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Comparative study of Cd(II) and Cr(VI) biosorption on *Staphylococcus xylosus* and *Pseudomonas* sp. in single and binary mixtures

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Abstract

Biosorption of Cd(II) and Cr(VI) ions in single solutions using *Staphylococcus xylosus* and *Pseudomonas* sp., and their selectivity in binary mixtures was investigated. Langmuir and Freundlich models were applied to describe metal biosorption and the influence of pH, biomass concentration and contact time was determined. Maximum uptake capacity of cadmium was estimated to 250 and 278 mg g^{-1}, whereas that of chromium to 143 and 95 mg g^{-1} for *S. xylosus* and *Pseudomonas* sp., respectively. In binary mixtures with Cd(II) ions as the dominant species, there is a profound selectivity for cadmium biosorption, reaching 96% and 89% for *Pseudomonas* sp. and *S. xylosus*, respectively, at 10 mg l^{-1} Cd(II) and 5 mg l^{-1} Cr(VI). Interesting, when chromium (VI) ions are the dominant species, there is selectivity towards chromium around 92% with *S. xylosus* only.

Keywords: Biosorption; Cadmium(II); Chromium(VI); *Pseudomonas* sp.; *Staphylococcus xylosus*

1. Introduction

Heavy metals have many industrial applications due to their technological importance. Wastewaters from these industries have permanent toxic effects to human and the environment. Cr(VI) and Cd(II) are common pollutants introduced into natural waters from a variety of industrial wastewaters. Sources of chromium pollution are reported to be electroplating, leather tanning, textile dyeing, and metal finishing industries. In metal cleaning, plating and metal processing industries, chromium concentration can approach 20,000–75,000, 15,000–52,000 and 100,000–270,000 mg l^{-1}, respectively (Sağ and Kutsal, 1996). On the other, cadmium is used in dipped coatings on metals-bearing and low-melting alloys, fire protection systems and batteries. Both metals are highly toxic elements and considered to be carcinogenic. Cadmium in humans can cause serious damage to kidney and bones, whereas hexavalent chromium is corrosive on tissue. Typical discharge requirements in secondary effluents for cadmium and chromium are 1.1 and 11 μg l^{-1}, respectively (Tchobanoglous et al., 2003).

Several physicochemical methods have been used for the removal of toxic metals, including adsorption on activated carbon, precipitation, membrane separation and ionic exchange. Alternative methods of metal removal and recovery based on biological materials have also been considered. Certain types of microbial biomass can retain relatively high quantities of metals on their cell wall due to its construction. This metabolism-independent mechanism is called biosorption (Alexander, 1999). Many factors such as, biomass type and concentration, metal concentration, pH, and biomass–metal contact time affect biosorption process.

Non-living cells are more advantageous than living cells, since they do not require the employment of a cultivation

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system, are not affected by toxic wastes and can be stored more easily. Biosorption experiments are usually being carried out using heat-killed cells. Heat treatment of the bacterial biomass causes breakage of the cell wall, revealing more functional groups, thus achieving maximum binding capacity of the biomass (Fehrmann and Pohl, 1993; Srinath et al., 2002). Bayramoğlou et al. (2005) have reported 1.7 times higher Cr(VI) ions biosorption capacity by heat treated fungal biomass of *Lentinus sajor-caju* mycelia than that with the untreated cells.

Fungi and yeasts are by-products of fermentation processes and have been studied extensively for the removal of toxic metals (Ferraz and Teixera, 1999; Dursun et al., 2003; Prakasham et al., 1999; Rapoport and Muter, 1995; Sağ and Kutsal, 1996; Bai and Abraham, 2002; Fourest and Roux, 1992). Bacterial biomass isolated from industrial wastewaters, activated sludge or contaminated soils has been used for toxic metals removal (Nourbakhsh et al., 2002; Ozdemir and Baysal, 2004; Hussein et al., 2004; Hassen et al., 1998; Boularbah et al., 1992).

The aim of this study was to compare the ability of a Gram negative, *Pseudomonas* sp. and a Gram positive bacterium *Staphylococcus xylosus* to biosorb Cd(II) and Cr(VI) in single ion solutions and investigate the selectivity of the above microorganisms towards Cd(II) and Cr(VI) adsorption from their binary solutions.

2. Methods

2.1. Bacteria and media

Pseudomonas sp. and *S. xylosus* strains were isolated from contaminated soil in a mining industry near Stratoni, Chalkidiki, Greece and identified according to the criteria described in Bergey's Manual of Systematic Bacteriology (Palleroni, 1984; Sneath et al., 1984), by professor E. Litopoulou Tzannetaki in the Microbial Laboratory of Agricultural School of Aristotle University, Thessaloniki. They were cultivated in Luria-Bertani broth containing 1% tryptone, 0.5% yeast extract and 0.5% NaCl (Scharlau Chemie, Barcelona) at 28 °C, using shake flasks in a water bath at 100 rpm (Julabo SW-20C). Cells were harvested by centrifugation (2000*g*; 20 min) at the static phase of growth after 24 h of incubation, and autoclavated at 121 °C for 20 min before their use. Moisture content was determined by drying a pre-weighted amount of the cells in oven at 100 °C for 10 h.

2.2. Biosorption experiments

Experiments with known concentrations of cadmium solutions at 200 mg l^{-1} were conducted to determine optimal pH, contact time and biomass concentration (dry weight). Cells were suspended in standard solutions of Cd(II), prepared from $Cd(NO_3)_2 \cdot 4H_2O$ (Merck, Germany). The effect of pH was investigated in the range of 3.0–7.0 at a biomass concentration of 1.0 g l^{-1} and contact time 1.5 h. Kinetics of Cd(II) sorption on *Pseudomonas* sp. and *S. xylosus* were also studied. Biomass loading was 1.0 g l^{-1} and pH was adjusted to 6.0 for *S. xylosus* and 7.0 for *Pseudomonas* sp. Samples were taken and analyzed every 15 min the first 5 h. Optimum biomass concentration was examined in the range of 0.5–7.0 g l^{-1}.

Optimum conditions of chromium biosorption were studied similarly. Standard solutions were prepared from $K_2Cr_2O_7$ (Merck, Germany). The effect of pH was investigated in the range of 1.0–6.0 at a biomass concentration of 1.0 g l^{-1} and contact time 1.5 h. Kinetics of Cr(VI) sorption on *Pseudomonas* sp. and *S. xylosus* were, respectively, studied the first 5 h. Biomass loading was 1.0 g l^{-1} and pH was adjusted to 1.0 for *S. xylosus* and 4.0 for *Pseudomonas* sp. Samples were taken every 15 min. Optimum biomass concentration was examined in the range of 0.5–11.0 g l^{-1}.

2.3. Effect of metal concentration

Biosorption experiments were conducted at initial Cd(II) concentrations from 10 to 1000 mg l^{-1}, at optimum pH values, biomass concentration and contact time previously determined. The effect of chromium concentration was studied at 5–1100 mg l^{-1} for *S. xylosus* and 5–450 mg l^{-1} for *Pseudomonas* sp., until equilibrium state is reached. At the end of each experiment the mixture was centrifuged (2000*g* for 20 min) and the remaining concentration of metals in the supernatant was determined. The experimental data were processed via Langmuir and Freundlich isotherms.

2.4. Competitive biosorption experiments

Two series of experiments were designed and conducted in order to study competitive biosorption with both microorganisms. In the first series cadmium was the dominant metal ion and its concentration varied between 10 and 500 mg l^{-1}, whereas that of chromium remained stable at 5 mg l^{-1}. In the other case, chromium was the dominant metal in the solution with concentration varying again between 10 and 500 mg l^{-1} and cadmium was constant at 5 mg l^{-1}. The experimental conditions were the optimum ones as they were determined in the former step of single ion biosorption. In the first series with cadmium as the dominant metal ion, biomass concentration was kept constant at 2.0 g l^{-1}, whereas in the case of chromium, biomass concentration was 1.0 and 8.0 g l^{-1} for *Pseudomonas* sp. and *S. xylosus*, respectively.

Furthermore, experiments were conducted in order to determine if there is any variation in optimum contact time of biomass and the metals, comparing to single ion biosorption, the first 5 h. In all cases the concentration of dominant metal was 400 mg l^{-1}, and that of competent 5 mg l^{-1}. Samples were taken and analyzed every 15 min.

Deviation bars in the figures represent the mean values of three independent experiments.