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Biosorption of Cr^{VI} supported on mordenite zeolite

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Abstract

This work reports the usage of a combined zeolite-biosorbent system for the removal and recovery of aqueous Cr^{VI}. The biosorption system consisted of a bacterium, *Arthrobacter viscosus*, supported on two mordenite (MOR) type zeolites with different Si/Al ratio, HMOR (Si/Al = 10) and NaMOR (Si/Al = 6.5). The results show that the biofilm of *A. viscosus* supported on MOR zeolite is able to recover chromium from dilute solutions. For both biosorption-MOR systems, the maximum removal was obtained for initial concentration of 20 mg_{Cr}/L. However, the best results were obtained for HMOR-system with a removal of 52.1 % for the diluted concentration and the best uptake, 3.3 $mg_{Cr}^{VI}/g_{zeolite}$, was achieved for the initial concentration of 100 mg_{Cr}/L. The Langmuir isotherm model was applied with good fitting to the experimental data.

1 Introduction

The emission of organic and inorganic pollutants from industrial sources into the environment is a well known risk factor. Pollution of the aquatic environment is mainly caused by the discharge of industrial effluents. The contamination with heavy metals is of great concern, where industries such as tanneries, electroplating and mining are found present. The continuous increase in emission of heavy metals into the environment poses a threat to human health, as the ingestion of several metals beyond admissible concentrations causes chronic disorders (Demir et al., 2007). Chromium is a metal of widespread industrial usage and is a common pollutant found in wastewaters. It is considered carcinogenic to humans in its Cr^{VI} oxidation state, whereas the Cr^{III} oxidation state is considered less dangerous.

From the different technologies available for the remediation of wastewaters containing heavy metals, biosorption has received considerable attention. The usage of microbial biomass for the removal of metals has been widely studied in recent years (Gavrilescu, 2004). Some studies refer that biosorbents require an adequate support to enhance good performance (Kratochvil et al., 1998). The employment of zeolites as supports for biosorbents has been reported (Figueiredo et al., 2006 and Tavares et al., 2006). Zeolites are widely known to be versatile materials, having found industrial application in various fields such as catalysis, adsorption, molecular sieving and ion exchange. In pollution control, the adsorption and ion exchange capacities have been exploited in the treatment of industrial effluents. The use of zeolites for the removal of heavy metals found in wastewaters has been proposed as a low-cost technique (Babel et al., 2003). However, zeolites can only be used as ionic exchangers for the removal of cationic species, due to the proprieties of the negatively charged aluminosilicate framework. While most metal species in water are cationic, aqueous Cr^{VI} is found in the anion form as chromate or dichromate ions. The repulsion between these ions and the zeolite framework avoids direct removal of Cr^{VI} by zeolite.

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The different method for the removal of Cr^{VI} from effluents proposed (Figueiredo et al., 2006; Tavares et al., 2006 and Silva et al., 2008) combines the biosorption capabilities of the *A. viscosus* bacteria with a robust support of faujasite (FAU) zeolite. The bacterium reduces Cr^{VI} to the cationic Cr^{III} species which are exchanged by the charge-balancing cations in the zeolite structure. The combined technology enables Cr recovery from contaminated effluents in a solid matrix that can be easily recovered from solution and reused as catalysts for several reactions. The oxidation of 1,2-dichlorobenzene in gas phase with Cr containing NaY and NaX zeolites recovered from biosorption essays was reported by Figueiredo et al. (2006).

As there are various zeolitic structures available, it is possible to draw a series of catalysts with recovered metals by simply changing the support for biosorption. The present work reports the usage of mordenite (MOR) type zeolites as supports for the *A. viscosus* bacteria. MOR zeolite differs from FAU zeolite as its structure has channels in a single axis orientation, whereas FAU zeolite has channels in all three axes (Čejka et al., 2005). FAU zeolite also has large supercages, unlike the tubular structure of MOR. Both zeolites present large 12-ring pore opening. MOR zeolites have been studied as catalysts for several reactions and it is common to find them associated to different transition metals. Yim et al. (2000) studied the oxidation of perchloroethylene over chromium supported on mordenite in gas phase, while catalysis in liquid phase reactions was also studied with these zeolites, as described by Kostrab et al. (2006).

This work presents the usage of a different zeolitic structure, mordenite type zeolite as support for the biosorption of Cr^{VI}. Two MOR zeolites, H-form (HMOR) and Na-form (NaMOR) were tested as supports for the biosorption of aqueous Cr^{VI} species.

2 Materials and Methods

a) *Preparation of the zeolitic supports*

Powder samples of HMOR (CBV 21A, Si/Al = 10, surface area of 500 m^2/g) and NaMOR (CBV 10A, Si/Al = 6.5, surface area of 425 m^2/g) were obtained from Zeolyst International and were previously calcined at 500 ºC during 8 h under dry air flow prior to use.

b) *Preparation of the A. viscosus*

A. viscosus was obtained from the Spanish Type-Culture Collection of the University of Valencia. The culture medium is composed by glucose (10 g/L), peptone (5 g/L), yeast extract (3 g/L) and malt extract (3 g/L). The medium is sterilized at 121 ºC, cooled to room temperature, inoculated with the bacteria and it is grown for 24 h at 28 ºC in an incubator prior to use in the Cr^{VI} removal essays.

c) *Cr^{VI} removal essays*

The removal of Cr^{VI} from aqueous solutions was performed in batch conditions: 1 g of either NaMOR or HMOR zeolite was transferred to 250 mL Erlenmeyer flasks, where 15 mL of the grown culture medium and 150 mL of each chromium solution were added. A total of 6 different Cr solutions were tested, with initial concentrations ranging from 20 to 120 mg_{Cr}/L, and were prepared by dilution of $K_2Cr_2O_7$ (Panreac. p.a.) in deionized water. All concentrations were tested in triplicate. The flasks were kept in an incubator at 28 ºC with moderate agitation for 8 days, for both zeolites. Samples were taken at a daily basis, centrifuged and the supernatant was analyzed for Cr^{VI} using the 1,5-diphenylcarbazide colorimetric method (Eaton et al., 1995).

3 Results

Cr^{VI} removal was observed for both NaMOR and HMOR based biosorption systems. Figure 1 presents the Cr^{VI} removal for both supports and the results are detailed in table 1:

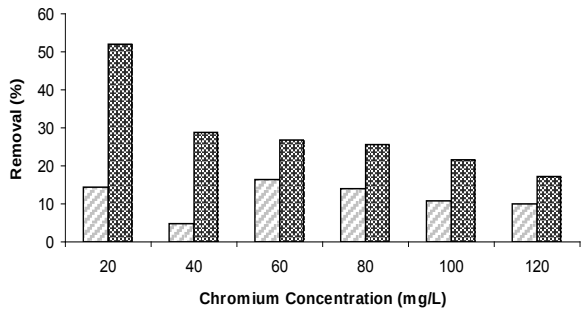

Figure 1: Cr^{VI} removal for NaMOR (light grey) and HMOR (dark grey), for the different chromium concentrations.

Table 1: Cr^{VI} removal and uptakes for both systems tested.

Support	NaMOR		HMOR	
Initial Cr^{VI} concentration (mg/L)	Removal (%)	Uptake ($mg_{Cr}^{VI}/g_{zeolite}$)	Removal (%)	Uptake ($mg_{Cr}^{VI}/g_{zeolite}$)
20	14.6	0.4	52.1	1.5
40	4.7	0.3	28.9	1.6
60	16.3	1.5	26.7	2.4
80	13.9	1.7	25.5	3.1
100	10.9	1.7	21.5	3.3
120	10.1	1.8	17.3	3.1

The best performance in terms of Cr^{VI} removal and uptake was achieved with the HMOR-*A. viscosus* system in all tested solutions with different Cr^{VI} concentrations. With this system, the best removal was obtained for diluted solutions and the uptake increased steadily up to the initial concentration of 80 mg_{Cr}/L and remained stable for the more concentrated solutions. For the NaMOR-based system, the removal appears to be better at the intermediate concentration solutions (40 to 60 mg_{Cr}/L), although the uptake progressed similarly to the HMOR-based system.

The efficiency of Cr^{VI} removal is related to the reduction performed by the *A. viscosus* bacterium (Silva et al., 2008). The ability of several bacteria to bio-reduce Cr^{VI} has been thoroughly studied. Namely, several *Arthrobacter* species are known to perform the reduction of Cr^{VI} (Tsibakhashvili et al., 2004. and Lin et al., 2006) and the reaction takes place in the electron-donor functional groups present in the polysacchararide chains. This reaction is pH-sensitive, as reported in the studies of Cr^{VI} removal by microbial biomass by Park et al. (2005, 2008), which suggest that acidic conditions favor the reduction of Cr^{VI}. Higher pH values limit the reduction capacity and the removal of Cr^{VI} species is performed by retention in the surface of the biomass. The pH values of the solutions were measured at the initial and final experimental time and the results are presented in table 2:

Table 2: Measured pH values for the different solutions

Solution	Initial Cr^{VI} solution	HMOR		NaMOR	
		Initial	Final	Initial	Final
20	5.21	3.60	3.35	7.03	7.85
40	5.20	3.52	3.27	6.31	8.19
60	4.30	3.53	3.21	6.22	7.83
80	5.02	3.29	3.10	6.08	5.41
100	4.83	3.39	3.11	6.12	5.18
120	4.72	3.31	3.07	6.09	5.34

The initial shift in the pH is related to the rapid ion exchange between the zeolite and the residual protons and potassium ions present in the aqueous media (K^+ originates from the chromium salt employed). For the biosorption-NaMOR, the system increases pH at the initial stages, with this effect being more notorious in the lower Cr^{VI} concentration solutions which have a lower K^+ concentration. In fact, this support has 6.5 % of Na_2O and most likely protons co-exchanged with Na^+ ions from the zeolite. For the biosorption-HMOR system the behavior is different. The principal charge balancing cation in its framework is the proton due to the absence of sodium (Na_2O = 0.05%). Charge compensation by co-exchange of protons and potassium leads to some residual acidity in the zeolite, so the shift in the pH of the solutions is towards a more acidic region. Therefore, the biosorption-HMOR system is more adequate to the reduction of Cr^{VI} by the *A. viscosus* bacterium and the differences in the uptake are related to this fact. It is expected that the HMOR zeolite recovered from solution will present a higher Cr loading when compared to the NaMOR.

The Langmuir adsorption isotherm model was applied to the experimental data obtained for the biosorption-MOR systems. The data was plotted (figure 2) and the parameter values were calculated and are presented in table 3:

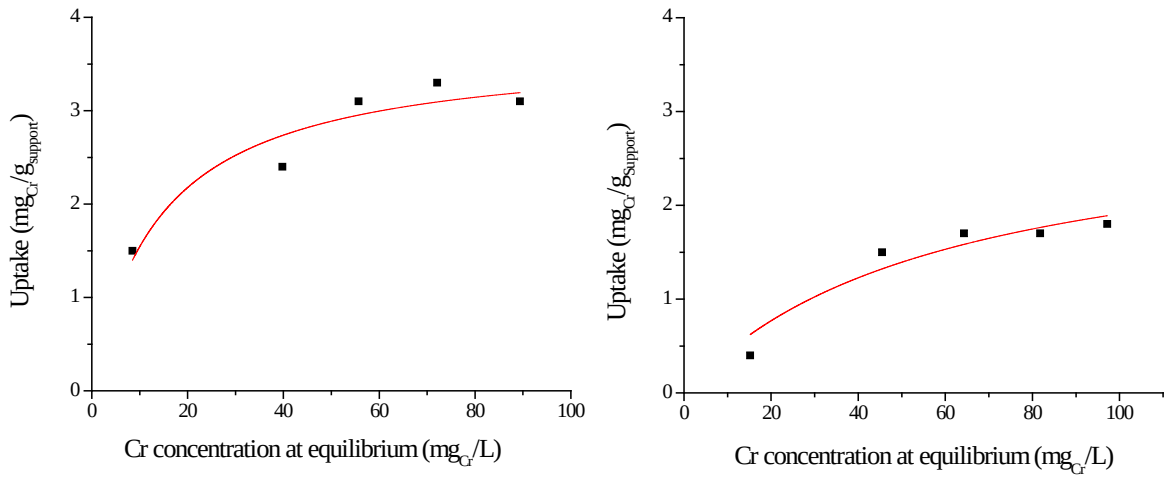

Figure 2: Uptake vs. equilibrium concentration for HMOR – bacteria (left) and NaMOR – bacteria (right), with plotted Langmuir fitting to experimental data for both systems.

Table 3: Langmuir model parameters

System	Parameters	
HMOR	q_{max}	3.5 $mg_{Cr}/g_{support}$
	b	0.37 $mg^{-1}.L$
NaMOR	q_{max}	2.0 $mg_{Cr}/g_{support}$
	b	0.33 $mg^{-1}.L$

The Langmuir adsorption model presented good fitting to experimental data for both systems, indicating that the Cr^{VI} removal performed by both systems is similar to an adsorption process. The calculated maximum uptakes (q_{max}) are similar to the obtained experimentally.

4 Conclusions

Both biosorption HMOR and NaMOR systems were able to recover Cr^{VI} from solution, with the biosorption-HMOR system being more efficient for all tested chromium solutions. The removal is higher for the lower concentration solutions. The pH regulation performed by the HMOR support increases the amount of Cr^{VI} reduced by the *A. viscosus* bacterium, whereas the pH shift into higher values performed by the NaMOR support hinders the reduction and therefore limits Cr^{VI} removal and uptake.

The Langmuir adsorption model was successfully applied to the experimental data making possible the modeling of the Cr^{VI} removal process by the combined *A. viscosus* - mordenite zeolite.

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