Abstract

The purpose of the work presented in this thesis is the implementation and development of biosorption systems for the fixation of heavy metals, aiming the resolution of important environmental problems caused by several industrial activities.

The biosorption system consists of a bacterial biofilm supported on granular activated carbon (GAC), placed in contact with the polluted solutions. The bacteria used for the formation of the different biofilms were *Arthrobacter viscosus*, *Bacillus coagulans*, *Escherichia coli* and *Streptococcus equisimilis*.

The metal selected for the experimental assays was chromium due to its high toxicity and to the fact that this element is used in several industrial activities with strong implementation on the North of Portugal. The hexavalent form of chromium, usually present in cromate (CrO_4^-) and dicromate ($Cr_2O_7^-$) forms, presents levels of toxicity significantly higher than other valent forms.

The production of polyssacharides and total polymers was quantified for the four bacteria selected and it is concluded that, in terms of total polymers, the biofilm of de *A. viscosus* reached the higher value (0.274 $g/g_{biosorbent}$), followed by the biofilm of *S. equisimilis* (0.173 $g/g_{biosorbent}$), *E. coli* (0.142 $g/g_{biosorbent}$) and *B. coagulans* (0.070 $g/g_{biosorbent}$).

Biosorption studies were made in open and batch systems, for the four selected bacteria. Batch experiments showed that the removal percentage of Cr (VI) varied between 46.9% and 17.2% for initial Cr (VI) concentration in the range 50–1000mg/l, for the biofilm of *B. coagulans*, between 36.6% and 10.8%, for the biofilm of *E. coli* and between 72% and 46.3%, for the biofilm of *S. equisimilis*. For the biofilm of *A. viscosus* the values of removal percentage were higher for the same initial concentrations used. So, for the concentration of 250 mg/l, the value of removal percentage was of 63.7 % using a biofilm of *A. viscosus*, while the value obtained with the *B. coagulans* biofilm was 31.4 %, for the *E. coli* biofilm was 19.5 % and for the *S. equisimilis* biofilm was 44.1%. For the concentration of 750 mg/l, the value of removal percentage was 46.2 % using a biofilm of *A. viscosus* while the value obtained with the *B. coagulans* biofilm was 22.0 %, for the *E. coli* biofilm was 11.9 % and for the *S. equisimilis* biofilm was 32.9%. The batch data were described using the Freundlich, Langmuir, Redlich-Peterson, Dubinin-Radushkevich, Sips and Toth model isotherms.

The results obtained in open experiments showed uptake values for Cr (VI) of 5.82 $mg/g_{biosorbent}$, 5.35 $mg/g_{biosorbent}$ and 4.12 $mg/g_{biosorbent}$, respectively for *S. equisimilis*, *B. coagulans* and *E. coli*, for the initial concentration of 100 mg/l, 2.33 $mg/g_{biosorbent}$, 1.98 $mg/g_{biosorbent}$ and 3.60 $mg/g_{biosorbent}$, for the initial concentration of 50 mg/l and 0.66 $mg/g_{biosorbent}$, 1.51 $mg/g_{biosorbent}$ and

1.12 mg/$g_{biosorbent}$, for the most diluted concentration (10 mg/l). These data were described by Adams-Bohart, Wolborska and Yoon and Nelson models.

The behaviour of the four different biofilms was also evaluated using an industrial effluent and it was concluded that the existence of a multiplicity of different ions affects negatively the biosorption performance of the biofilms.

The performance of a biofilm of *Arthrobacter viscosus* on the biosorption of organic compounds was also evaluated and there are clear differences towards phenol, *o*-cresol and chlorophenol. The batch assays for the organic compounds showed that the removal percentage of organic compound decreases with the increase of the initial concentration. The removal percentage of phenol varied between 99.3% and 61.6% and the removal percentage of o-cresol, varied from 98.7% to 73.5%, for the range of initial concentrations used. The batch data were described using the same six isotherm models referred.

The maximum uptake values obtained for the biosorption of organic compounds by the biofilm of *Arthrobacter viscosus* suported on granular activated carbon were 5.52 mg/g for phenol, 5.67 mg/g for chlorophenol and 13.99 mg/g for *o*-cresol, for the monocomponent solutions and 9.94 mg/g for phenol, 9.70 mg/g for chlorophenol and 11.30 mg/g for *o*-cresol, for the binary solution (chromium+organic compound). After 15h of experimental assay, the affinity between the organic compound and the biofilms followed the order: phenol > chlorophenol > *o*-cresol. The removal percentage was of 97, 93 and 87%, respectively for phenol, chlorophenol and *o*-cresol, for the initial concentration of 10 mg/l (monocomponent solution) and after 15 h of experimental assay.

The maximum uptake values obtained for the biosorption of Cr (VI) obtained by the biofilm of *Arthrobacter viscosus* suported on granular activated carbon were of 5.27 mg/g, for the chromium solution and for the higher initial concentration tested (100 mg/l) and 5.44 mg/g on the presence of phenol for the combination 100 mg/l phenol/100 mg/l Cr (VI), 5.83 mg/g on the presence of chlorofenol for the combination 100 mg/l chlorofenol/60 mg/l Cr (VI) and 5.62 mg/g on the presence of *o*-cresol for the combination 50 mg/l *o*-cresol/60 mg/l Cr (VI). The removal percentage of Cr (VI) for the experimental assays on the presence of organic compounds was, normally, lower than those obtained with single chromium solutions. The removal percentage was of 35%, after 15 h of experimental assays, for the chromium solution with initial concentration of 10 mg/l (monocomponent solution), and a maximum value of 23.1%, for the combination 100 mg/l of phenol with 10 mg/l of Cr (VI). Data from column runs were described by Adams-Bohart, Wolborska and Yoon and Nelson models.

The aplicability of a biofilm of *Arthrobacter viscosus* to the treatment of large amount of efluent was also evaluated in a pilot reactor. Two concentration of chromium were used: 10 mg/l and

100 mg/l, with a flow rate of 25 mg/l. In terms of removal percentage, for the initial concentration 10 mg/l, the value was 100 % during the first 26 days of experimental assay. When the initial chromium concentration used was 100 mg/l, the value of removal percentage was 100 % during the first 6 days of experimental assay.

The presence of functional groups on the cell wall surface of the biomass that may interact with the metal ions, was confirmed by FTIR.

Key words: *Arthrobacter viscosus*, Biofilm, Biosorption, *Bacillus coagulans*, *Escherichia coli*, Hexavalent chromium, *Streptococcus equisimilis*, Volatile organic compounds