



BIOSORPTION OF HEXAVALENT CHROMIUM BASED ON MODIFIED Y ZEOLITES OBTAINED BY ALKALI-TREATMENT

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Abstract

The structural modification of external surface of NaY was investigated in order to enhance efficient biosorption systems consisting of a bacterial biofilm, *Arthrobacter viscosus*, supported on that zeolite, for removing hexavalent chromium from aqueous solutions. The supported bacterial biofilm reduces Cr(VI) to Cr(III) and this cation is then retained in the zeolite by ion exchange. NaY zeolite was modified by alkali-treatments using NaOH 2.0 M, with two different contact periods of time between the zeolite and the alkaline solutions, resulting in NaY_A and in NaY_B. The biosorbents supported on the modified NaY zeolite were tested in solutions with low concentration of chromium. The results showed that the modification of external surface of NaY zeolite allows an efficient Cr removal, and the maximum removal efficiency was observed for NaY_A sample that was submitted to a smoother chemical treatment.

Key words: alkali-treatment, *Arthrobacter viscosus*, biosorbent, Cr(VI), NaY Zeolite

1. Introduction

A wide variety of toxic inorganic elements (heavy metal) and organic chemicals (volatile organic compounds - VOCs) is discharged into the environment as industrial wastes, causing serious pollution problems in water, air and soil. Cadmium (Cd), chromium (Cr) and lead (Pb) are common toxic pollutants found in wastewater coming from chemical manufacturing, painting, coating, mining operations and leather tanneries. One of the potential solutions for this problem is the use of adsorption technologies (Bailey et al., 1999; Gavrilescu, 2004; Sag and Kutsal, 1995). In this regard, zeolites have a great potential for removing heavy metals from industrial wastewater, specially the faujasite structures like Y and X zeolites (Figueiredo et al., 2005).

Y zeolite is a microporous aluminosilicate based on sodalite cages joined by O bridges between the hexagonal faces. Eight such sodalite cages are linked together, forming a large central cavity or supercage, with a diameter of 12.5 Å. The supercages share a 12-membered ring with an open diameter of 7.4 Å. The peculiar adsorptive properties of Y zeolite are due to the positively charged exchangeable ions, which are located inside the three-dimensional pore structure of the solid to balance the negative charge of the framework AlO₄⁻ tetrahedrons (van Santen and Kramer, 1995). The existence of this net negative structural charge promotes a strong affinity for metal ions giving good adsorption properties to these supports.

Among different heavy metals that may be removed from liquid solutions by sorption, chromium demands special attention as it may present several

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oxidation states. Chromium exists in oxidation states from +2 to +6, but only two states, +3 and +6, are of environmental significance (Ghiaci et al., 2006).

These two oxidation states have widely contrasting toxicity and transport characteristics: hexavalent chromium is more toxic, with high water solubility and mobility, while trivalent chromium is less soluble in water, less mobile and less harmful (Tsibachashvili et al., 2004). While the positive ion is easily exchangeable by the zeolite itself, the chromate or dichromate ions are negatively charged which prevents the direct ion exchange by NaY. It was reported in previous work that NaY can be used as a support for a biofilm of *Arthrobacter viscosus* bacteria, and the combined biofilm – zeolite system is able to remove Cr(VI) from aqueous solutions (Ghiaci et al., 2006; Figueiredo et al., 2005; 2008; Tsibachashvili et al., 2004; van Santen and Kramer, 1995). *A. viscosus* bacterium is a good exopolysaccharide producer, which allows foreseeing good qualities for support adhesion and for metal ions entrapment (Quintelas et al., 2001). The bacterial biofilm supported on the zeolite reduces Cr(VI) to Cr(III) and Cr(III) is retained by ion exchange. In this way, the bacteria allow metal loading of the zeolite, as sterical limitations and charge repulsions would not permit the zeolite loading with the anionic species, $\text{Cr}_2\text{O}_7^{2-}$ (Figueiredo et al., 2008).

Nevertheless, one of the characteristics of the zeolites is their small external surface in contrast with their high internal surface which limits the adhesion of the *A. viscosus* bacterium to the support, as the characteristic dimension of bacteria ranges from 1 to 10 μm . The zeolites exhibit large specific surfaces areas, typically higher than 300 m^2/g and most of this area is internal, with an internal void volume above 0.1 cm^3/g . In order to enhance a better adhesion of the bacteria, the external surface of NaY zeolite was modified by chemical treatments.

The most common modifications in the structure of the zeolites are the ion exchange treatment (Neves et al., 2009), the dealumination by the acid treatment (Fan et al., 2007) and the hydrothermal treatment (Nagamori and Kawase, 1998). However these treatments affect the whole structure of the zeolite. Contrarily, the modification by alkali-treatment is poorly documented, despite to be known for several years (Breck and Skeels, 1980; Engelhardt and Lohse, 1984; Aouli et al., 1988). The first works (Breck and Skeels, 1980) on basic media showed that NaOH treatment reduces the surface area of the zeolite. Several authors (Cherif et al., 2003) studied the dealumination by hexafluorosilicate when treated with acids or bases and observed the formation of an amorphous phase in Y zeolite. Recent works (Suzuki and Okuhara, 2001) reported that NaOH treatment of MFI zeolite leads to the extraction of silicon and little aluminum and to the formation of mesopores larger than 18 Å. However, the treatment of MFI zeolite in NaOH aqueous solution enhanced the catalytic activity for cumene cracking and changes in the pore volume and pore-size distribution of

mesopores (Ogura et al., 2001). SEM and XRD measurements revealed that the microcrystallites were not affected by the NaOH treatment, but amorphous phases present at the boundary of the crystallites were dissolved. Some authors (Song et al., 2006) describe the post-treatment of ZSM-5 with sodium hydroxide to enhance on-stream stability for butane aromatization.

In the present work, the structural evaluation of NaY zeolite has been studied after alkali-treatment using NaOH 2.0 M and two different contact periods of time between the zeolite and the treatment solution (NaY_A and NaY_B). The stability of the samples was followed by X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy (FTIR), chemical analysis (ICP-AES) and nitrogen adsorption at 77 K. The biosorbents based on the modified Y zeolite were tested in solutions with low concentration of chromium.

2. Experimental

2.1. Materials

NaY zeolite ($\text{Si}/\text{Al} = 2.88$) in powder form was obtained from W. R. Grace. It was calcined at 500 °C during 8 h under a dry air stream prior to use. *Arthrobacter viscosus* was obtained from the Spanish Type Culture Collection of the University of Valencia. Aqueous chromium solutions were prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ (Riedel) in distilled water and the alkaline solution was prepared by dissolving NaOH (Aldrich). All the materials used were reagent grade. Glassware used for experimental purposes was washed in 10 % nitric acid to remove any possible interference by other metals. Atomic absorption spectrometric standards were prepared from 1000 $\text{mg}_{\text{Cr}}/\text{L}$ solution.

2.2. Methods

2.2.1. Alkaline Chemical Treatment of the NaY zeolite

The alkali-treatment of the starting NaY was performed with NaOH solution. Two modified samples were prepared with 25 g of NaY zeolite and with 250 mL of 2.0 M solution of NaOH (10 mL of solution/g zeolite). The resulting mixtures were refluxed for 1 h. After the reflux, NaY_A sample was separated immediately from the solution, while NaY_B sample was kept in contact with the alkaline solution for an additional 8 h. The modified samples were separated by filtration, washed with distilled water and dried in an oven at 60 °C for 8 h. They were calcined in the same conditions of the starting NaY zeolite.

2.2.2. Biosorption Assays

The whole experimental work was conducted in triplicate. *A. viscosus* bacteria were grown 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 121 °C

for 20 min, cooled to room temperature, inoculated with the bacteria and kept at 28 °C for 24 h with moderate stirring in an incubator. 1.0 g of NaY zeolite and of the modified zeolite samples were placed in Erlenmeyer flasks to which 15 mL of *A. viscosus* culture media (3.0 g_{biomass}/L) above described were added. Finally, 150 mL of the different aqueous chromium solutions were added: 100, 150 and 250 mg_{Cr}/L. All flasks were closed and kept at 28 °C with moderate stirring.

Control of the pH solution was made at the beginning and at the end of the biosorption assays. Samples of 1 mL were taken, centrifuged and analyzed for metals using a Varian Spectra AA-400 Atomic Absorption Spectrophotometer (AAS). Samples were filtered and washed off with distilled water. Afterwards, the samples were calcined using the same procedure described for the starting NaY zeolite.

2.2.3. Characterization

Si, Al and Na contents of modified zeolite samples were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Philips ICP PU 7000 Spectrometer. Powder X-ray diffraction patterns (XRD) were recorded using a Philips Analytical X-ray model PW1710 BASED diffractometer system. Scans were taken at room temperature, using Cu K α radiation in a 2 θ range between 5° and 70°. Scanning Electron Microscopy (SEM) was performed using a LEICA Cambridge S360 Scanning Microscope. Samples were coated with Au in vacuum to avoid surface charging using a Fisons Instruments SC502 sputter coater. The textural characterization of the samples was based on the N₂ adsorption isotherms, determined at 77 K with a Quantachrome Instruments Nova 4200e. Samples were previously outgassed at 300 °C for 3 h.

Room temperature FTIR spectra were obtained from powdered samples on KBr pellets, using a Bomem MB104 spectrometer in the range 4000–500 cm⁻¹ by averaging 20 scans at a maximum resolution of 4 cm⁻¹.

3. Results and Discussion

3.1. Alkali-treatment of the starting NaY zeolite

The textural characterization, structure and chemical composition before and after the alkaline treatments of NaY zeolite were determined by scanning electron microscopy (SEM), nitrogen adsorption-desorption isotherm at 77 K, X-ray diffraction (XRD), infrared spectroscopy (FTIR) and chemical analysis. SEM analysis of the samples confirms the effect of the alkali-treatment on the morphology of NaY zeolite. Fig. 1 shows SEM micrographs of NaY and of the modified zeolite samples after the alkali-treatment.

Comparison of microphotographs of NaY and of the modified samples indicates that the morphology changed during the alkali-treatment, for

the two treated zeolites. The SEM microphotographs of all samples are typical of a microporous crystalline aluminosilicate with regular small particles.

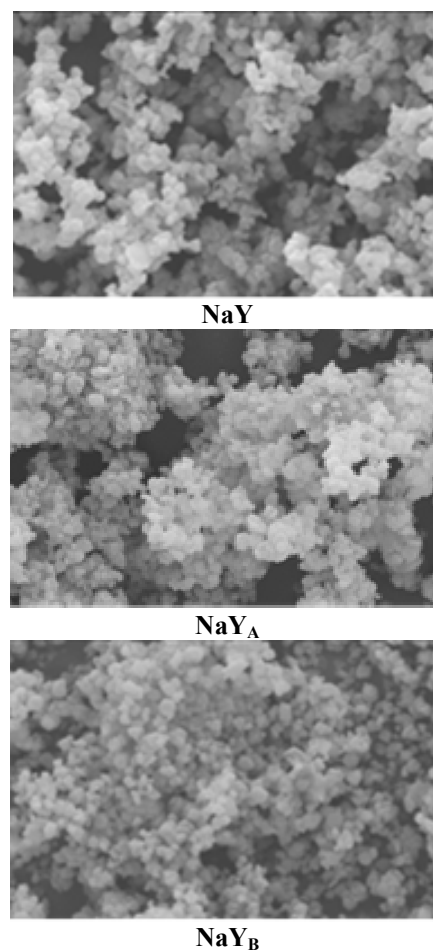


Fig. 1. SEM photographs with a 5000x resolution of NaY, NaY_A and NaY_B samples

The surface of NaY zeolite became rougher after a severe alkali-treatment and the edges of particles of NaY zeolite seem to become more irregular. The particle size of starting NaY was about 1 μ m, the one of NaY_A was 0.7–1 μ m and the other of NaY_B was 0.3–1 μ m. The nitrogen adsorption-desorption equilibrium isotherms at 77 K for NaY, NaY_A and NaY_B samples are illustrated in Fig. 2.

The N₂ adsorption isotherms for all samples are of Type-I, according the IUPAC classification, which is typical of solids with a microporous structure (Gregg and Sing, 1982). The shape of both adsorption and desorption isotherms of the modified zeolites were very similar to that of the starting NaY.

A decrease of all textural parameters was observed for both modified samples. These results indicate that the alkali-treatment does not affect the whole structure, but only the external surface, apparently blocking partially the access of some pores. It is possible that damages on the surface structure and on the pores accesses are dependent on the NaOH treatment conditions (Suzuki and Okuhara, 2001).

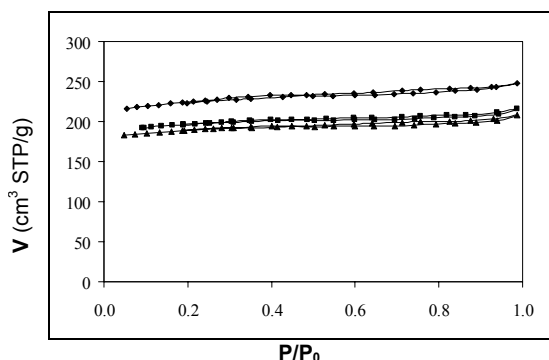


Fig. 2. Nitrogen adsorption-desorption equilibrium isotherms at 77 K of the samples:
 (♦) NaY, (■) NaY_A and (▲) NaY_B

The micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) were calculated by the *t*-method and the total surface areas (S_{BET}) were calculated through the BET equation. These values are summarized in Table 1.

Table 1. Si/Al ratios, specific area, pore volume and textural parameters of the zeolite samples.

	NaY	NaY _A	NaY _B
S_{BET} (m ² /g)	787	665	651
V_{micro} (cm ³ /g)	0.35	0.29	0.30
S_{meso} (m ² /g) ^a	18.90	12.70	13
a_0 ^b (Å)	24.63	24.71	24.77
Si/Al ^c	2.88	2.72	2.51
Si/Al ^d	2.80	2.22	1.89
Si/Al ^e	2.74	2.45	2.33
Crystallinity (%)	100	94.30	91.80

^aFrom *t*-plot; ^bUnit cell parameter determined from XRD; ^cBulk Si/Al ratio determined from ICP-AES; ^dFramework Si/Al ratio determined from XRD, $N_{Al} = 115.2(a_0 - 24.191)$; ^eFramework Si/Al ratio determined from FTIR, $\chi = 3.857 - 0.0621w_{DR}$ (cm⁻¹), where $\chi = [1 + (Si/Al)]^{-1}$ and w_{DR} is the zeolite specific double ring vibration mode between $v_{max} = 570-600$ cm⁻¹.

In agreement to these observations, the preservation of the zeolitic structure after alkali-treatment was shown by X-ray diffraction and Infrared spectroscopy analysis. Fig. 3 and Fig. 4 show the XRD and FTIR analyses of NaY, NaY_A and NaY_B, respectively.

The powder XRD patterns of NaY and the modified zeolite samples were recorded at 2θ values between 5 and 45°. All samples exhibited the typical and similar pattern of highly crystalline Y zeolite. The relative crystallinity was estimated by comparing the peak intensities of the modified sample with those of the starting NaY (100 % of crystallinity). The total intensities of the six peaks assigned to [3 3 1], [5 1 1], [4 4 0], [5 3 3], [6 4 2] and [5 5 5] reflections were used for the comparison according to ASTM D-3906-80 method (the reflection peaks positions are indicated in Fig. 3). After the alkali-treatment, the modified zeolites maintained over 90 % of crystallinity as compared to the respective starting

NaY zeolite. The unit cell parameters (a_0) were calculated from the [5 3 3], [6 4 2] and [5 5 5] reflection peak positions that were determined using quartz as an internal standard, according to ASTM D-3942-80 method. The framework Si/Al ratio was obtained from the calculated unit cell parameters by using the Breck and Flanigen equation (Breck and Flanigen, 1968). The infrared region between 570 and 600 cm⁻¹ exhibits the most structure sensitive band in NaY zeolite spectra and can be used to calculate also the framework Si/Al ratio (Ghesti et al., 2007) (Fig. 4). The bulk Si/Al ratio was determined by chemical analysis (ICP-AES) (Table 1).

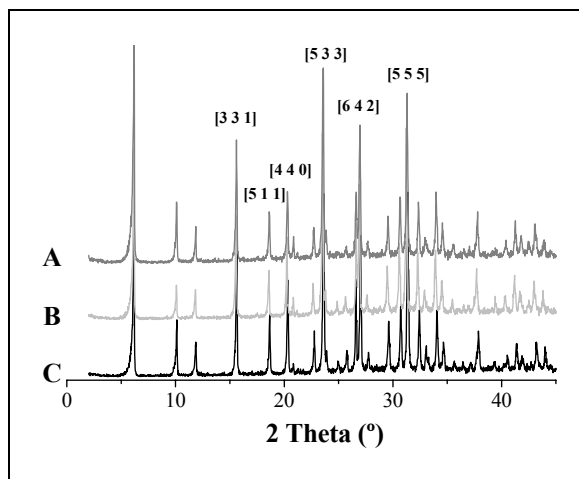


Fig. 3. XRD patterns of NaY_A (A), NaY_B (B) and NaY (C) zeolite samples

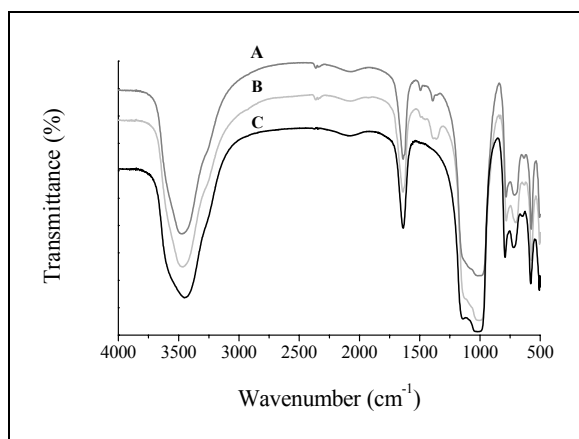


Fig. 4. FTIR spectra of NaY_A (A), NaY_B (B) and NaY (C) zeolite samples

The unit cell parameters and the framework Si/Al atomic ratio for both modified zeolite samples changed substantially upon alkali-treatment. The increase in the unit cell parameters indicates the enrichment of aluminum in the framework (Cherif et al., 2003). In the case of the starting NaY, the Si/Al ratios of the bulk and the framework (determined by XRD and FTIR analysis) were similar. This indicates that the Si/Al atomic ratio was uniformly distributed throughout each zeolite particle and the presence of extra-framework alumina species was excluded.

Each characterization method showed different Si/Al ratios, i.e., the bulk Si/Al ratio (given by chemical analysis) and the framework Si/Al ratio (given by XRD and FTIR) were different for each zeolite, after the alkali-treatment. The bulk and framework ratios of Si/Al on the modified zeolite samples decreased with the increasing severity of the alkali-treatment. This one provokes a preferential migration of silicon species (Cherif et al., 2003) from surface and leads to the formation of the mesopores in the structure (Suzuki and Okuhara, 2001).

It may be observed in Fig. 4 that the FTIR spectra of the starting NaY zeolite and the modified zeolites are dominated by the strong zeolite bands: the broad band at $3700\text{--}3300\text{ cm}^{-1}$ is attributed to surface OH in Si-(OH)-Al groups of the framework and bands corresponding to the lattice vibrations are observed in the spectral region between $1300\text{--}450\text{ cm}^{-1}$ (Imelik and Vedrine, 1999; van Bekkum et al., 2001). No shift or broadening of these Y zeolites vibrations are observed after the alkali-treatment and even after the inclusion of chromium through the biosorption process (data not included). This provides further evidence that the microcrystallinity of the zeolite remains unchanged in agreement with other works (Figueiredo et al., 2006; Oguna et al., 2001).

The infrared spectra of NaY_A (A) and of NaY_B (B) exhibit two bands at 1390 and 1490 cm^{-1} which are probably assigned to the presence of sodium after the alkali-treatment. For NaY_B, the broad bands are more intense due to the long exposition of the sample to the NaOH solution.

3.2. Biosorption data

The removal of chromium by the combined system (biofilm/zeolite) presents a typical and well known biosorption kinetics (Figueiredo et al., 2006; Quintelas et al., 2001), which includes a very fast initial stage occurring at the very beginning of the process, Figs. 5 and 6. This step is associated with the external cell surface action, biosorption itself (Tavares et al., 1995).

Intra-cellular accumulation/reaction or processes depending on the cellular metabolism do not seem to promote further Cr removal from solution.

The peculiar adsorptive properties of zeolites are originated from the negative charge of the framework AlO_4^- tetrahedra, which are located inside the three-dimensional pore structure of the solid. The role of the biofilm is the reduction of the negative Cr(VI) to a smaller cation, Cr(III), being this ion easily exchanged on the internal surface of the zeolite (Figueiredo et al., 2006; Quintelas et al., 2001). The reduction can only occur on the outer surface of the zeolite as $\text{Cr}_2\text{O}_7^{2-}$ is not able to get inside of the zeolite framework.

The results of Cr removal from aqueous solutions in batch assays showed that the modification in external surface of Y zeolite enhances Cr removal in both samples and the

maximum removal efficiency was observed for NaY_A sample that was submitted to smoother alkali-treatment.

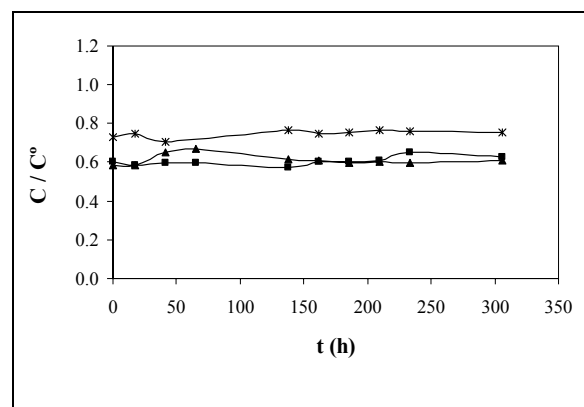


Fig. 5. Instant over initial Cr concentration (C/C^0) versus time of contact, for NaY_A based biosorbent, for different initial metal concentrations: (*) $100\text{ mg}_{\text{Cr}}/\text{L}$, (▲) $150\text{ mg}_{\text{Cr}}/\text{L}$ and (■) $250\text{ mg}_{\text{Cr}}/\text{L}$.

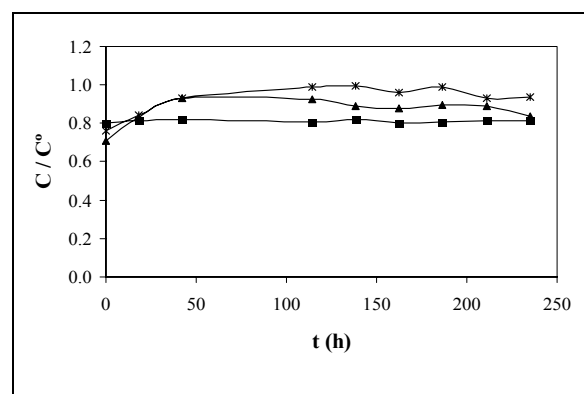


Fig. 6. Instant over initial Cr concentration (C/C^0) versus time of contact, for NaY_B based biosorbent, for different initial metal concentrations: (*) $100\text{ mg}_{\text{Cr}}/\text{L}$, (▲) $150\text{ mg}_{\text{Cr}}/\text{L}$ and (■) $250\text{ mg}_{\text{Cr}}/\text{L}$.

Fig. 7 presents the ratio between residual and initial Cr concentration for the 100, 150 and 250 $\text{mg}_{\text{Cr}}/\text{L}$ solutions, for the unmodified support NaY and the samples submitted to alkali-treatment. In terms of Cr removal, NaY_A sample was more efficient than the unmodified support (Figueiredo et al., 2006) for all tested solutions. NaY_B sample was less efficient than NaY for most of the tested Cr solutions.

The results of chromium elemental analysis show that the biosorption process allowed the retention of chromium in the modified zeolites. In fact, the entrapment of the chromium in the framework zeolite by ion exchange was strongly affected by the alkali-treatment. Table 2 presents the chemical analysis obtained after biosorption process, filtration and calcination of the modified samples compared with starting NaY (Figueiredo et al., 2006). The three different samples included herein were tested as biosorbents in Cr solutions with initial concentrations of 100 and 250 $\text{mg}_{\text{Cr}}/\text{L}$.

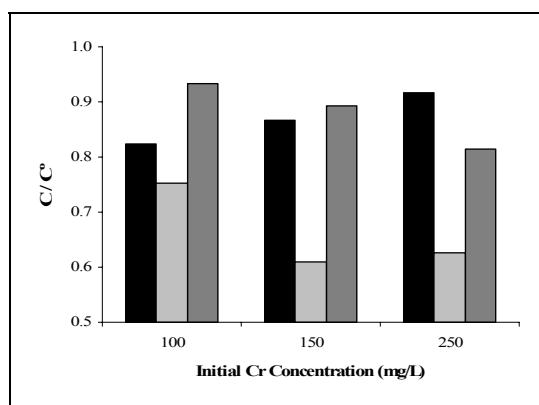


Fig. 7. Instant over initial Cr concentration (C/C^0) versus initial metal concentrations, 100, 150 and 250 mg_{Cr}/L for NaY (■), NaY_A (■) and NaY_B (■).

Table 2. Chemical analysis of the zeolite samples after biosorption studies

Samples	Cr (%) ^a	Na (%) ^a	Cr (UC) ^b	Si/Al ^c
NaY	—	7.82	—	2.88
CrNaY 100	0.14	5.56	0.45	2.93
CrNaY 250	0.22	4.81	0.70	2.94
NaY _A	—	8.61	—	2.72
CrNaY _A 100	0.02	7.09	0.06	2.29
CrNaY _A 250	0.03	6.18	0.10	2.36
NaY _B	—	8.96	—	2.52
CrNaY _B 100	0.08	7.37	0.24	2.32
CrNaY _B 250	0.12	6.05	0.38	2.39

^aChromium and sodium loading on zeolite samples (wt %) after biosorption process; ^bNumber of chromium ions per unit cell determined from the chromium loading on zeolites after biosorption process; ^cBulk Si/Al ratio determined from ICP-AES.

As expected, the alkaline treatment provokes the reduction of the amount of chromium retained in the structure of the zeolites. However, this decrease is more accentuated for the NaY_A, the sample that was submitted to a smoother chemical treatment.

After the biosorption and the calcination treatments, the bulk Si/Al ratios obtained by chemical analysis of the tested samples changed (Table 2). The Si/Al ratio of the unmodified support did not change significantly (Figueiredo et al., 2006) and the one of the modified samples decreased. This decrease is more pronounced for NaY_A sample, when compared with initial and final Si/Al ratio obtained after Cr(VI) biosorption (0.40 for NaY_A and 0.20 for NaY_B).

During the alkali-treatment, the silicon hydroxides formed diffuse to the external surface of the zeolite and bind to the structure, in agreement with combined XRD and chemical analysis (Table 1). As it can be seen, the framework Si/Al ratio is lower than the bulk Si/Al ratio for both modified zeolites. This fact is related to the formation of a layer of amorphous silica (Oguna et al., 2001) and this may cause pore blocking (Cizmek et al., 1995; 1997).

The pore blocking in the surface of the zeolite limits the access of Cr^{III} ions to the zeolite inner structure and the cation probably remains in the

bacteria walls. The filtration of the samples with distilled water removes the bacteria and the Cr ions retained in the biostructures. A smaller amount of Cr is effectively retained by the zeolite, compared to results obtained with the starting NaY.

In general, the alkali-treatment, aiming the optimization of the adhesion of the bacteria to the external surface of NaY zeolite, allows an improved removal performance for the most concentrated solutions tested, but it is possible that the process may lose its adsorption character with a reduced ion-exchange capacity of the zeolite. While a smoother alkali surface treatment of the base zeolite promotes the definition of a good support for the biofilm to be used as a biosorbent (by increasing its external surface area and its chemical ability to support the bacteria), a more aggressive treatment allows an improved entrapment process for metal ions (by increasing the mesoporosity of the support). The alkali-treatment in NaY zeolite modifies its external surface and enhanced a better adhesion of *A. viscosus* bacteria to the zeolite. Chromium removal can be improved by this method in detriment of the retention by ion exchange capacity of the support.

4. Conclusions

The alkali-treatment of NaY zeolite is a helpful procedure to modify its external surface and can enhance a better adhesion of *Arthrobacter viscosus* bacteria to the zeolite. The increase in external surface was ascribed to the removal of siliceous species by the alkali-treatment while the intrinsic microcrystallinity of NaY zeolite remains unchanged. The results showed that the modification in external surface of Y zeolite allows an efficient Cr removal. The maximum removal efficiency was observed for NaY_A sample that was submitted to smoother alkali-treatment, while NaY_B sample, subjected to a more aggressive treatment revealed higher metal ions entrapment ability.

The biofilm supported on modified zeolite is able to remove Cr(VI) from dilute solutions and can be applied in wastewater remediation.

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