CO-ADSORPTION OF CR(VI) AND PHENOL, O-CRESOL AND CHLOROPHENOL BY AN *ARTHROBACTER VISCOSUS* BIOFILM SUPPORTED ON GAC

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Introduction

The presence of heavy metals and organic compounds in the environment can be detrimental to a variety of living species, including man [1]. Chromium is used in the manufacture of inks, industrial dyes and paint pigments, in chrome tanning, aluminium anodising and other metal cleaning, plating and electroplating operations. Frequently, the major source of waste chromium is the chromic acid bath and rinse water used in such metal plating operations [2]. Organic compounds are present in most useful and economically important chemicals available to industry and agriculture, being extensively used as herbicides, insecticides, fungicides, heat transfer media, insulatores and lubricants [3].

Biosorption of heavy metals is one of the most promising technologies aiming at the removal of toxic metals from industrial waste streams and natural waters. It is a potential alternative to conventional processes for the removal of metals such as precipitation [4]. The retention of these contaminants by a biofilm supported on granular activated carbon is a promising technology for the treatment of diluted solutions, as the biofilm is able to retain the metallic ions and the support will help to fix them for further catalytic applications. GAC was chosen by the fact that this material is a versatile adsorbent due to its high surface area, porous structure, high adsorption capacity and surface chemical nature [5]. *Arthrobacter viscosus* is a good exopolysaccharide producer which, by itself, would allow to foresee good qualities for support adhesion and for metal ions entrapment [6].

The aim of this work was the study of the addition of three different organic compounds, phenol, o-cresol and chlorophenol, to the metallic solution to better describe the real industrial effluent. The ion under consideration is chromium (VI) for its peculiar ionisation state mutability, with concentrations of 60 mg/l, to be removed by a matrix composed of biofilm of *Arthrobacter viscosus* supported on GAC, in expanded bed. The individual effect of such compounds on the metal fixation, as well as the synergetic effect of their combination will be presented in terms of ion and organic removal and in terms of uptake.

Experimental

Materials

The bacterium *Arthrobacter 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 and the organic solutions were prepared with extra pure o-cresol, phenol and chlorophenol. All glassware used for experimental purposes was washed in 60% nitric acid and subsequently rinsed with deionised water to eliminate any possible interference by other metals. Atomic absorption spectrometric standards were prepared from 1000 mg_{Cr} l^{-1} solution. The support was granular activated carbon (GAC) with a Langmuir area of 1270 m^2g^{-1} and an average pore diameter of 2 nm, and was characterized by N_2 adsorption (77K), with a ASAP Micromeriticcs 2001.

Methods

All experimental work was conducted in duplicate. GAC was placed in an Erlenmeyer flask of 250 ml to which was added 150 ml of distilled water. It was sterilized at 120^0C for 20 min to release the air inside the pores. Then it was placed in column. Minicolumns (internal diameter = 2.0 cm, ht = 30 cm) were used for open systems studies, partially filled with GAC (14 g). The microorganism culture and the nutrient broth were pumped through the bed aiming the formation of the biofilm. Two different media, with different concentrations of peptone, were used to grow the microorganism for 3 d, aiming the optimization of the adhesion. The formation of the biofilm was observable by naked eye. After this period of time the bed was washed out and the metal and organic solutions were passed through the column with a flow rate of 10 ml/min. The metal concentration was fixed at a value of 60 mg/l and the organic compounds concentrations varied between 10 and 100 mg/l. Samples (5 ml) were taken, centrifuged and analyzed for metal using atomic absorption spectrophotometry, AAS, and for organic compounds using spectrometry by the 4-aminoantipyrine method. At the end of each run the column was washed out and samples of the effluent were seeded in Petri plates with nutrient agar to assess the metabolic activity of the microorganism.

Results and Discussion

The amount of biosorved species increased significantly with the initial organic compound concentration (Figure 1). The uptake of phenol and chlorophenol increased in the presence of Cr(VI), for all the initial concentations of phenol and chlorophenol tested. This can be explained by the fact that although chromate reduction is thermodynamically favorable, Cr(VI) reduction to Cr(III) may be limited by reaction conditions. On the other hand, the kinetics of Cr(VI) reduction may be improved by coupling Cr(VI) reduction to other energy yielding reactions such as phenol and chlorophenol degradation [7]. In fact we believe that two mechanisms were responsible for the removal of organic compounds: biodegradation and carbon adsorption.

There are clear differences in the adsorption behaviour of phenol, o-cresol and chlorophenol (Figure 1a, 1b and 1c). The differences in molecular size, solubility, dissociation equilibrium and benzene ring reactivity, may explained this [8].

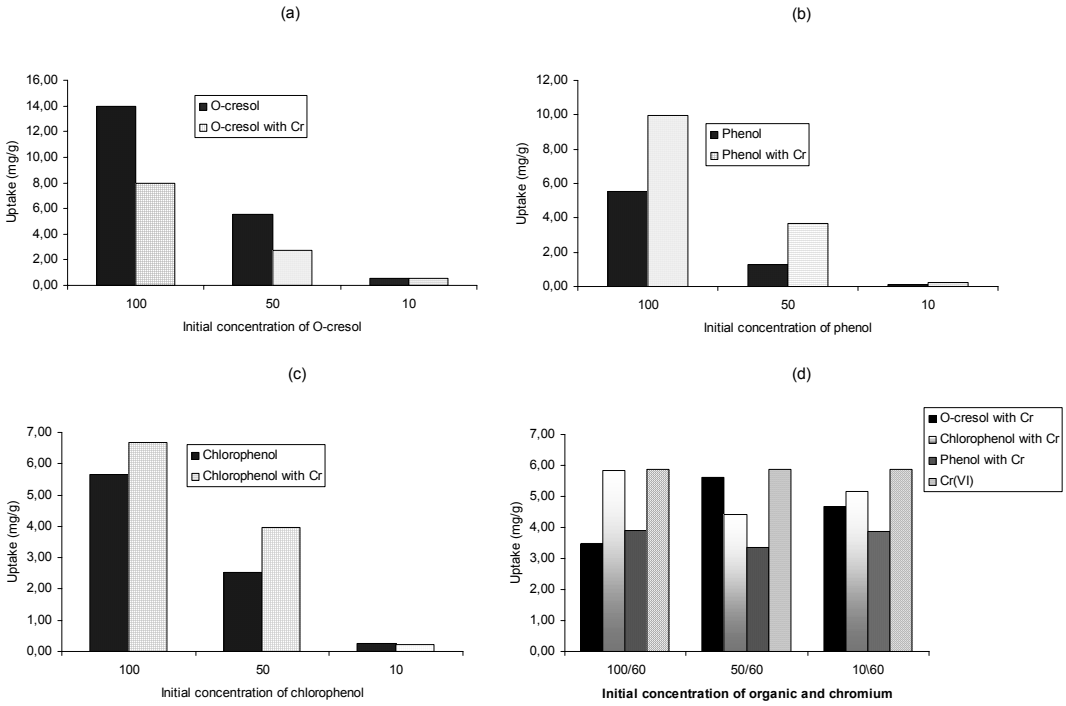

Figure 1. Specific uptake values for organic compounds at different initial concentratios in the presence and absence of Cr(VI) and for Cr(VI) in the presence and absence of organic compounds. The initial concentration of Cr(VI) was 60 mg/l in all the experiments. The time of experiments is 15 hours. (a) O-cresol, (b) Phenol, (c) Chlorophenol and (d) Chromium (VI).

The removal percentage was high for all the organic compounds tested, with values between 100% and 40% for chlorophenol, between 100% and 30% for O-cresol and between 100% and 10% for phenol.

The uptake for Cr(VI) presents best results when this heavy metal is a single solute (Figure 1, d). The maior reason for that is probably the competition between the organic compounds and the ion for the same active sites.

Conclusions

A biofilm of *Arthrobacter viscosus* supported on granular activated carbon was used to remove chromium and organic compounds (o-cresol, phenol and chlorophenol) from aqueous solutions with sucess. The maximum value of uptake obtained with the initial

concentration 100 mg/l in the presence of 60 mg/l of Cr(VI) is 9.94 $mg_{phenol}/g_{biosorbent}$, 7.99 $mg_{ortocresol}/g_{biosorbent}$ and 6.67 $mg_{chlorophenol}/g_{biosorbent}$. The system present best results for chlorophenol which indicates more affinity between this organic compound and the biosorbent used.

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