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Original Research Paper

Removal of Heavy Metals from Industrial Effluent by Biomass of *Aspergillus flavus*

P. S. Raut and P. P. Wani
MET's Institute of Engineering, Bhujbal Knowledge City, Adgaon, Nashik-422 003, Maharashtra

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ABSTRACT

Biosorption is a potential alternative to traditional processes of metal ions removal. Therefore, the capacity to biosorb cadmium and lead by *Aspergillus flavus* strain 44-1 was investigated. Batch-scale experiments were conducted to study the effect of design parameters such as pH, retention time and initial metal concentration. Fixed dried *Aspergillus flavus* strain 44-1 dose of 2g/L was applied through the study. The highest removal for Cd and Pb were 50% and 70% respectively. For both metals, uptake increased by increasing the initial metal concentration. The experimental biosorption equilibrium data were in good agreement with those calculated by Freundlich model. The maximum sorption capacities determined from the experimental equilibrium isotherms by applying the Freundlich model showed that the *Aspergillus flavus* has best ability at pH 4 and pH 6 for Cd and Pb respectively. By applying Freundlich model at pH 6, k was 28 for Pb and 21 for Cd, and at pH 4, k was 20 for Pb and 30 for Cd. This means that treated adsorbents show good adsorption capacities for Cd and Pb.

INTRODUCTION

One of the main causes of tannery pollution is the discharge of effluents containing heavy metals. Heavy metals can have serious effects on human and animal health. Beside the health effects, heavy metals are nonrenewable resources. Therefore, effective recovery of heavy metals is as important as their removal from waste streams.

Disposal of tannery wastewater has always been a major environmental issue. Pollutants in tannery wastewater are almost invariably so toxic that wastewater has to be treated before its reuse or disposal in water bodies. Tannery processes generate wastewater containing heavy metal contaminants. Since heavy metals are non-degradable into non-toxic end products, their concentration must be reduced to acceptable levels before discharging them into environment otherwise these could pose threats to public health and/or affect the aesthetic quality of potable water. According to World Health Organization the metals of most immediate concern are chromium, zinc, iron, mercury and lead (WHO 1984). Maximum allowable limits for contaminants in "treated" wastewater are enforced in developed and many developing countries.

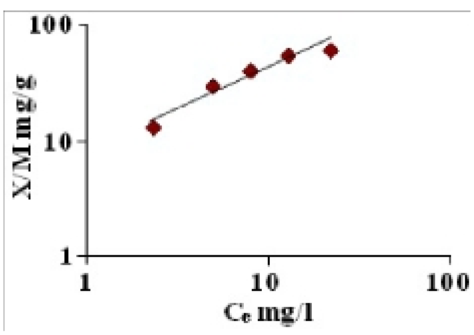
The treatment of contaminated waters is as diverse and complicated as the operation from which it comes. A number of conventional treatment technologies have been considered for treatment of wastewater contaminated with heavy metals. Previous investigations on the removal of heavy metals from wastewater (Howari & Garmoon 2003, Shwarts & Ploethner 1999, El-Awady & Sami 1997) suggest that systems containing calcium in the form CaO or $CaCO_3$ and carbonates, in general, are particularly effective in the removal of heavy metals from wastewater. Some of the conventional techniques for removal of metals from tannery wastewater include chemical precipitation, adsorption, solvent extraction, membrane separation, ion exchange, electrolytic techniques, coagulation/

flocculation, sedimentation, filtration, membrane process, biological process and chemical reaction (Blanco et al. 1999, Blanchard et al. 1984, Gloaguen & Morvan 1997, Jeon et al. 2001, Kim et al. 1998, Lee et al. 1998, Mofa 1995, Lujan et al. 1994, Gardea-Torresdey et al. 1996). Each method has its merits and limitations in application. Similarly, use of biomass in treatment of effluent containing metals has effective results in removal of metals like Cd, Pb.

MATERIALS AND METHODS

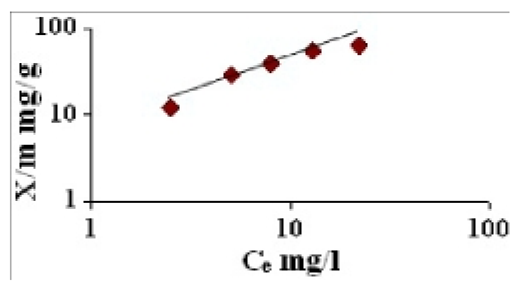
Preparation of biosorbent: *Aspergillus flavus* strain 44-1 was collected from tannery effluent. The biomass was washed several times with deionized water to remove dirt, and other impurities present in the raw materials. All the samples were dried in an oven at 100°C for 24h or until constant weight and ground with a mortar. Fractions of particle size in the range between 0.5 and 1 mm were selected for the metal uptake experiments. The concentration of added biomass was 2 g/L.

Metal solutions: Cadmium and lead solutions and standards were prepared by using analytical grade cadmium chloride ($CdCl_2$) and lead chloride ($PbCl_2$). Solution of 5000 mg/L was prepared with deionized water. Solutions of varying concentrations were prepared by diluting the stock solution with deionized water. The freshly diluted solutions were used for each biosorption study.



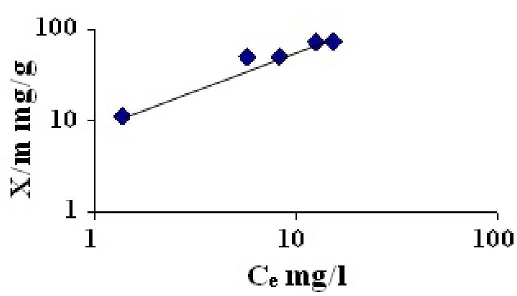
(A)

Fig. 1: Freundlich sorption isotherm for Cd by *Aspergillus flavus* strain 44-1 at pH 4.



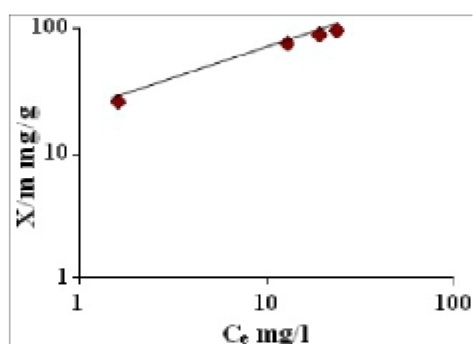
(B)

Fig. 2: Freundlich sorption isotherm for Pb by *Aspergillus flavus* strain 44-1 at pH 4.



(C)

Fig. 3: Freundlich sorption isotherm for Cd by *Aspergillus flavus* strain 44-1 at pH 6.



(D)

Fig. 4: Freundlich sorption isotherm for Pb by *Aspergillus flavus* strain 44-1 at pH 6.

Experimental procedure: Batch equilibrium experiments were performed in 125 mL Erlenmeyer flasks, containing 100 mL of metal solution. The initial concentrations of cadmium were 4, 7, 9, 28, 36 and 44 mg/L and that of lead were 4, 9, 16, 18, 27 and 30 mg/L. All the experiments were conducted with a control test without metal. Samples were taken from solutions after 5, 15, 30, 50, 60, 90, 120, 150 min to determine optimal contact time. The separation of the biomass from experimental solution was achieved by membrane filtration (Whatman 40) in all cases. The pH values were adjusted at 6 and 4 for biosorption using 10% NaOH and 10% HCl. During the adsorption process, the flasks were agitated on a shaker at 200 rpm under ambient temperature (25±2°C). Heavy metal concentrations were measured in the filtrate by atomic absorption spectrophotometer (AAS) (Varian, Model 220) according to standard methods.

Data analysis: The Freundlich isotherm model below is commonly used to describe the sorption of metals onto microbial surface.

Freundlich equation:

$$\text{Log } (Co - Ce/m) = \log k + 1/n \log Ce$$

Where, Co = the initial concentration
Ce = the metal concentration remaining in solution
m = weight of adsorbent (g)
k reflects adsorption capacity of adsorbent as it increases with the adsorption capacity.
1/n = measure of affinity of adsorbate to adsorbents and its value decrease as 1/n value increases.

RESULTS AND DISCUSSION

The biosorption process has been analysed through batch experiment with regard to the influence of initial metal concentration and pH on biomass. The removal process is rapid taking only a few minutes. From preliminary experiment, to reach equilibrium 2 h were chosen for best removal of cadmium and 3 h for lead.

Key quantitative information on biosorption performance can be obtained from batch equilibrium studies. Small sample doses (2 g/L) of the biosorbent, prepared of dried biomass of *Aspergillus flavus* strain 44-1, enabled 46% removal of Cd and 72% removal of Pb from diluted water solutions. Mahamadia & Torto (2007) found that lead biosorption by *Aspergillus flavus* occurred rapidly, with 80% of total uptake occurring within 50 minutes.

Biosorption time: The results indicate that the metal concentration decreased rapidly during the first 5 min and remained nearly constant after 2 h for Cd and 3 h for Pb suggesting that the biosorption was fast and reached saturation within 2 and 3 h. After this equilibrium period, the amount of adsorbed metals did not significantly change with time. Similar equilibrium times were obtained for many algae. Equilibrium times of 2 or 3 h were employed with macroalgae *Sargassum genus* (Cruz et al. 2004, Munoz et al. 2006). This equilibrium time is shorter than those usually employed for the adsorption of cadmium by other adsorption materials. Aksu (2001) reported 4 h adsorption tine with macroalgae *Chlorella vulgaris*.

Freundlich model effectively described the sorption of cadmium and lead by *Aspergillus flavus.* In Figs. 1, 2, 3, and 4, k and 1/n are empirical constants and indicative of sorption capacity and intensity, respectively. Tien (2002) found that the magnitude of k and n show easy uptake with increase in surface area and dry weight of algal cells. They were found to be the main factors influencing metal sorption and indicate favourable adsorption. So the ratio of surface area and dry weight was determined, it was 2.65. The Freundlich constant k was 30 and 21 at pH 4 and 6 respectively for cadmium, which reflects higher adsorption capacity at lower pH. The k for lead was 20 and 28 at pH 4, 6 respectively which reflects that adsorption capacity for lead is higher at pH 6. Affinity of the adsorbate (1/n) for lead was 0.8 and 0.88 at pH 6 and 4 respectively denoting greater affinity at pH 6; for cadmium 1/n was 0.49 and 0.4 at pH 6 and 4 respectively which means greater affinity at pH 4.

It can be from the study that the *Aspergillus flavus* strain 44-1 could be used as an efficient biosorbent material for the treatment of cadmium and lead ions bearing wastewaters.

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