Available online at www.sciencedirect.com

ScienceDirect

Microporous and Mesoporous Materials 109 (2008) 163–171

MICROPOROUS AND MESOPOROUS MATERIALS

www.elsevier.com/locate/micromeso

Immobilization of Fe(III) complexes of pyridazine derivatives prepared from biosorbents supported on zeolites

Hugo Figueiredo [b], Bruna Silva [b], M. Manuela M. Raposo [a], António M. Fonseca [a], Isabel C. Neves [a,*], Cristina Quintelas [b], Teresa Tavares [b,*]

[a] *Departamento de Química, Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal*
[b] *IBB – Instituto de Biotecnologia e Bioengenharia, Centro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal*

Received 8 September 2006; received in revised form 12 April 2007; accepted 19 April 2007
Available online 3 May 2007

Abstract

Immobilization of Fe(III) complexes of pyridazine derivatives was achieved in NaY zeolite, loaded with iron through the action of a robust biosorption mediator consisting of a bacterial biofilm, *Arthrobacter viscosus*, supported on the zeolite. The objective of this study is the preparation and characterization of new catalytic materials to be used in oxidation reactions under mild conditions. The biosorption of Fe(III) ions was performed starting from aqueous solutions with low concentrations of iron and the highest values of biosorption efficiency for Fe(III) were reached at the beginning of the contact period with the sorbents. The Fe(III) biosorption process was compared with the one of Cr(III) under the same experimental conditions, as this latter case has been well characterized. The sample used in the immobilization of Fe(III) complexes of pyridazine derivatives was prepared from an aqueous solution of 100.0 $\mathrm{mg_{Fe}/L}$, without the competing effect of other metals. Fe(III) is retained in the zeolite by ion exchange and coordination with two different pyridazine derivative ligands, 3-ethoxy-6-chloropyridazine (A) and 3-piperidino-6-chloropyridazine (B). The resulting materials were fully characterized by different spectroscopic methods (EPR, FTIR and UV–vis), chemical analysis (CA), surface analysis (XRD and SEM) and thermogravimetric (TGA) analysis and the results indicated that the Fe(III) complexes of pyridazine derivatives were effectively immobilized in NaY inside the supercages, without any modifications of the morphology and structure of the zeolite. The EPR spectra of the Fe(III) complexes in *Y* zeolite show signals at $g = 4.3$ and 2.3, attributed to Fe(III) species coordinated to pyridazine derivative ligands.

Keywords: NaY; *Arthrobacter viscosus*; Biosorbents; Fe(III); Pyridazine derivative ligand; Immobilization

1. Introduction

Concern regarding sustainable development is responsible for the concentration of research efforts on the effects of toxic metals on the environment, since they ultimately reach and accumulate in animal and human tissues. In accordance with water standard procedures used in most countries, heavy metal ions in wastewater must be controlled and reduced to below fixed reference values. Wastewater treatment, including the removal of heavy metal ions, generally depends on the size and type of the emission plant, as well as on the characteristics and flow rate of wastewater. Numerous processes exist for removing heavy metal ions including chemical precipitation, chemical oxidation and reduction, ion exchange, membrane filtration and carbon adsorption [1]. These processes however have significant disadvantages such as incomplete metal removal, high reagent or energy requirements, generation of toxic sludge or other waste products and are generally very expensive when the contaminant concentrations are in the range 10.0–100.0 mg/L [2]. Cost effective alternative technologies or sorbents for treatment of metal-contaminated waste streams are needed. In this respect, zeolites

---

[*] Corresponding authors. Tel.: +351 253604057; fax: +351 253678983 (I.C. Neves).
E-mail addresses: ineves@quimica.uminho.pt (I.C. Neves), ttavares@deb.uminho.pt (T. Tavares).

1387-1811/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2007.04.038

have a great potential for removing heavy metal from industrial wastewater. The peculiar adsorptive properties of zeolites result from the ability of positively charged exchangeable ions, which are located inside the three-dimensional pore structure of the solid, to balance the negative charge on the framework Al atoms. These atoms can be replaced by heavy metals [3].

Biosorption is the accumulation of metals by biological materials without active uptake and can be considered to be a collective term for a number of passive accumulation processes which may include ion exchange, coordination, complexation, chelation, adsorption and micro-precipitation [4]. Other authors [5] have defined biosorption as the ability of biological materials to accumulate heavy metals from waste streams by either metabolical mediation or by purely physico-chemical uptake pathways.

The biosorption of heavy metals by microorganisms is a promising process with potential for industrial application, suitable for natural environments and of low cost. *Arthrobacter viscosus* is a good exopolysaccharide producer, an aspect which would permit prediction of good adhesion to the support and metal ion entrapment [6] through capture by the polysaccharide net developed by the biofilm. The new systems herein presented combine the biosorption properties of the microorganism with the metal ion immobilization ability of the zeolite due to its ion exchange properties and shape selectivity. The role of the biofilm mediator is the enhancement of an alternative, efficient and quite competitive path for metal ion immobilization.

During the last two decades the preparation and catalytic activity of transition metal complexes encapsulated in micro- and meso-structures have been extensively investigated due to their industrial significance [7–12]. Encapsulation of transition metal complexes that may act as homogeneous catalysts, within the structure of zeolites provides a way to greatly simplify their separation from the reaction mixture and to improve the recycling of expensive catalysts. These heterogeneous systems provide information at the molecular level about the interactions between the zeolite and their guest complexes [13–18].

The present work associates biosorption studies to the immobilization of transition metal complexes in zeolites for applications in heterogeneous catalysis in mild conditions. Presently, we are interested in the study of the immobilization of iron metal complexes on Y zeolite for oxidation reactions. The iron metal complexes imitate the role of the active site and the zeolite replaces the protein moiety of metalloenzymes [19]. The synthesis of Fe(III) complexes of pyridazine derivatives immobilized in supercages of Y zeolite was carried out by free diffusion of the pyridazine derivative ligands through the zeolite pores exchanged with the Fe(III) metal ion, obtained by the previous use of the biosorption process [20,21].

The ability of pyridazine to form metal complexes has led to applications in the growing area of molecular self-assembly. The pyridazine skeletons are commonly found in compounds exhibiting a wide range of biological activity [22,23]. The derivatives of pyridazine could also find application as ligands in supramolecular chemistry and in metallic complexes which exhibit catalytic properties [24,25].

The present work deals with the multi-step synthesis and characterization of new heterogeneous materials, specifically Fe(III) complexes of pyridazine derivatives prepared through a robust biosorption mediator consisting of a bacterial biofilm supported on Y zeolite. The preparation procedure includes: (i) the sorption of Fe(III) from aqueous solutions by *A. viscosus* bacterium, a biosorbent supported on NaY, in batch experiments; (ii) the synthesis of pyridazine derivative ligands, 3-ethoxy-6-chloropyridazine (A) and 3-piperidino-6-chloropyridazine (B) and (iii) the immobilization procedure of the Fe(III) complex in Y zeolite. The samples obtained have been fully characterized by spectroscopic methods (FTIR, EPR and UV–vis) chemical analysis (ICP-AES), X-ray power diffraction (XRD), scanning electron microscopy (SEM) and by thermogravimetric analysis (TGA). The material so prepared may be used as catalyst under mild conditions and its activity and selectivity have been described elsewhere [26]. What would be a solid residual material for many industries working with iron in solution may therefore be transformed into an active and selective catalyst, by the procedure described in this paper.

2. Experimental section

2.1. Materials and reagents

A. viscosus was obtained from the Spanish Type Culture Collection of University of Valência. Aqueous iron chloride solutions were prepared by dissolving $FeCl_3 \cdot 6H_2O$ (Riedel) in distilled water, in concentrations up to 100.0 mg_{Fe}/L. Aqueous chromium chloride solutions were prepared by dissolving $CrCl_3 \cdot 6H_2O$ (Riedel) in distilled water, in concentrations up to 100.0 mg_{Cr}/L. NaY zeolite ($Si/Al = 2.88$) was obtained from W.R. Grace (previously calcined at 500 °C during 8 h under a dry air stream). Chemicals for the synthesis of the pyridazine derivative ligands, 3-ethoxy-6-chloropyridazine (A) and 3-piperidino-6-chloropyridazine (B) and for the immobilization procedure were purchased from Aldrich. All the materials used were reagent grade.

2.2. Sample preparation

2.2.1. Preparation of the biofilm supported on Y zeolite

All experimental work was conducted in triplicate. *A. viscosus* bacteria were grown for 24 h in 500 mL of the following culture medium: 10.0 g/L glucose, 5.0 g/L peptone, 3.0 g/L yeast extract and 3.0 g/L malt extract. The medium was sterilized at 120 °C for 20 min, cooled to room temperature, inoculated with bacteria and kept at 28 °C for 24 h with moderate stirring in a incubator.

1.0 g of the NaY zeolite was placed in an Erlenmeyer flask to which 15 mL of *A. viscosus* culture media above