Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

*Available online at*www.jcbsc.org

Section B: Environmental Biotechnology

CODEN (USA): JCBPAT

Research Article

Biosorption of Hexavalent Chromium Using Inactive Biomass of *Aspergillus* sp.

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Abstract: In this study Aspergillus sp. cells were cultivated using nutrient broth media at room temperature and 150 rpm. The media was inoculated with about 2 x 106 conidies/mL. Cultivation period was about 7 days. After cultivation, cells were harvested by centrifugation (4000rpm/15 min) and then dried in oven at 60°C for 48 h. Stock solutions (1000 ppm) of Cr^{6+} was prepared by dissolving analytical grade of K_2CrO_4, in distilled water.The effect of pH on adsorption was studied and found that the results at pH 6 the removal percentage of Cr^{6+} was small. The removal percentage increased rapidly with decreasing pH, and reached a plateau around 90% at pH 2. The results showed strong pH dependence of biosorption.

Keywords: Ecosystems, biosorption, *Aspergillus* sp, heteropolysaccharides

INTRODUCTION

Extensive industrialization and unplanned disposal of industrial effluents have led to increase the emission of pollutants into ecosystems[1]. Heavy metals in wastewaters come from industries and municipal sewage, and they are one of the main causes of water and soil pollution. Chromium is one of the most widely used metals in industry[2] since it is an essential trace element for all living organisms. Accumulation of Cr in humans has several consequences such as growth and development abnormalities, carcinogenesis, neuromuscular control defects and wide range of other illnesses.

Traditional technologies for the removal of heavy metals, especially in low concentrations (below 10 ppm) are often inefficient and/or expensive, usually generating great volume of sludge containing high level of heavy metals, which need to be disposed of somehow[3]. New technologies are necessary so that the concentration of heavy metals liberated to the environment is within the levels allowed by law, at an acceptable cost. The biosorption, is a process by which solids of natural origin or their derivatives are used to retain heavy metals, has great potential to achieve this objective[4]. Microbial metal removal has received much attention due to the potential use of microorganisms for cleaning metal polluted water[5]. The aim of the present work was to study the removal of Cr^{6+} from solutions using inactive biomass of *Aspergillus* sp. isolated from of soil of the metropolitan area of Nuevo León, México.

METHODS

In this study *Aspergillus* sp. cells were cultivated using nutrient broth media at room temperature and 150 rpm. The media was inoculated with about 2 x 10^6 conidies/mL. Cultivation period was about 7 days. After cultivation, cells were harvested by centrifugation (4000rpm/15 min) and then dried in oven at 60°C for 48 h. Stock solutions (1000 ppm) of Cr^{6+} was prepared by dissolving analytical grade of K_2CrO_4, in distilled water. A series of experiments with Cr^{6+} set to 30 ppm, were conducted under different pH to investigate the effect of pH on the adsorption. The pH was first adjusted to a specific value, from 2.0, 4.0 and 6.0. The pH adjustment was done with addition of either 0.1M NaOH or 0.1M HCl. Then it was measured and maintained steady throughout the experiment. Samples were take a different times during 2 hours of contact for determining the equilibrium time needed for biosorption process.

These experiments were performed using 10 mg of biomass with 10 mL from the initial metal concentrations of Cr^{6+} ions in 10 mL of metal solution at pH 2.0, 4.0 and 6.0. All experiments were performed in triplicate and results shown are mean values with less than 5 % error. The contents were filtrated on 0.45 um filter membranes and the filtrates were analyzed by UV-vis spectroscopy (Model Evolution 60 S, Thermo Scientific) for residual metal content. The metal specific uptake (q in $mg \cdot g^{-1}$) was calculated according to equation 1

$$q = [(C_o - C)/X] \qquad (1)$$

Where: q (mg of metal·g of $biomass^{-1}$) is the metal specific uptake, Co ($mg \cdot L^{-1}$) is the initial metal concentration, C is the residual metal concentration and X($g \cdot L^{-1}$) is the biomass concentration.

RESULTS

Many studies showed that pH is an important factor affecting biosorption of heavy metals.[6,7] It is well know that pH could affect the protonation of the functional groups on the biomass as well as the metal chemistry. The effect of pH on adsorption was studied and the results were shown in Fig 1. At pH 6 the removal percentage of Cr^{6+} was small. The removal percentage increased rapidly with decreasing pH, and reached a plateau around 90% at pH 2. The results showed strong pH dependence of biosorption. The cell wall matrix of filamentous fungi contains complex heteropolysaccharides that can provide amino, carboxyl and sulphate groups.

At low pH, cell wall ligands are protonated and increase the biosorption of $[CrO_4]^{2-}$ as a result of the attractive force.

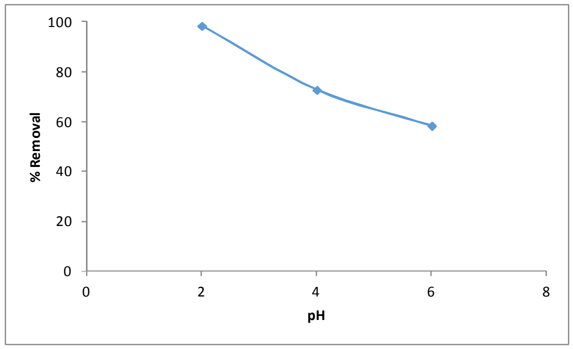

Figure 1: Removal efficiencies of Cr^{6+} by *Aspergillus* sp. at different pH

The pseudo-second order kinetic model based on the sorption capacity of solid phase can be used in this case assuming that measured concentrations are equal to cell surface concentrations. The linearized form of the pseudo-second order model was proposed by Ho and McKay[8,9,10] and has been widely applied to the sorption of metal ions.[11] The pseudo-second order kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2)$$

Integrating for the boundary condition conditions $q_t = 0$ at $t = 0$ and q_t at time t, the linearized form of pseudo-second order model is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where k_2 is the second order biosorption rate constant (g/mmol/min); q_e and q_t are the amounts of adsorbed metal ions on the biosorbent at the equilibrium and at any time t, respectively.

The removal rate of Cr^{6+} by *Aspergillus* sp. rapid in the first 5 min, (Fig. 2). The kinetic data were analyzed in term of the pseudo-second order. Figure 3 showed the plots of t/q vs. t at various pH values. The values of k_2 and q_e were presented in Table 1. The adsorption of Cr^{6+} by *Aspergillus* sp. followed the second order model very well at pH 2 (R^2 > 0.999), and based on the assumption that the rate limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

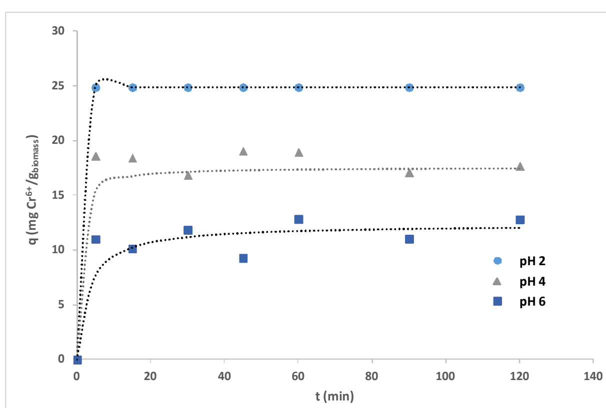

Figure 2: Adsorption kinetics of Cr^{6+} at different pH values by *Aspergillus* sp.

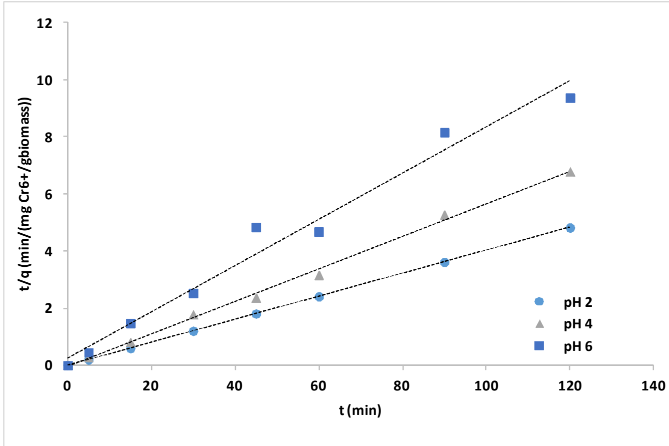

Figure 3: Linearized pseudo-second order kinetics at different pH values by *Aspergillus* sp.

Table 1: Comparison of the second-order rate constants for different pH values.

pH	k_2 (g/mg·min)	q_e (mg Cr/g biosorbent)	%R^2
2	8.0802	24.877	99.99
4	0.0538	17.483	99.65
6	0.0177	12.579	97.19

CONCLUSIONS

From the laboratory based experiments, the following conclusions can be reached: the biosorption processes were pH dependent; the optimum pH for Cr^{6+} biosorption is 2.0, after 5 min at room temperature. Kinetics followed the pseudo-second order kinetic model. The results demonstrate that inactive biomass of *Aspergillus* sp. could be used as promising biosorbent for the removal of Cr^{+6} ions from aqueous solutions.

ACKNOWLEDGEMENTS

Authors thank Mr J.M. Tijerina-Martínez and Mrs. A. Díaz de León-Vivar for his work and support. This work was supported by the project PROMEP/103.5/12/3585.

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