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Short communication

Competitive biosorption of ortho-cresol, phenol, chlorophenol and chromium(VI) from aqueous solution by a bacterial biofilm supported on granular activated carbon

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Abstract

A biofilm of *Arthrobacter viscosus* supported on granular activated carbon was used to remove chromium and organic compounds (chlorophenol, phenol and *o*-cresol) from aqueous solutions. The compounds were studied as single solutes and in different combinations between them and Cr(VI). Optimum Cr(VI) adsorption was observed at a phenol concentration of 100 mg/l and at an initial concentration of the metal of 60 mg/l. The maximum values of biosorption of organic compounds were 9.94 mg/g for phenol, 9.70 mg/g for chlorophenol and 13.99 mg/g for *o*-cresol. In terms of removal percentage, after 15 h of experiment, the affinity order was as follows: phenol > chlorophenol > *o*-cresol > chromium(VI).

Keywords: Activated carbon; *Arthrobacter viscosus*; Biofilm; Biosorption; Chromium(VI); Organic compounds

1. 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 industrial applications such as tanning, metallurgy, plating and metal finishing [2]. Frequently, the major source of waste chromium is the chromic acid bath and rinse water used in such metal plating operations [3]. Organic compounds are pollutants of priority concern that enter water bodies through discharge from pharmaceutical, petrochemical and other chemical manufacturing processes [4].

Biosorption is an alternative to conventional or traditional methods of heavy metals removal such as precipitation, ion-exchange, catalytic reaction, etc. As a consequence, this process is presented as one of the most promising technologies for the simultaneous removal of organic compounds and heavy metals from wastewater. The use of non-expensive waste biomass, the low cost of biomass immobilization and the possibility of biomass regeneration are some of the most important key factors that should be considered in the application of biosorption in the removal of toxic metals from industrial waste solution [5,6]. The applicability of bacteria as biosorbents have some advantages due to their small size, their ubiquity, their ability to grow under controlled conditions and their resilience to a wide range of environmental situations [7,8]. The biosorptive sites on these microorganisms are carboxyl, hydroxyl, sulphydryl, amino and phosphate groups [9].

During the last decades several studies were made aiming the removal of organic compounds and/or chromium(VI): with fungi [9–11], yeasts [12,13], microalgae [14], bacteria [6,8,15], consortia of bacteria [16], anaerobic activated sludge [1], activated carbon [17–20] and granular activated carbon with biofilm [21,22].

The use of activated carbon as a support is justified by its characteristics like its high surface area, porous structure, high adsorption capacity and surface chemical nature [23].

A biosorption system consisting of a biofilm supported on granular activated carbon combines the ability of the biofilm to remove heavy metals with the ability of the activated carbon to remove organic compounds.

The aim of this study is the investigation and development of an innovative process for the simultaneous removal of heavy metals and organic compounds. *Arthrobacter viscosus* supported on granular activated carbon was chosen as biosorbent

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material due to the relative lack of information about its sorption properties and its evident ability to produce exopolysaccharides that may determine the efficiency of the whole process [24]. The effect of the initial concentrations of metal and organic compounds and the effect of the competition between metal and organic compound were tested and the uptake values and removal percentage were quantified.

2. Material and methods

2.1. Materials

The bacterium *A. viscosus* proceed from the Spanish Type Culture Collection of the University of Valência. Aqueous chromium solutions were prepared by diluting $K_2Cr_2O_7$ (Riedel-de Haen) in distilled water and the organic compounds solutions were prepared with extra pure *o*-cresol (Riedel-de Haen), phenol and chlorophenol (Merck). Atomic absorption spectrometric standards were prepared from 1000 mg_{Cr}/l solution. The support was granular activated carbon (GAC) from Merck, with a Langmuir area of 1270 m^2/g and an average pore diameter of 2 nm as it was determined by N_2 adsorption (77 K), with a ASAP Micromeriticcs 2001.

2.2. Methods

The methods used were well described in previous work published by this group [6,8], with all the assays performed in minicolumns with 2 cm internal diameter and of 30 cm height, filled with 14 g of GAC. 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 sequentially used to grow the microorganism for 3 days, 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. Samples (5 ml) of the outflow were taken, centrifuged and analyzed for metals using atomic absorption spectrophotometry, AAS, and for organic compounds using spectrometry with the 4-aminoantipyrine method [25]. Each run was repeated at least four times. 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.

3. Results and discussion

A biofilm represents a stable ecosystem. The main compositions of biofilms are bacterial cells, extracellular polymers produced by bacteria (exopolymers), lysis and hydrolysis products, attached matter and some inorganic compounds. Exopolymers consist mainly of polysaccharides, proteins, uronic acids, humic acids, nucleic acids, lipids and cell fragments. In biofilms, possible sorption sites are extracellular polymeric substances, cell walls, cell membranes and cytoplasm. These sites contribute to the sorption properties of biofilms for organic and inorganic substances [26].

3.1. Single and dual biosorption of organic compounds

There are clear differences in the adsorption behaviour of phenol, *o*-cresol and chlorophenol (Figs. 1, 2 and 5). The differences in molecular size, solubility, dissociation equilibrium and benzene ring reactivity can explain these observations (Table 1) [17]. Brasquet et al. [27] showed that adsorbability of

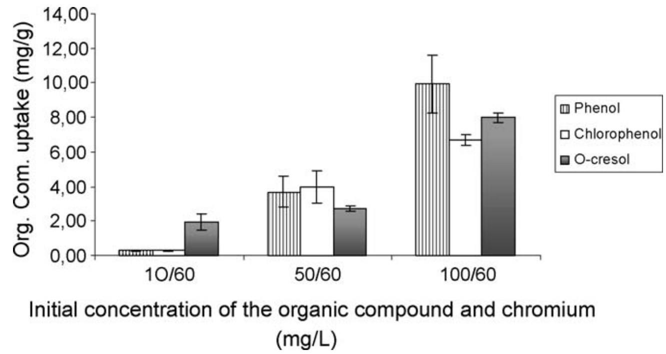

Fig. 1. Uptake values for organic compounds at different initial concentrations (10, 50 and 100 mg/l) in the presence of Cr(VI). The initial concentration of Cr(VI) was 60 mg/l in all the experiments. The time of experiments is about 15 h.

activated carbon in the presence of 14 aromatic compounds increased with increasing molecular size and decreased with increasing number of heteroatoms and degree of insaturation. Our results, in terms of uptake, showed best results for the chlorophenol and *o*-cresol than for phenol.

Biosorption was increased significantly with the initial organic compound concentration (Figs. 1 and 2, Tables 2 and 3). The uptake of phenol and chlorophenol increased in the presence of Cr(VI), for all the initial concentrations of phenol and chlorophenol tested (Tables 2 and 3). For *o*-cresol, the uptake increased in the presence of Cr(VI) only for the more diluted concentration (10 mg/l). Two mechanisms were responsible for the removal of organic compounds: biodegradation and carbon adsorption. Phenol is very degradable; *o*-cresol and chlorophenol are much less degradable and the major contribution to their removal is carbon adsorption [28]. Mattson et al. [29] also suggested that organic compounds adsorption on carbon occurs by a donor–acceptor complex mechanism involving carbonyl oxygen groups on the carbon surface acting as the electron donor and the aromatic ring as the acceptor. On the other hand, phenol, 4-chlorophenol and *o*-cresol have a pK_a of 9.89, 9.18 and 10.2, respectively [30]. The solution pH was always less than 8 during all the experiments, so the compounds stayed mostly in the undissociated forms. The adsorption reaction may mainly result from hydrogen-bonding between the

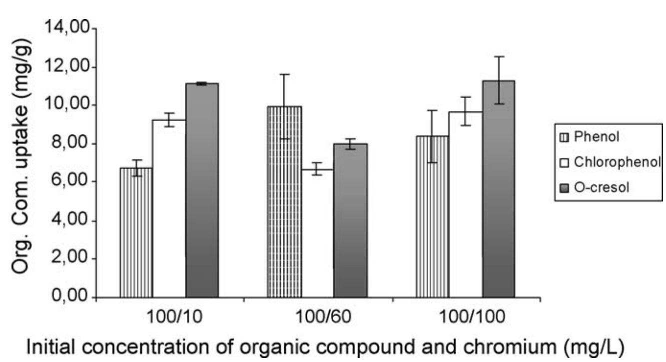

Fig. 2. Uptake values for organic compounds in the presence of Cr(VI) at different initial concentrations (10, 60 and 100 mg/l). The initial concentration of organic compound was 100 mg/l in all the experiments. The time of experiments is about 15 h.

Table 1
Aqueous solubility of chlorophenol, phenol and *o*-cresol

Organic compound	Formula	Molecular weight (g/mol)	Solubility (g/l)
Chlorophenol	C_6H_5ClO	128.56	28
Phenol	C_6H_6O	94.11	70
o-Cresol	C_7H_8O	108.14	26

Table 2
Removal percentage, after 15 h of experiment, for the single solutions

Compound	Initial concentration (mg/l)	Removal percentage (%)
Phenol	10	97
	50	85
	100	40
Chlorophenol	10	93
	50	74
	100	71
o-Cresol	10	87
	50	42
	100	36
Chromium(VI)	10	35
	60	8
	100	12

hydroxyl groups of phenols and functional groups such as carboxylic on the carbon surfaces [19].

The maximum uptake of organic compounds onto the *A. viscosus* biofilm supported on granular activated carbon was

Table 3
Removal percentage for Cr(VI) and organic compounds, after 15 h of experiment, for the dual solutions

Compound	Initial concentration (mg/l)	Removal of Cr(VI) (%)	Removal of organic compound (%)
Phenol/Cr(VI)[a]	10	7.7	63
	50	6.6	38
	100	11.3	7
Chlorophenol/Cr(VI)[a]	10	3.6	81.2
	50	9.9	60.4
	100	0	55.5
o-Cresol/Cr(VI)[a]	10	4.6	52.8
	50	8	50.6
	100	8.5	33.2
Cr(VI)/Phenol[b]	10	23.1	57
	60	13.9	7
	100	12.2	40.2
Cr(VI)/Chlorophenol[b]	10	16	64.3
	60	0	60.4
	100	9.8	49.1
Cr(VI)/*o*-Cresol[b]	10	5.2	67
	60	8.5	33.2
	100	14.1	46.9

[a] The initial concentration of Cr(VI) was 60 mg/l and the initial concentration of organic compound varied between 10 and 100 mg/l.
[b] The initial concentration of organic compound was 100 mg/l and the initial concentration of Cr(VI) varied between 10 and 100 mg/l.

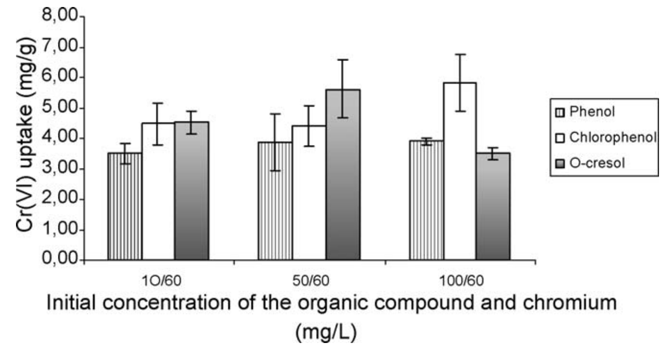

Fig. 3. Uptake values for Cr(VI) in the presence of organic compounds at different initial concentrations (10, 50 and 100 mg/l). The initial concentration of Cr(VI) was 60 mg/l in all the experiments. The time of experiments is about 15 h.

5.52 mg/g for phenol, 5.67 mg/g for chlorophenol and 13.99 mg/g for *o*-cresol, for the single solutions and 9.94 mg/g for phenol, 9.70 mg/g for chlorophenol and 11.30 mg/g for *o*-cresol, for the dual solutions, that is, with organic compound and chromium. The adsorption capacity for the chlorophenol and *o*-cresol is higher than that for the phenol, probably because of the higher solubility of phenol in water (Table 1) [31].

In terms of removal percentage, after 15 h of experiment, the affinity order was as follows: phenol > chlorophenol > *o*-cresol. The removal percentage reaches 97, 93 and 87%, respectively, for phenol, chlorophenol and *o*-cresol and for the initial concentration of 10 mg/l (as single solute). This values decreased on the presence of Cr(VI), after 15 h of experiment, probably because the organic compounds suffer from competition with the ion for the same active sites and because of the lower level of active sites available.

3.2. Single and dual biosorption of Cr(VI)

The maximum adsorption of Cr(VI) onto the *A. viscosus* biofilm supported on granular activated carbon was 5.27 mg/g, for the single solute and for the higher initial concentration tested (100 mg/l) and 5.44 mg/g in the presence of phenol with an initial concentration of 100 mg/l, 5.83 mg/g in the presence of chlorophenol with an initial concentration of 100 mg/l and

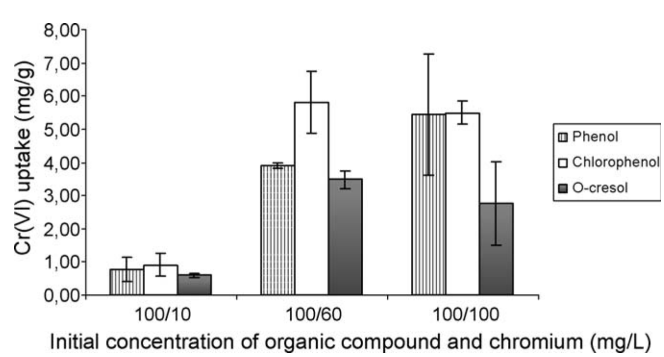

Fig. 4. Uptake values for Cr(VI) at different initial concentrations (10, 60 and 100 mg/l) in the presence of organic compounds. The initial concentration of organic compound was 100 mg/l in all the experiments. The time of experiments is about 15 h.

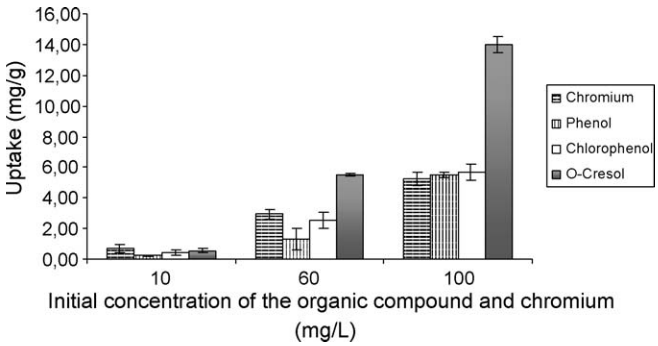

Fig. 5. Uptake values for organic compounds and Cr(VI) as single solute. The initial concentrations were 10, 60 and 100 mg/l in all experiments. The time of experiments is about 15 h.

5.62 mg/g in the presence of *o*-cresol with an initial concentration of 50 mg/l, for the dual solutions. Generally, the uptake of Cr(VI) increased in the presence of organic compounds (Figs. 3–5). This can be explained by the fact that kinetics of Cr(VI) reduction may be improved by coupling Cr(VI) reduction to other energy yielding reactions such as phenol and chlorophenol degradation [16].

The Cr(VI) removal percentage reaches 35%, after 15 h of experiment, for the single solution of initial concentration of 10 mg/l, and a maximum of 23.1%, at the end of the experiment, for the dual solution of 100 mg/l of phenol and 10 mg/l of Cr(VI). For higher concentrations of Cr(VI) the final removal percentage decreased. One possible explanation is that the chromate (CrO_4^{2-}) with its toxicity and high oxidative potential may inhibit biological activity of the biofilm.

4. Conclusions

Wastewater containing organic compounds and heavy metals present a serious problem because of the high toxicity of these compounds. A biofilm of *A. viscosus* supported on granular activated carbon is able to remove organic compounds (phenol, chlorophenol and *o*-cresol) and Cr(VI) and can be applied in wastewater remediation. The differences in molecular size, solubility, dissociation equilibrium and benzene ring reactivity can be explained the differences in the adsorption behaviour of phenol, *o*-cresol and chlorophenol. Generally, the uptake of Cr(VI) increased in the present of organic compounds, a possible reason for that is the fact that 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.

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