

Biorecovery of Cr(VI) from wastewater and its catalytic reutilization

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Abstract: The performance of two zeolites with different structures and acidity properties was evaluated on the biosorption of Cr(VI) and catalytic oxidation of ethyl acetate. The starting zeolites, HY and HZSM5, were modified by ion exchange treatments in order to obtain zeolites with different acidity and sodium content. *Arthrobacter viscosus* supported on the different zeolites was used for Cr(VI) recovery from solution. The best removal efficiencies and uptake of chromium were achieved for the Y zeolites due to their higher ion exchange capacity. The Y and ZSM5 zeolites were characterized by ICP-AES, SEM, NH₃ chemisorption, XRD and N₂ adsorption. Y and ZSM5 zeolites obtained after biosorption of chromium were successfully reused as catalysts in the oxidation of ethyl acetate. The chromium-loaded ZSM5 zeolites were considerably more active and selective towards CO₂ than chromium-loaded Y zeolites, essentially due to its different framework structure, textural and acidity properties.

Keywords: Y zeolite, ZSM5 zeolite, Cr(VI) biosorption, Catalytic oxidation

Introduction

Wastewater pollution with heavy metals is an important issue of great environmental concern. The discharge of effluents with toxic metals from many industrial activities into water bodies could lead to serious health hazards due to the accumulation of metals in the food chain (Gravilescu, 2004). Among the different heavy metals, chromium is one of the most toxic and is released into the environment through a variety of industrial activities. The two oxidation states of environmental significance, +3 and +6, have widely contrasting toxicity characteristics. Chromium in hexavalent oxidation state, Cr(VI), is very toxic and carcinogenic, while trivalent chromium, Cr(III), is an essential trace element to living beings (Mohan and Pittman, 2006).

Intensive efforts towards heavy metals removal from effluents have been done, to overcome the drawbacks of traditional treatments such as high cost and generation of toxic sludge. In recent years, biosorption has gained importance due to its advantages, such as cost-effectiveness and possibility of metals recovery. Several microorganisms, such as bacteria, are found to be able of efficiently accumulating heavy metals. In the field of metals recovery, low cost ion exchangers such as zeolites are also widely used due to their unique properties in terms of selectivity and exchange capacity. For the recovery of Cr(VI), this work proposes a conjugate biosorption system that combines simultaneously the biosorption properties of a bacterium with the ion exchange capacity of a zeolite.

It has been demonstrated that zeolites containing transition metal ions are promising heterogeneous catalysts in pollution abatement and selective oxidation reactions (De Vos et al., 2002). In the present work the metal-loaded zeolites obtained after the biosorption studies were reutilized as catalysts in the oxidation of ethyl acetate. Therefore, the treatment system described in this work presents a double

advantage, since it allows the removal of metals from aqueous solutions, as well the recycling of the metals by their reutilization in catalytic oxidation reactions. The aim of this work is to evaluate the effect of the zeolite structure (FAU and MFI) and the modification of their acidity, obtained by ion exchange treatments, in Cr(VI) biosorption and in their further catalytic reutilization in the oxidation of ethylacetate.

Material and Methods

HY and HZSM5 zeolites were used as the starting materials and were modified by ion exchange treatments with NaNO₃. The modified zeolites were prepared by two ion exchange treatments (Neves et al., 2006), designated as A and B. A medium with glucose, peptone, malt extract and yeast extract was used for the growth of *A. viscosus*. Batch experiments were conducted in 250 mL Erlenmeyer flasks using 15 mL of the *A. viscosus* suspension previously prepared, with a biomass concentration of 5 g/L, 150 mL of a potassium dichromate solution, with an initial concentration of 100 mgCr/L, and 1.0 g of each zeolite. Samples were taken and analyzed for chromium quantification. Hexavalent chromium that remained in solution was quantified by measuring absorbance at 540 nm of the purple complex of Cr(VI) with 1,5-diphenylcarbazide, in acidic solution. The different zeolites were characterized by ICP-AES, SEM, NH₃ chemisorption, XRD and N₂ adsorption. After the biosorption experiments, the chromium-loaded zeolites were used as catalysts in the oxidation of ethyl acetate. The catalytic tests were performed using similar conditions as reported by Bastos et al. (2009).

Results and Discussion

The ion exchange treatments with NaNO₃ performed to the starting HY and HZSM5 zeolites led to the increase of sodium content and consequently to the decrease of total acidity, as it can be seen in Table 1.

Table 1 Sodium content and total acidity of the starting and modified zeolites

Sample	Na _{initial} (%) ^(a)	Total acidity (cm ³ NH ₃ /g) ^(b)
HY	1.80	25.5
H(Na) _A Y	1.95	20.1
H(Na) _B Y	2.50	19.4
HZSM5	0.08	23.3
H(Na) _A ZSM-5	0.79	18.4
H(Na) _B ZSM-5	1.10	17.9

^(a) Determined by chemical analysis (ICP-AES)

^(b) Determined by NH₃ chemisorption

An improvement on the removal of total Cr can be observed with the modified zeolites H(Na)_AY and H(Na)_BY, in comparison to the starting HY zeolite. However, with ZSM5 zeolites it was not observed the same trend, as the decrease of acidity did not produce considerable changes on the uptake process. During biosorption process, the Y zeolites presented higher efficiencies of chromium removal due to their higher ion exchange capacity in comparison with ZSM5 zeolites (see Figure 1). After the

biosorption of Cr(VI), the different chromium-loaded zeolites (Table 2) were successfully used as catalysts for the complete oxidation of ethyl acetate.

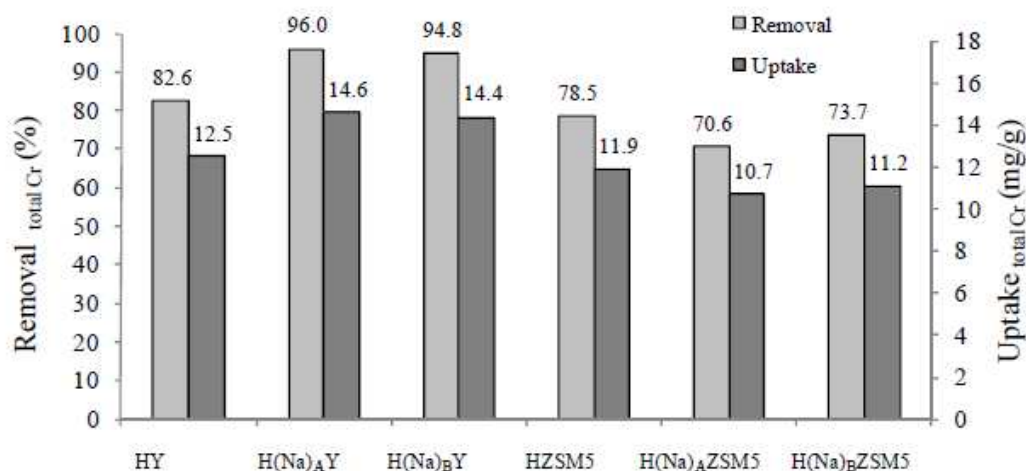


Figure 1 Removal efficiencies and uptake of total Cr for the biosorption assays performed with *A. viscosus* supported on Y and ZSM5 zeolites. Experiments at pH 4, initial Cr(VI) concentration of 100 mg/L and biomass concentration of 5 g/L.

Table 2 Sodium and chromium content of the zeolites after biosorption

Sample	Na _{final} (%) ^(a)	Cr (%) ^(a)
Cr-HY	0.22	1.10
Cr-H(Na) _A Y	0.24	1.10
Cr-H(Na) _B Y	0.44	1.20
Cr-HZSM5	0.07	0.93
Cr-H(Na) _A ZSM-5	0.11	0.95
Cr-H(Na) _B ZSM-5	0.18	0.92

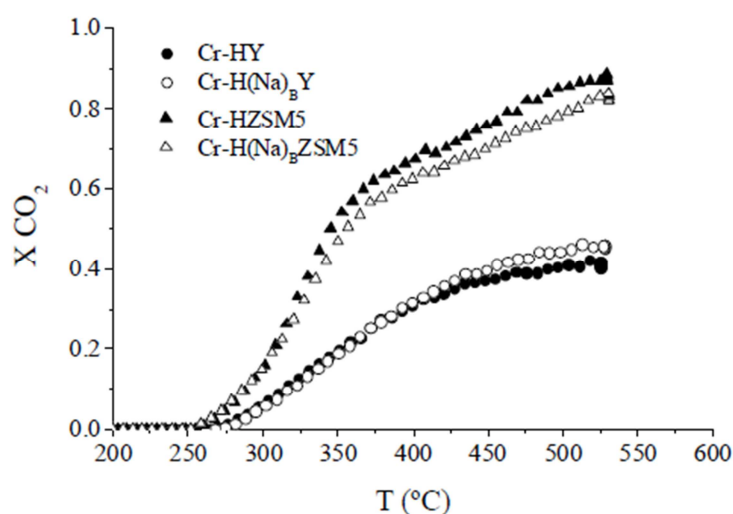


Figure 2 Removal Light-off curves for the oxidation of ethyl acetate on Cr-HY, Cr-H(Na)BY, Cr-HZSM5 and Cr-H(Na)BZSM-5 for the cooling step, at a VOC concentration of 4000 mg_C/m³.

The ZSM5 catalysts showed higher activity and selectivity towards CO₂ than Y zeolites, as it can be observed in Figure 2. No considerable differences were observed in the catalytic behaviour of Y and ZSM5 catalysts with different content of sodium, which reveals that the extension of sodium exchange did not affect substantially the catalytic properties of the zeolites. Other important factors such as structural and textural properties as well as the acidity of the supports played an important role in the activity and selectivity of the catalysts during ethyl acetate oxidation.

Conclusions

A combined biosorption system consisting of a bacterium, *A. viscosus*, supported on Y and ZSM5 zeolites revealed to be efficient on the removal of Cr(VI) from aqueous solution. The increase of Na content in the zeolites after the ion exchange treatments led to the decrease of total acidity, although this modification did not change significantly the removal efficiency of total Cr. During Cr(VI) biosorption, Y zeolites showed better uptake performances, while ZSM5 catalysts showed higher activity and selectivity towards CO₂ during the catalytic oxidation of ethyl acetate. The different performances observed are explained by the distinct framework structure, textural and acidity properties of the tested zeolites.

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