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CATALYTIC REUTILIZATION OF Cr(VI) BIOSORPTION SUPPORTS

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KEYWORDS

Chromium, zeolite, biosorption and catalysis.

ABSTRACT

This work reports the application of a biosorbent, *Arthrobacter viscosus*, to a zeolitic support (FAU zeolites) as a method for the treatment of Cr(VI)-containing solutions that allows the recovery of the Cr-laden supports as catalysts for liquid-phase oxidation reactions.

INTRODUCTION

Contamination of aqueous media with heavy metals is a direct consequence of human activity, mainly industrial. This pollution type poses a risk for human health, as high concentrations of heavy metals can be toxic or even lethal. Moreover, heavy metals accumulate in organisms, meaning that this contamination may reach human beings through the food chains.

In order to limit the impact of heavy metals on human health, many remediation options were successfully developed and implemented. These are mostly physico-chemical processes such as adsorption, ion-exchange, chemical precipitation or solvent extraction. However, some of these processes fail to meet with affordable energetic or economic restraints. Additionally, a current push for “recovery-reuse” technologies is in place, in order to minimize the demand on the mining and processing of mineral ores (Agrawal et al. 2006).

Biosorption has received considerable attention from both academia and industry as a remediation option for the treatment of heavy-metal contaminated effluents, where inexpensive and environmentally-friendly biomaterials are used (from bacteria, yeast or complex materials such as fermentation or agricultural wastes).

Biosorption consists in a multitude of physico-chemical phenomena that occur on the cellular surface, by which metal ions may be adsorbed, complexed or chemically reduced. The latest is of great importance when anionic metal ions are present, which are difficult to treat with other established methodologies. One of these elements is chromium, a widespread used metal which is commonly found as chromate and dichromate anions in effluents of electroplating, tanning or textile dyeing industries. The common treatment method for this element in its hexavalent form, Cr(VI), is chemical reduction followed by precipitation, which presents the downside of chemical sludge generation and its disposal.

The combination of the *Arthrobacter viscosus* bacterium with a zeolitic support was reported to be effective on the removal of Cr(VI) from aqueous solutions, while the retention of Cr ions by the zeolitic supports enabled the reuse of the Cr-laden inorganic matrix as a catalyst (Figueiredo et al. 2006). The interaction between bacteria and the zeolitic supports is synergetic: zeolites are robust supports for the bacteria. While being intrinsically ion-exchangers for cations, zeolites lack the ability for Cr(VI) species. This is compensated by the known Cr(VI) reduction capacity of bacteria (Park et al. 2007), which reduce Cr(VI) to Cr(III), being the latest possible of ion-exchange by the zeolite. Through thermal treatment of the exhausted system, the biomass can be effectively removed resulting in a purely inorganic Cr-containing matrix which is ideal for the preparation of catalysts for oxidation reactions. This matrix can be directly used in gas-phase reactions, whereas for liquid-phase reaction, efficient immobilization of the Cr species in the zeolite supercages is required to overcome the known leaching proneness of Cr ions to the reaction medium. The latest is achieved through *in-situ* coordination of the Cr ions with adequate ligands by a method called “ship-in-a-bottle synthesis” (Corma and Garcia 2004). This work reports the latest results in the application of FAU



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zeolite (Y zeolite) as a support for the *Arthrobacter viscosus* bacterium and later recovery of the supports for liquid-phase oxidation of organic substrates.

RESULTS AND DISCUSSION

The *Arthrobacter viscosus*-FAU zeolite system was tested for the treatment of Cr(VI) solutions in batch processes, being a single of sequential-batch reactor (SBR) operation. Each reactor contains 150 mL of Cr(VI) solution (or the Cr(VI) solution recovered from previous cycles in SBR operation), 1.0 g of either NaY or HY zeolite and a biomass concentration of 5.0 g/L. The pH of each reactor was monitored and maintained at 4.0.

It was confirmed that the biomass promoted the reduction of Cr(VI) to Cr(III), presenting typical biosorption kinetics (Figueiredo et al. 2010). For an initial concentration of 100 mg_{Cr}/L, Cr(VI) concentration decreases rapidly during the first 24 h of experimental time (up to 50 % decrease), whereas a secondary reduction phase occurs subsequently with a much lower reduction rate. The composition of HY and NaY zeolites has a distinct effect on the medium pH, given the interference of the supports in H⁺ availability. HY zeolite was found to increase the Cr(VI) reduction during the first 24 h due to the release of H⁺ ions which assist the acid reduction of Cr(VI), while increased ion-exchange capacity of NaY allowed this zeolite to perform better in the secondary reduction stage. Maximum total Cr removal from an initial 100 mg_{Cr}/L solution in single-batch experiments was 77.6% using NaY zeolite as support (uptake of 11.6 mg_{Cr}/g_{zeolite}), after 27 days of experimental time. For SBR operation (3 cycles of 96 h), the swifter Cr(VI) reduction achieved with HY support proved determinant for a better performance of the HY-biomass system, reaching complete Cr(VI) reduction on cycle 2 and a final concentration of total Cr below 2.0 mg_{Cr}/L (accumulated total Cr removal of 98.2%). However, individual cycle Cr uptakes are lower in SBR, given the shorter contact time between the zeolite support and the reduced Cr species.

The biosorption supports were collected from the respective reactors and calcined at 500 °C to yield a Cr-containing zeolite, the precursor for the liquid-phase catalysts. These supports underwent treatment with diphenyltriazene ligands to immobilize the Cr(III) ions

in the FAU supercages, by “ship-in-a-bottle” immobilization of Cr-ligand complexes. This was confirmed through the combination of several analytical techniques, such as IR and Raman spectroscopy, thermogravimetry, XPS and EPR analysis.

The catalysts were tested on the oxidation of cyclohexanol into cyclohexanone and the oxidation of cyclohexene to 2-cyclohexene-1-ol and 2-cyclohexene-1-one. Both reactions employed *tert*-butylhydroperoxide as oxidant with temperatures of 60 °C for cyclohexanol and 50 °C for cyclohexene, during 23 hour reaction cycles. The prepared catalysts showed increased catalytic activity for both reactions, achieving maximum conversions of 61 % for cyclohexanol (TON of 198) and 72 % for cyclohexene (TON of 269).

REFERENCES

- Agrawal, A.; Kumar, V.; Pandey, B.D. 2006. “Remediation options for the treatment of electroplating and leather tanning effluent chromium – a review.” *Mineral Processing & Extractive Metallurgy Reviews*, No.27, 99-130.
- Corma, A.; Garcia, H. 2004. “Supramolecular Host-Guest Systems in Zeolites Prepared by Ship-in-a-Bottle Synthesis.” *European Journal of Inorganic Chemistry*, Issue 6 (Mar), 1143-1164.
- Figueiredo, H.; Neves, I.C.; Quintelas, C.; Tavares, T.; Taralunga, M.; Mijoin, J.; Magnoux, P. 2006. “Oxidation catalysts prepared from biosorbents supported on zeolites.” *Applied Catalysis B: Environmental*, No.66, 274-280.
- Figueiredo, H.; Silva, B.; Quintelas, C.; Neves, I.C.; Tavares, T. 2010. “Effect of the supporting zeolite structure on Cr biosorption: Performance of a single-step reactor and of a sequential batch reactor—A comparison study.” *Chemical Engineering Journal*, No.163, 22-27.
- Park, D.; Lim, S.-R.; Yun, Y.-S.; Park, J.M. 2007. “Reliable evidences that the removal mechanism of hexavalent chromium by natural biomaterials is adsorption-coupled reduction.” *Chemosphere*, No.90, 298-305.

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