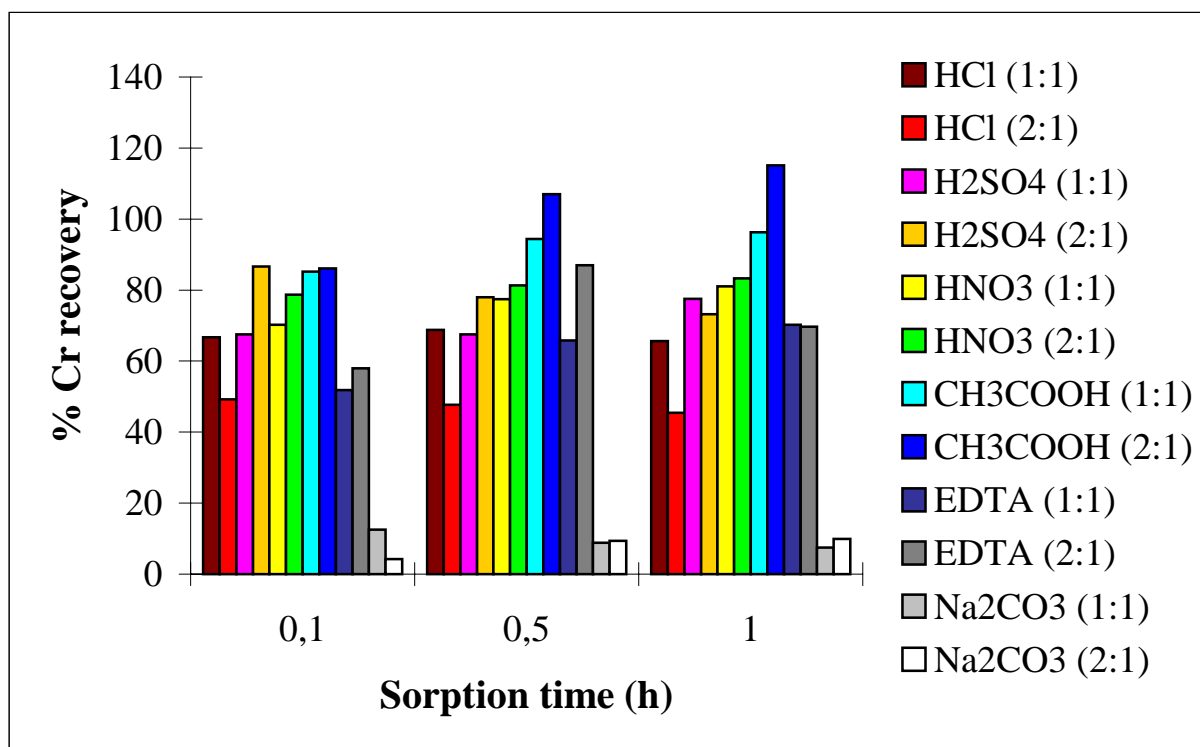


Figure 5 – Cr (III) recovery (15 min; Ci = 25 mg/L)

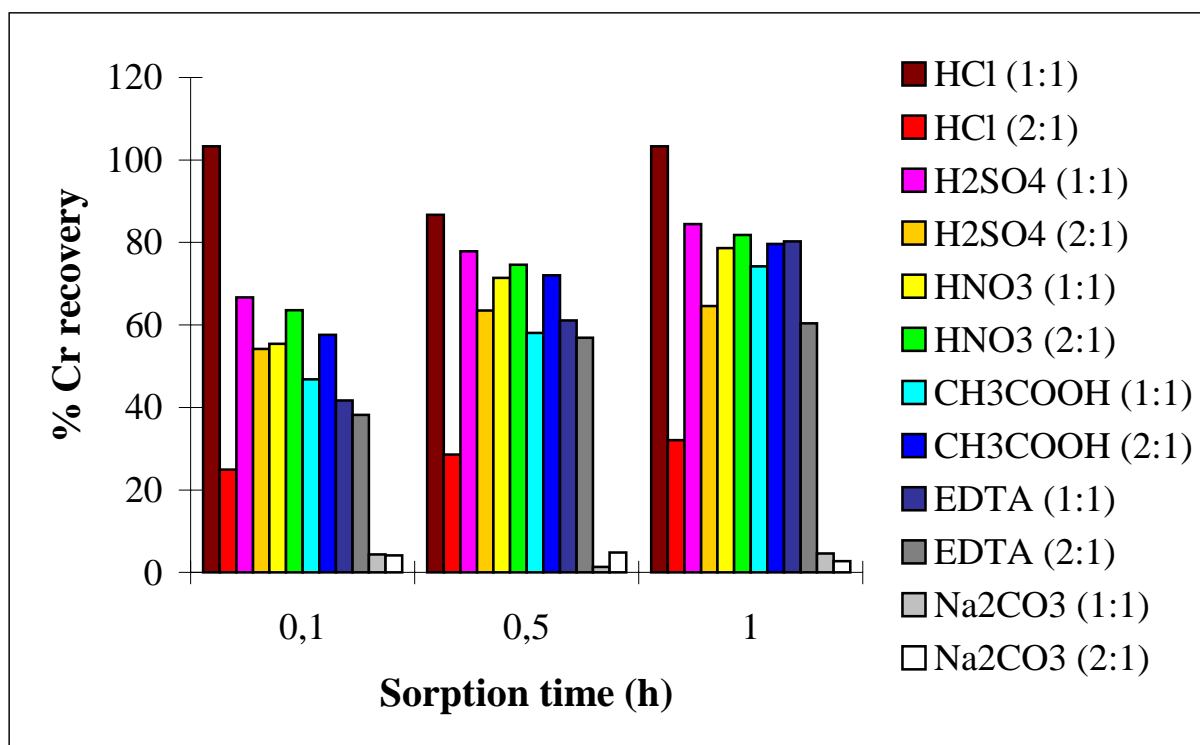


Figure 6 – Cr (III) recovery (15 min; Ci = 10 mg/L)

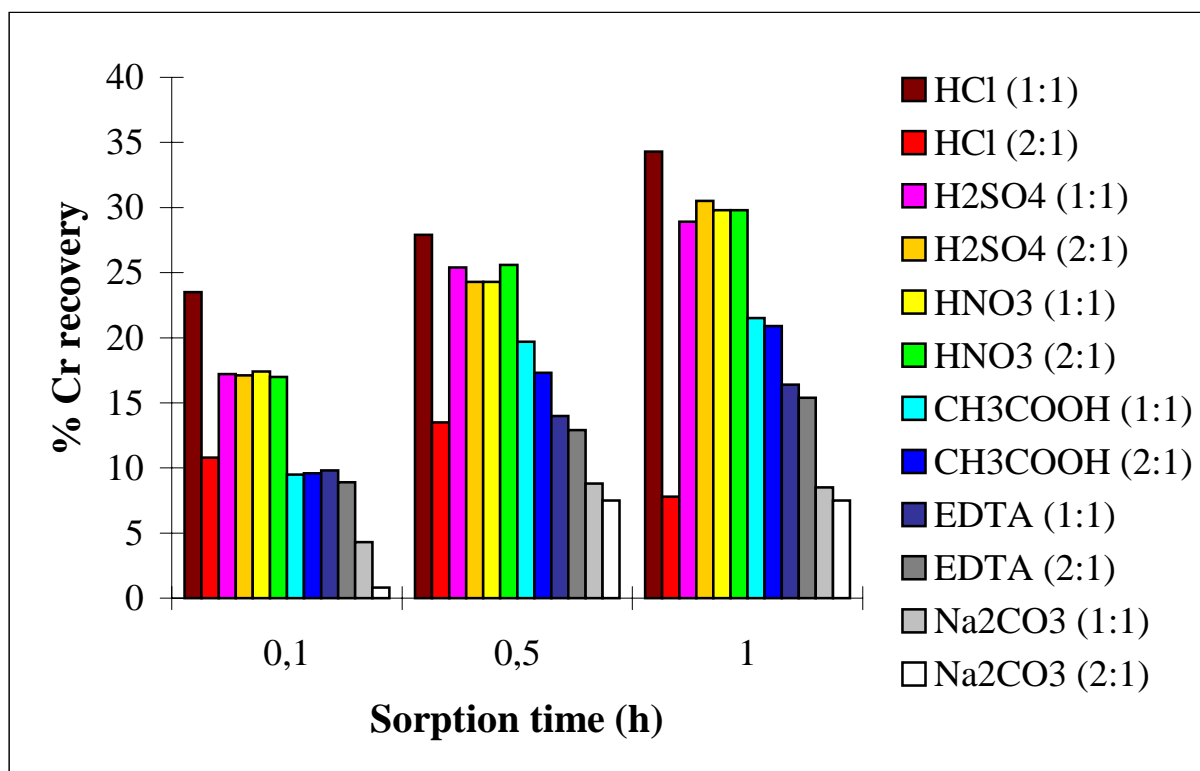


Figure 7 – Cr (III) recovery (2 h; Ci = 50 mg/L)

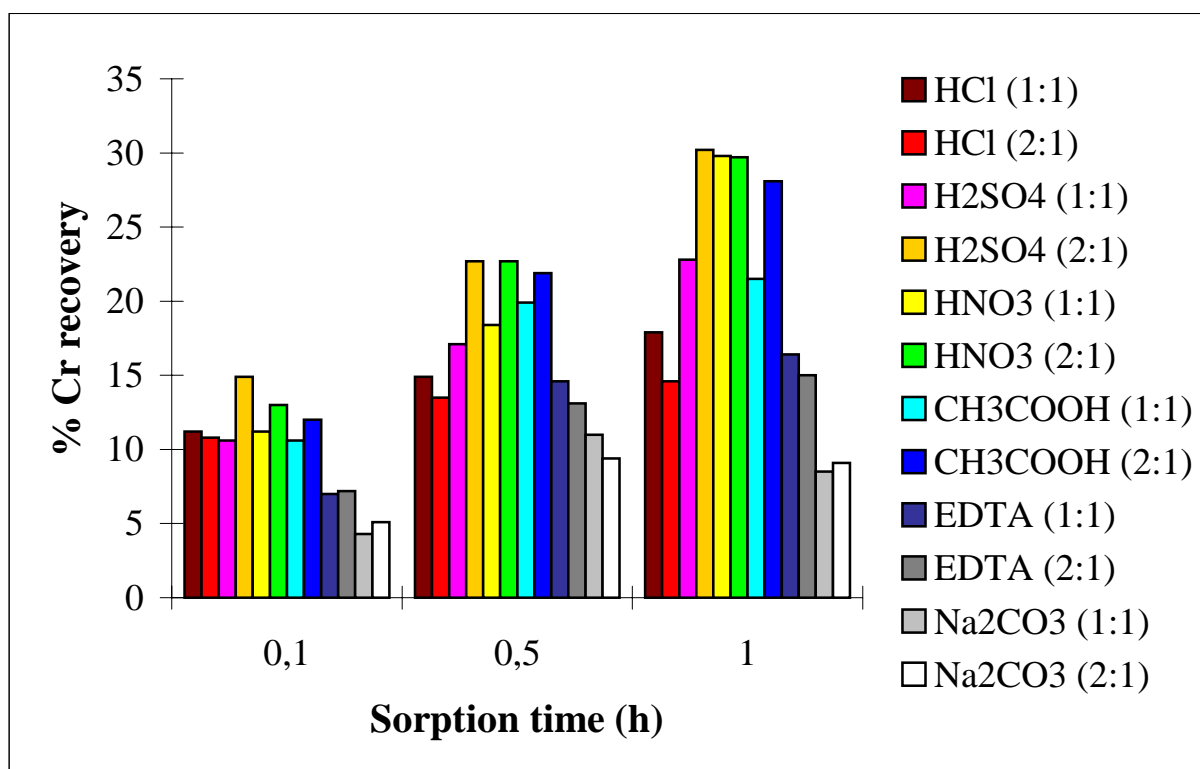


Figure 8 – Cr (III) recovery (2 h; Ci = 25 mg/L)



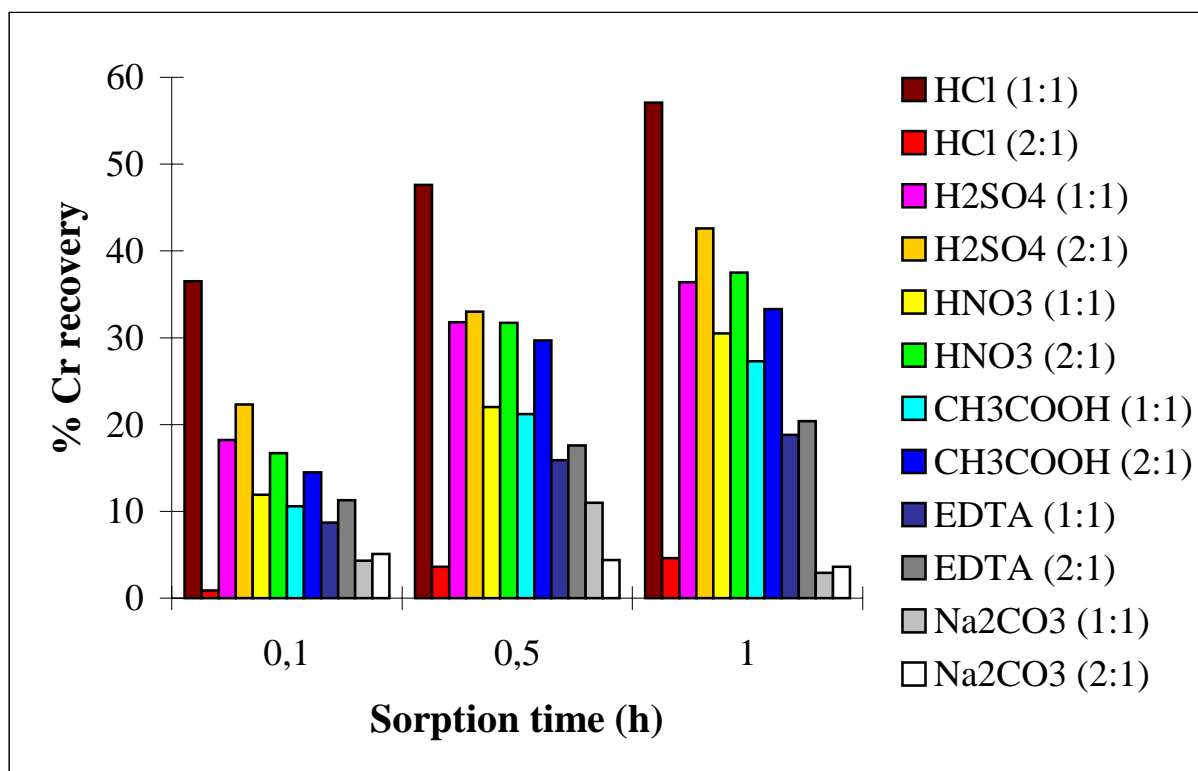


Figure 9 – Cr (III) recovery (2 h;  $C_i = 10 \text{ mg/L}$ )

## CONCLUSIONS

This preliminary study of Cr (III) desorption from *Saccharomyces cerevisiae* indicates that metal recovery is possible, with high efficiency, for short sorption periods (15 minutes). Sorption time proved to have great influence in metal recovery. From the 6 eluants tested, acids may be considered to have the best desorption capacity, more assays being necessary to evaluate eventual damages in biomass affecting its uptake capacity in subsequent sorption cycles. Concerning the S/L ratio, in general best recovery was obtained with a metal solution/eluant volume proportion of 2:1 (S/L ratio = 8 g/L). Considering this evidence it is likely that the use of low quantities of eluant doesn't harm metal recovery, allowing for eluant economy, producing a recovered solution with higher metal concentration, thus increasing process economical competitiveness.

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