Biosorption of Cr (VI) using a bacterial biofilm supported on granular activated carbon and on zeolite

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Abstract

Two mini-columns partially filled with granular activated carbon (GAC) and/or a natural zeolite, covered by a bacterial biofilm of *Arthrobacter viscosus*, were used in a continuous flow system to remove Cr (VI) from solutions with initial concentration of 70 mg/l and a working pH ranging between 4.5 and 5.5. Three different set-up's were used: two columns in series filled GAC covered with a biofilm, two columns in series filled with zeolite covered with a biofilm and a column filled with GAC followed by another column filled with zeolite, both supports covered with biofilm. Comparatively, the biosorption system supported on GAC reaches similar removal values, 19%, as the one supported on the zeolite, 18%, but when these two beds are used in combination better performances are reached, i.e. 42% removal. The maximum uptake values ranged from 0.57 $mg_{Cr}/g_{Support}$ to 3.58 $mg_{Cr}/g_{Support}$. The interactions between metal ions and functional groups on the cell wall surface of the biomass were confirmed by FTIR. GAC was regenerated with steam draughting and reused twice. The first regeneration caused a decrease in the removal capacity of 38% and the second regeneration caused a total decrease in the removal capacity of 76%.

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1. Introduction

Environmental pollution by heavy metals is mainly caused by industrial and agricultural processes. Removal of heavy metals from wastewater is usually achieved by physical and chemical processes which include precipitation, coagulation, reduction, membrane processes, ion exchange and adsorption (Pagnanelli et al., 2001).

This work aimed at the definition of a sustainable, low-cost environmental technology targeted at small but locally vibrant industries producing wastewater with low concentration of heavy metals. These units work within tight budgets and are not really motivated to treat their wastes by conventional pollution abatement technology, as it is too expensive and not completely effective when applied to diluted solutions.

The development of a robust biosorption system consisting of a bacterial biofilm supported on activated carbon and on a naturally occurring zeolite is proposed. On one hand, the ability of GAC to remove organic compounds that usually are also present in this kind of industrial wastewater seems to be a good property to be taken in consideration, in actual applications of the system under study. On the other hand, naturally occurring zeolite is not as expensive as GAC and may work as a good support for the biofilm in a second treatment unit, performing the residual metal removal that was not accomplished by the first bed.

The uptake of heavy metals ions can take place by entrapment in the cellular structure of many materials of biological origin and subsequent sorption onto the binding sites present in the cellular structure. This uptake method is independent of the biological metabolic cycle and is known as biosorption or passive uptake (Kapoor et al., 1999). Microorganisms are quite adequate for heavy metals

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biosorption, due to their ability to sorb metal ions, suitability for natural environments and low cost (Nakajima, 2002). There are several chemical groups present in biomass that could attract and sequester metals. These groups include acetamide groups of chitin, structural polysaccharides, amino and phosphate groups of nucleic acids, amide, amine, sulfhydryl and carboxyl groups in the proteins (Ahluwalia and Goyal, 2006). Studies made by Mohanty et al. (2006) and Pradhan et al. (2007) confirm the role played by various functional groups in biosorption of different heavy metals. *Arthrobacter viscosus*, a Gram-positive aerobe from the family of *Micrococcaceae* and order of *Actinomycetales* is a good exopolysaccharide producer, which, by itself, would allow foreseeing good qualities for support adhesion and for metal ions entrapment (Scott and Palmer, 1988; Melo and D'Sousa, 2004).

Activated carbon is frequently used in adsorptive separation processes. Many of the most recently developed biosorption systems are presented in a comparison basis with similar removal systems based on sorption by activated carbon (Sharma and Forster, 1996; Aksu et al., 2002; Kobya et al., 2005). The regeneration of such material is very important if these processes are to be considered economically attractive. Since adsorption is an exothermal process, raising temperature will favour surface regeneration by liberating adsorption sites. On the other hand, steam treatment will deactivate the biofilm, preparing the support for a new cycle of biofilm formation followed by ions fixation. Accordingly, the best results are usually obtained with thermal regeneration, vapour regeneration and wet air oxidation (Salvador and Sánchez Jiménez, 1999).

Zeolites are hydrated aluminosilicate minerals with a cage-like structure that offers large internal and external surface areas for ion exchange. These cages are filled with ions and water molecules with high freedom of movement. They possess a net negative structural charge due to isomorphic substitution of cations in the mineral lattice. Hence they have a strong affinity for transition metal cations, but only little affinity for anions and non-polar organic molecules (Mier et al., 2001). This may be changed by surface pre-treatment or surface coverage by a specific biofilm. Zeolites are quite common in nature and naturally occurring zeolites from Cuba were tested in this study. They are mainly composed of clinoptilolite (80%), one of the most efficient materials in terms of heavy metals fixation (Arriagada et al., 2001).

This study aims the development of a system of two mini-columns in series for the removal of chromium (VI) using a biofilm of *A. viscosus* supported on two different materials: granular activated carbon and natural zeolite. Although these materials are already good sorbents for metals, the dichromate ion is quite large and negatively charged which prevent adsorption on these surfaces. An easier fixation on the matrix may be allowed by a possible reduction of Cr (VI) to Cr (III) by the microorganism (Figueiredo et al., 2006). Functional groups present in the biomass that may have some role in biosorption process

were examined by FTIR. The effect of the regeneration of granular activated carbon was also studied.

2. Methods

2.1. Materials

The bacterium *A. viscosus* was obtained from the Spanish Type Culture Collection of the University of Valência. Aqueous chromium solutions were prepared by diluting $K_2Cr_2O_7$ in distillated water. All glassware used for experimental purposes was washed in 60% nitric acid and subsequently rinsed with deionised water to reduce any possible interference by other metals. Atomic absorption spectrometric standards were prepared from 1000 mg_{Cr}/l solution.

The supports were granular activated carbon (GAC) from MERCK with an average particle size of 2.5 mm, characterised by N_2 adsorption (77 K) with an ASAP Micromeritics 2001 which indicated a Langmuir area of 1270 m^2/g and an average pore diameter of 2 nm, and naturally occurring zeolite from Cuba, mainly composed by clinoptilolite, $Al_2O_3 \cdot SiO_2$, with a pore diameter between 0.2 and 1.2 nm and a internal surface smaller than 10^3 m^2/g. This last support was randomly smashed and only particles with a size between 2 and 5 mm were used. Any attempt to reduce more the size of these particles would reduce to powder an important amount of the material. The option for granular supports is justified by the fact that this kind of biofilm demands detached particles that allow the bed to expand, avoiding the gluing by the exopolysaccharides produced by the bacteria. The selection of GAC was due to its high surface area, porous structure, high adsorption capacity and surface chemical nature (Radovic and Rodrígues-Reinoso, 1997), making it a versatile adsorbent and the zeolite was chosen due to its capacity for immobilising microorganisms (Milán et al., 2001) and its ability to remove heavy metals from industrial wastewater (Mier et al., 2001).

2.2. Methods

The whole experimental work was conducted in duplicate. GAC and the zeolite were placed separately, in Erlenmeyer flasks of 250 ml with 150 ml of distilled water. They were sterilised at 120 °C for 20 min to release the air inside the pores. Then, those materials were placed in mini-columns (internal diameter = 0.9 cm, ht = 30 cm) for open system studies. Three different set-ups were used: two columns in series filled with granular activated carbon, two columns in series filled with zeolite and a column with GAC (23 g) followed by another column with zeolite (40 g). The microorganism culture and the nutrient broth were pumped through at a flow rate of 25 ml/min, firstly to a mixture reactor and afterwards through the set-up of sequential beds, aiming the formation of the biofilm. Two different media, with different concentration of peptone, were used to grow the microorganism for 4 d, aiming the

Table 1
Composition of growth medium and cultivation conditions (microorganism culture and nutrient broth)

Component (g/l) or condition	Microorganism culture	Nutrient broth
Malt extract	3	0.015
Yeast extract powder	3	0.015
Peptone	5	0.025
Glucose	10	0.05
pH	7	7
T (°C)	26	26

optimisation of the adhesion, Table 1. The high flow rate used allows the formation of a compact biofilm and consequently a resistant one to the erosion stress resultant from the hydrodynamic forces.

After the biofilm formation, beds were washed out and the metal solution with concentrations between 10 and 150 mg/l, with pH ranging from 4.5 to 5.5 and a temperature of 26 °C, was passed through the columns with a flow rate of 10 ml/min. At the end of each run, columns were washed out and samples of the effluent were seeded in Petri plates with nutrient agar to assess the metabolic activity of the microorganism. The GAC was recovered with steam and reused twice. Cr (VI) concentration at the inlet and at the outlet of the sequential columns was measured by Atomic Absorption Spectroscopy, Varian Spectra AA-250 Plus, by acetylene flame emission and wavelengths of 357.9 nm, 425.4 nm and 520.8 nm.

Infrared spectra of the unloaded biomass and chromium loaded biomass, both in suspension, were obtained using a Fourier transform infrared spectrometer (FTIR BOMEM MB 104). For the FTIR study, biomass was centrifuged and dried, followed by weighting. Then 20 mg of finely ground biomass was encapsulated in 200 mg of KBr (Riedel) in order to prepare translucent sample disks.

3. Results and discussion

3.1. Biofilm formation

The differences in concentration between the microorganism culture and the nutrient broth aimed the maximization of the exopolysaccharides production by the bacteria. The stress conditions of the biofilm formation in the presence of the diluted medium increased the production of those saccharides and this allowed the formation of a coherent biofilm with a strong adhesion to the support surface. On the other hand, previous work indicated that fixation of the metallic ions on the polysaccharide net is an important step in the overall mechanism of ions entrapment (Scott and Palmer, 1988). The relatively high flow rate of nutrient broth, compared to the metallic solution flow rate, lead to the formation of a consistent biofilm, resistant to the hydrodynamic erosion.

In spite the fact that the amount of biofilm produced at each run could not be quantified, it has to be considered that the seeding material and the growth conditions were the same for all the runs, that the support was fully covered by the biofilm which could be observed by naked eye and that the biosorption results (removal and uptake of the metal) were reproducible and quite different from those obtained in the absence of the biofilm.

3.2. Chromium (VI) sorption mechanisms due to pH

During these experiments it was noticed that at pH $\geqslant$ 12, Cr (VI) was not adsorbed on activated carbon and that at pH < 6, Cr (VI) was adsorbed and reduced to Cr (III) by the possible catalytic action of the activated carbon (Huang and Wu, 1977; Alaerts et al., 1989). On the other hand, studies developed by Leyva Ramos et al. (1994) show that the maximum adsorption occurred at pH 6 and the adsorption capacity was reduced about 17-fold when pH was increased from 6 to 10. At lower pH values, where the concentration of H_3O^+ is high, the competition for the negative sites on the zeolite and GAC surface is enhanced and the metal sorption is reduced accordingly (Dal Bosco et al., 2005). The fact that the optimum pH for the viability of *A. viscosus* is 7 and as clinoptilolite is known to partially degrade and lose its ion exchange capacity in alkaline media (X-ray diffraction analysis showed that clinoptilolite crystals are destroyed at pH > 10) (Mier et al., 2001), reinforced the decision of using metal solutions with pH of 6.5. At these pH values the Cr is in an anionic state as a strong oxidizing agent. Its fixation occurs mainly on the biofilm surface, as its relatively big anionic radius enhanced by hydration status would not allow direct adsorption on GAC internal surface (Quintelas and Tavares, 2001). Eventual reduction to Cr (III) must occur metabolically, that is accumulation and reaction inside the cells, as no precipitate was detected inside or at the outlet of the column, as observed by centrifugation of samples to be analysed for safety of the equipment. The effluent of the column always kept the characteristic yellow colour of the hexavalent form. Besides, the quantification method used in this work, AAS, detects the total amount of metal, no matter the oxidation state it is in.

The biofilm seems to have an initial fixation role of the anionic chromium to the matrix, followed by local reduction of the metal and by fixation on internal GAC surface of smaller chromium ions. The local reduction may be a consequence of the pH variation with the proximity and eventual metabolism of the biofilm.

3.3. Biosorption studies

In all the experiments the removal of Cr (VI) was fast and presented a typical biosorption kinetics, which includes two phases: the first one is associated with the external cell surface, biosorption itself, and the second one is an intracellular accumulation/reaction, depending on the cellular metabolism (Tavares et al., 1995).

The applicability of such retention system on practical situations depends on many factors, one of which is the

initial concentration of metal on the liquid solution. As this process is to be applied to diluted solutions, the tested range of initial concentrations was defined bellow 100 mg/l. Fig. 1 shows the dependence of the total uptake of the metallic ion as a function of the initial concentration on the water solution. There is a clear maximum around 70 mg/l and this value established the initial conditions of the following experiments. This maximum is probably defined by the balance between the effect of the increasing driving force in terms of concentration difference between the bulk solution and the biosorbent surface and the effect of the saturation of the surface matrix.

When the biosorption system support is composed exclusively by GAC, some recovery of the metal removal percentage is observed around 500 min of flow time. In fact, metal removal falls from 100%, at initial moments, to 20% and rises again till 45% removal, Fig. 2. This unique behaviour, that is the recovery of its performance as ion retainer, is not observable with the zeolite support. It may be due to the synergetic effect of the biofilm that, after ion enrichment, allows the transportation of the metallic

ions to deeper sites of the support through the exopolysaccharides net liberating some external surface sites. This recovery is rapidly lost as even deeper sites are quickly saturated, as the spatial geometry of the complex Cr (VI) limits the access to most sites inside of such a microporous carbon. Karthikeyan et al. (2005) investigated the adsorption capacity of Cr (VI) onto activated carbon and obtained a value of 44.05 mg/g of adsorption capacity but for an initial concentration of 200 mg/l. Mohanty et al., 2005 studied the effect of contact time on the removal percentage of Cr (VI) at different initial concentrations and concluded that the optimum period is about 600 min when the removal percentage reaches 21% and 23% for an initial concentration of 10 mg/l and 20 mg/l, respectively.

The zeolite, not as good adsorbent as GAC, does not show this behaviour, as its open cage structure is not so sensitive to the biofilm effect. The combination of the two supports shows a similar trend to the one of the two GAC beds, more accentuated, as residual metal ions in bulk solution will be entrapped easier in the second bed.

After 27 h of continuous treatment, the removal of Cr (VI) by two beds of zeolite reaches 18%, and 19% with two beds of GAC. It increases to 42% when both supports were used in series connection, with an initial concentration of 70 mg$_{Cr}$/l (Fig. 2, Table 2). These relatively humble results may be explained by the little affinity between the net negative structural charge, some charge of bacteria and the anionic form of chromium. However, it should be notice that this research work aims the definition of a treatment process end-of-line, applied to dilute solutions, for which a 42% removal of residual heavy metal may make a difference between forbidden wastewater and the respect of environmental legislation. There is room for improvement in this area by previous modification of the surface charge. The best results obtained with the combined system GAC and zeolite may be explained by the fact that the main amount of the metallic ion present in the solution in retained by the first bed, that is the one made of GAC covered with biofilm, allowing a more refined surface distribution of the remaining ions on the surface of the second bed, that is the one made of clinoptilotite covered with biofilm. The uptake values do follow the same trend as the percentage removal. They ranged from 0.57 mg$_{Cr}$/g$_{support}$ to 3.58 mg$_{Cr}$/g$_{support}$ (Fig. 4).

On one hand the biofilm supported on the activated carbon retains more ions than the one supported on the zeo-
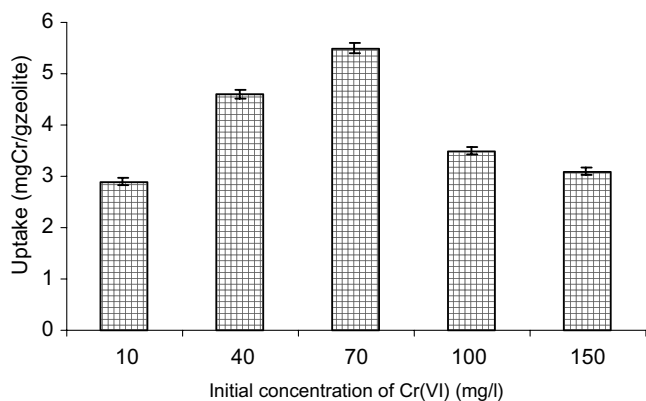

Fig. 1. Uptake of Cr (VI) by a biofilm of *Arthrobacter viscosus* supported on a zeolite as a function of the initial concentration of the metal in the water solution to be treated.
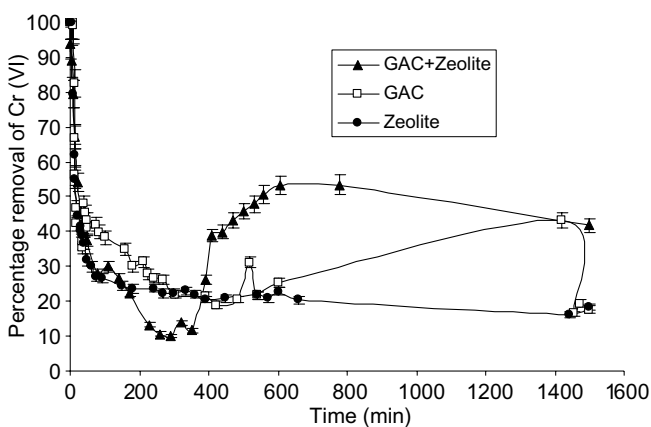

Fig. 2. Removal of chromium by a biofilm of *Arthrobacter viscosus* supported on: GAC, zeolite and GAC + zeolite. The initial concentration of chromium was 70 mg/l, with a flow rate of 10 ml/min.

Table 2
Removal percentage values for the three different supports after 27 h

Support	Removal percentage of Cr (VI) (%)
Zeolites	18
GAC	19
GAC + Zeolite	42
GAC (1st) + Zeolite	26
GAC (2nd) + Zeolites	10

The initial concentration of chromium was 70 mg/l, with a flow rate of 10 ml/min.

lite. On the other hand, this second bed behaves better than the first one for low metal concentrations in the bulk solution, as it is more permissive in terms of surface adsorbate rearrangement due to its open structure, quite different from GAC with an average pore radius of 2 nm.

Several studies show that the possible modifications of the surface of zeolites give them positive charge, which can increase the efficiency of the system to remove chromium. Batista et al. (2000), prepared an organo-zeolite by modification of the surface adsorptive properties of natural zeolites (clinoptilolite) from Cuba, with a cationic surfactant, Br-HDTMA, and obtain an adsorbent with a maximum removal capability of Cr (VI) of 30 mg/g$_{organo-zeolite}$, without biosorption.

Barros et al. (2001) justified the low efficiency of zeolites on the removal of chromium with the presence of impurities on the natural zeolites, the difference between the relative big anionic radius of chromium and the porous diameter of the zeolite and the strong propensity of chromium to form complexes.

3.4. Effect of regeneration of GAC

The GAC is frequently used in biosorption systems. The regeneration of such material is important to reduce the high costs associated to activated carbon. The steaming of GAC reduced the removal capability of the system in 38% and 76%, respectively for the 1st and 2nd regeneration (Figs. 3 and 4). After its first use, the binding sites present on GAC were probably saturated. The regeneration of GAC aimed the cleaning of the binding sites and allowed a new adsorption cycle. The results show that the regeneration process used may not been good enough to clean all the binding sites. This was partially achieved during the second regeneration. Besides, like most of the regeneration processes, there is a loss of porosity that may responsible for the recovery of the metal removal in Fig. 2 and dis-

Fig. 4. Uptake values for two beds of zeolite support, two beds of GAC support, mixed system, mixed system after 1 regeneration of GAC bed and mixed system after two regenerations of GAC bed.

cussed above. Accordingly, the effect was not observable in Fig. 3 for the regenerated supports. Hu et al. (2005) studied the Cr (VI) adsorption capacity of maghemite nanoparticles during six cycles and observed that the Cr adsorption capacity of this material remained almost constant for the six cycles, which indicated that there was no irreversible adsorption on the surface of the adsorbent.

3.5. FTIR spectral analysis

The FTIR spectra of unloaded and metal loaded A. viscosus biomass in the range of 500–4000 cm^{-1} were performed to find out which functional groups are responsible for the biosorption process and are presented in Fig. 5. As seen in this graph, unloaded biomass displays a number of absorption peaks, reflecting the complex nature of the biomass. The spectrum pattern of unloaded biomass showed slight changes of certain bands in the region of 1700–750 cm^{-1} as compared to Cr (VI) loaded biomass. Band shifts were observed for the signals at 3400 cm^{-1}
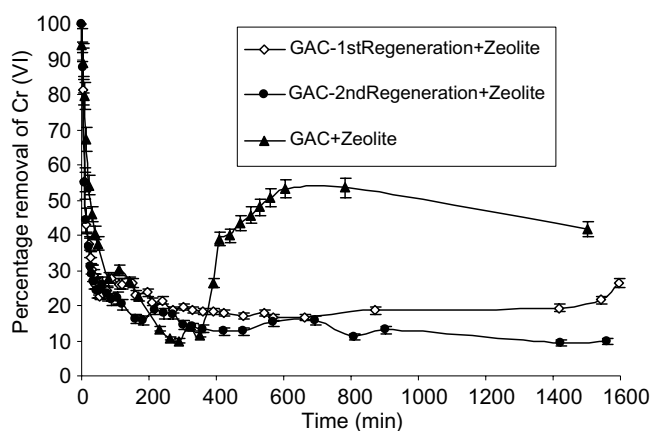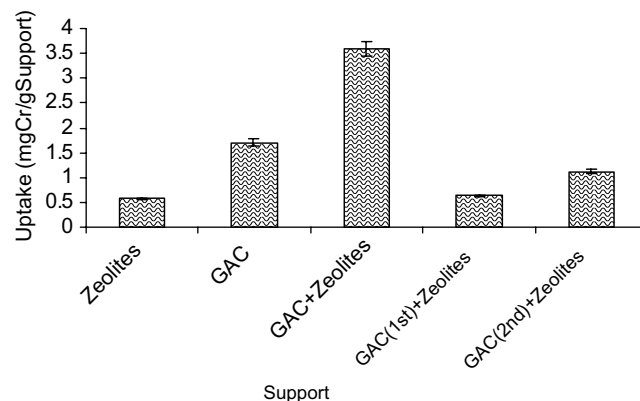

Fig. 3. Removal of chromium by a biofilm of *Arthrobacter viscosus* supported on: GAC and zeolite, GAC-1st regeneration and zeolite, GAC-2nd regeneration and zeolite. The initial concentration of chromium was 70 mg/l, with a flow rate of 10 ml/min.
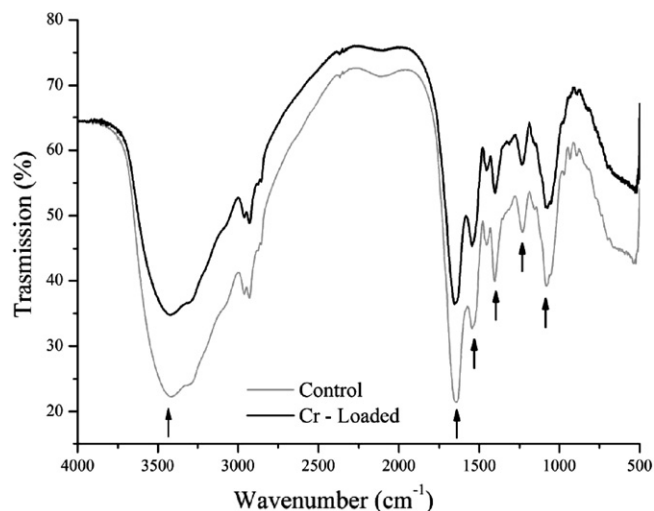

Fig. 5. FTIR spectra of *Arthrobacter viscosus* before and after metal loading.

(indicative of bonded hydroxyl group and –NH stretching peak) (Park et al., 2005), 1546 cm^{-1} (indicative of C–N stretching and N–H deformation), 1398 cm^{-1} (indicative of COO− anions), 1238 cm^{-1} (indicative of –SO$_3$ groups) and at 861 cm^{-1} (aromatic –CH stretching peak) (Tunali et al., 2006). These changes observed in the spectrum indicated the possible involvement of those functional groups on the surface of the biomass in biosorption process.

Acknowledgements

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