REMOVAL OF CHROMIUM FROM WASTEWATER BY ADSORPTION AND BY BIOSORPTION

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The objective of this work is the definition of an efficient biosorption system based on the ability of some microorganisms, metabolically active or not, to retain heavy metals, specially the hexavalent form of Cr. Metallic solutions were passed through mini-columns in which a biofilm was developed at pre-established conditions. As industrial wastewater usually contains organic and inorganic compounds, besides metallic ions, it would be desirable to co-extract several pollutants at the same time. The utilization of granular activated carbon (GAC) as a support for the biofilm seems to be advantageous, as it can retain other substances while the biofilm removes the heavy metal. To quantify the contribution of GAC to the overall removal of chromium, adsorption studies were carried out with the determination the effect of pH and of the presence of concurrent species on the adsorption isotherms. Biosorption studies were done with three different bacteria, *Pseudomonas fluorescens*, *Escherichia coli* and *Arthrobacter viscosus*. Among microorganisms, bacteria are particularly interesting for the purpose as they are able to excrete polysaccharides allowing a good adhesion to the support, implementing the retention capacity of the biosystem and protecting the cells from the xenobiotic effect of the heavy metal ions. Removal efficiencies were compared between the three biosystems.

KEY WORDS - Biosorption, adsorption, heavy metals, chromium.

INTRODUCTION

The presence of chromium in industrial wastewater is still a problem for small and medium size local industries. Traditional physico-chemical processes are used to treat highly concentrated effluents [1] as those from electroplating and tannery industries, but they become too costly when aiming the reduction of small concentrations to values accepted by environmental legislation. Usually the treated effluent has a final metal concentration less than 10 $mg.l^{-1}$ [2], but although very efficient those techniques imply large reagent and/or energy costs. The potential of live or dead microorganisms to accumulate certain ions is already recognized and biosorption, defined as the capture of metal ions by solid materials of natural origin [3] is an alternative technology to the classical ones. It is known that the ratio of the metal weight in the biosystem to that in the surrounding aqueous phase for mercury, cadmium and zinc at equilibrium ranged from 4000 to 10000 [4]. There are now several biosorption systems in operation treating low metal contamination [5].
Besides metallic ions there are organic and inorganic compounds in the waste streams of the electroplating unites and tanneries, so it would be desirable to co-extract several pollutants. The utilization of granular activated carbon as the support of the biofilm seems to be advantageous, as it can retain other substances while the biofilm remove the heavy metal [6,7].

MATERIALS AND METHODS

The granular activated carbon used as a support for the biofilm was charcoal with an average particle diameter of 1.5 mm, a density of 2.34 $g.cm^{-3}$, a Langmuir specific area of 1270 $m^2.g^{-1}$ and an average pore diameter of 20 angstrom. Adsorption isotherms were determined in batch studies where 5 g of GAC were placed in contact with 200 ml of Cr (VI) solutions with concentrations ranging from 40 to 1000 $g.cm^{-3}$. These solutions were placed in Erlenmeyer flasks, in a rotary shaker at 27 °C and the concentration of the metallic ion in the liquid phase was followed for several days. The Cr (VI) concentration in the supernatant of the centrifuged samples was determined by a colorimetric method using diphenylcarbazide and a spectrophotometer (JASCO 7850) at 540 nm. The total Cr concentration was measured by Atomic Absorption Spectroscopy (VARIAN SPECTRA AA-250 PLUS).

The columns have a height of 30 cm and diameter of 0.9 cm . They were partially filled with GAC and different bacterial suspensions (*Pseudomonas fluorescens*, *Escherichia coli* and *Arthrobacter viscosus*) in the exponential growth phase and in the stationary growth phase were circulated through the carbon, slowly enough to allow the biofilm attachment but expanding the bed enough to avoid the gluing of pellets. Nutrient broth was then circulated at the same flow rate for two days in such conditions that a polysaccharide net was developed. These optimized biofilms supported on GAC were used in biosorption studies allowing the contact of these systems with aqueous solutions of Cr (VI) of concentrations between 4 and 20 $g.cm^{-3}$. Determinations of the concentrations of the hexavalent and of the total Cr were systematically made by the methods referred above. Similar studies were made with GAC without the biofilm so the participation of this adsorbent may be quantified.

Samples of GAC, with and without biofilm, and with retained metal ions were observed by SEM (LEICA S 320) and elementary analysis was performed by Energy Dispersive Spectrometry. Samples to be observed were prepared for a good fixation of the biomass with glutaraldehyde (5%) and chilled cacodylate buffer (0.1M). Dehydration was obtained using a graded ethanol series and drying in a airtight container for 12 hours.

RESULTS AND DISCUSSION

The adsorption of hexavalent chromium on GAC was thoroughly characterized and Langmuir adsorption isotherms describe quite well the experimental results. They indicated a maximum uptake of 140 mg of Cr/ g of GAC. The pH of the solution is a critical parameter as it determines the speciation of the metal and while Cr (III) hardly adsorbs and tends to precipitate, Cr (VI) adsorbs as an anionic species, thus easily attracted by the H^+ present on the GAC surface. An acid pre-washing of the GAC, as well as the maintenance of the bed

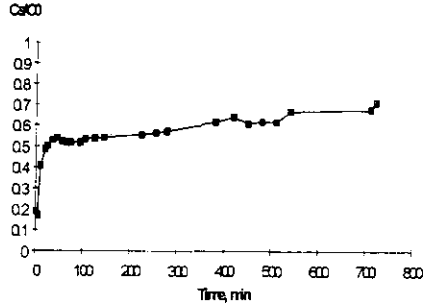

Fig. 1 - Effluent of a GAC column treating a 50 mg/l Cr (VI) solution.

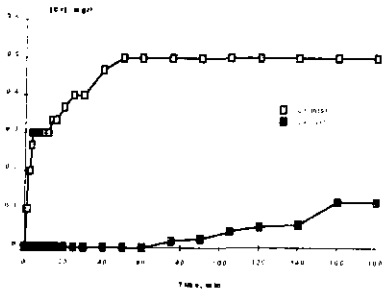

Fig. 2 - Effluent of a GAC/BIOFILM column treating a 5 mg/l Cr (VI) solution.

pH value at 3.0 seems to enhance Cr adsorption. The presence of other metallic ion, Cd, was also considered and there are indications that other factors besides pure competition may rule the adsorption of several species [8]. In fact, the addition of the two final uptakes, Cd and Cr, was significantly less than the maximum uptake of individual elements. Fig.1 reports the ability of an open GAC column to retain Cr (VI) with some reduction to Cr (III), which may precipitate and accumulate on the carbon surface. Steady state is achieved at 70% of the initial influent concentration.

A similar system was used, this time with a *Pseudomonas fluorescens* biofilm covering the GAC support and the steady state was achieved with an effluent concentration having 10% of the initial value, Fig. 2. In most of the runs some reduction of the original ionic species occurs as the metabolic activity of the biofilm lowers the pH.

The effect of the biofilm in the metal fixation is otherwise described by EDS analysis of two samples: GAC/Cr and GAC/BIOFILM/Cr [9]. The analysis was performed at different depths and it was observed that the fixation of Cr ions occurs at a deeper level than the first micrometers and that the concentration profile is accentuated in the presence of the biofilm, Fig.3.

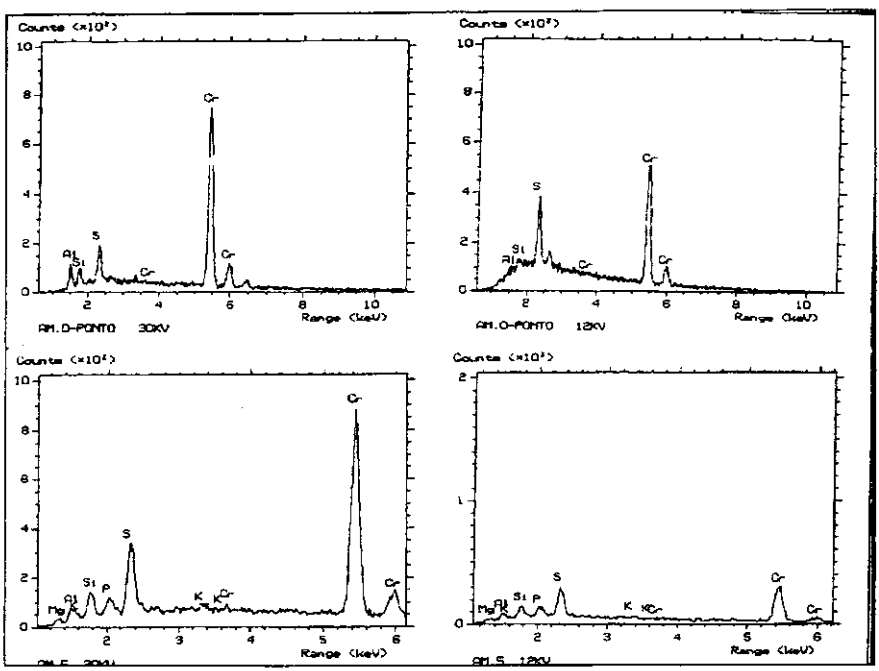

Fig. 3 - Elementary analysis by EDS in depth for two different samples: GAC/Cr (top two) and GAC/Biofilm/Cr (bottom two); the left profiles being obtained at 8.5 μm and the right ones at 1.7 μm.

There is room for further improvement as other biofilms are being studied. *Arthrobacter viscosus* is a very good polysaccharide producer and this enables it to be a good biosorber. Preliminary results with this bacteria indicate that the kind of nutrient broth (mainly a deficient one) as well as the hydrodynamic conditions of the biofilm formation determine the removal efficiency of the biosystem. The performance of other bacteria, adapted to higher concentrations of Cr, as well as the performance of a consortium of microorganisms isolated from sludges of treatment stations receiving Cr effluents are also under study.

Studies of the effect of flow rate and of the initial Cr concentration on the removal efficiency of a biosorption system (GAC/*Pseudomonas fluorescens*) are resumed in Table 1.

Table 1 - Total Cr removal efficiency of the biosorption system (GAC *Pseudomonas fluorescens*) for different flow rates and concentrations of the metallic solution.

Flow rate ($cm3.min^{-1}$)	7	15	25	31
Concentration ($4mg.l^{-1}$)	87%	74%	61%	58%
Concentration ($10mg.l^{-1}$)	-	68%	-	-
Concentration ($20mg.l^{-1}$)	-	64%	-	-

CONCLUSIONS

This work reports some results of a project that aims the definition and optimization of a biosorption system able to treat low concentrations of Cr (VI) in industrial or municipal wastewater. The main conclusions are: i) there is an evident improvement on the total Cr uptake when an adsorbent as GAC is covered with a bacterial biofilm; ii) initial pH of the solution to be treated as well as bed pH during Cr fixation is critical for the overall process, as it determines the metal ionic form; iii) total uptake is sensitive to the amount of polysaccharide production as it increases when changing the biofilm from *E. coli* to *P. fluorescens* and finally to *A. viscosus*; iv) nutrient broth as well as hydrodynamic conditions of the biofilm formation are important parameters in the biofilm optimization; v) the best hydrodynamic conditions for the biosorption process are achieved with low flow rates, which may allow some bed expansion.

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