

Short Communication

Sorption of Cr(VI) from dilute solutions and wastewater by live and pretreated biomass of *Aspergillus flavus*K.K. Deepa^a, M. Sathishkumar^{b,c,*}, A.R. Binupriya^{a,b},
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Abstract

Sorption of Cr(VI) was carried out from dilute solutions using live and pretreated biomass in a batch mode. Effects of agitation time, adsorbent dosage and pH were examined. The autoclaved biomass that showed maximum adsorption capacity ($Q_0 = 0.335 \text{ mg g}^{-1}$) was used as an adsorbent in column studies. The optimized flow rate of 2.5 ml min^{-1} and bed height 10 cm were used to determine the effect of metal ion concentration on removal of Cr(VI). Applying the BDST model to calculate the adsorption capacity (N_0) of column, which showed 4.56×10^{-5} , 7.28×10^{-5} , 6.89×10^{-5} , 3.07×10^{-5} , $2.80 \times 10^{-5} \text{ mg g}^{-1}$ for 4, 8, 12, 16 and 20 mg dm^{-3} of Cr(VI), respectively. Batch sorption proved to be more efficient than the column sorption and hence batch sorption was used to remove Cr(VI) from a textile dyeing industry wastewater. The phytotoxic effect of treated and untreated wastewater was studied against *Zea mays*. Toxicity was reduced by 50% in the treated effluent.

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1. Introduction

The toxicity of Cr(VI) makes its removal highly necessary. But, physico-chemical methods presently in use have several disadvantages such as unpredictable metal ion removal, high reagent requirements, formation of

sludge and its disposal and high installation and operational costs (Ranganathan, 1993). Adsorption by activated carbon appears to be particularly effective in the removal of trace levels of metals. However, activated carbon is expensive and the higher the quality, the greater the cost. Biosorption is an alternative technology, and has been the focus of a number of recent studies (Kaesarn, 2002). Extensive investigations are being carried out to identify suitable and cheap adsorbents capable of removing Cr(VI). The use of microbial biomass as a potential sorbent for removal of metals from industrial

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and municipal wastewater has been proposed and bacterial removal of Cr(VI) has already been reported (Srinath et al., 2002). Fungal biosorption is an alternative method for treatment of wastewater bearing toxic metal ions (Kapoor and Viraraghavan, 1998). This has been proved efficient in treating wastewaters containing metals in dilute concentrations. Several researchers have reported the sorption of Cr(VI) using fungi (Bai and Abraham, 2001, 2002; Dursun et al., 2003; Sag et al., 2001). In the present investigation efficiency of the live and pretreated biomass of the fungi, *Aspergillus flavus* to adsorb Cr(VI) from dilute solutions was studied in batch and column modes and batch studies were conducted for the treatment of Cr(VI) containing textile dyeing wastewater. Phytotoxicity studies were also carried out in treated and untreated wastewaters.

2. Materials and methods

2.1. Adsorbent

One ml (10^6 spores) of *A. flavus* spore suspension was inoculated into Czapek-Dox broth in 250 ml Erlenmeyer flasks and incubated at room temperature ($27 \pm 3^\circ\text{C}$) for 5 days in an orbital shaker at 125 rpm. At the end of the fifth day, the mycelial pellets were separated by filtration through Whatman No. 1 filter paper. Biomass was then washed with a generous amount of deionised water till it was free from the media components. The washed, live mycelial pellets were used as an adsorbent after squeezing out the excess water with the use of filter paper. The biomass was also subjected to various pretreatments to test its efficacy to adsorb Cr(VI). Similar pretreatments have been used in studies of the removal of other metals such as Pb, Cd, Cu and Ni (Kapoor and Viraraghavan, 1998). The various pretreated biomasses were as follows:

- Autoclaved biomass: the biomass was autoclaved for 30 min at 121°C at 124 kPa.
- Acid treated biomass: the biomass was boiled for 15 min in 500 ml of 10% (vol/vol) *o*-phosphoric acid.
- Alkali treated biomass: the biomass was boiled for 15 min in 500 ml of 0.5 N sodium hydroxide solution.
- Formaldehyde treated biomass: the biomass was boiled for 15 min in 500 ml of 15% (vol/vol) formaldehyde solution.
- Detergent treated biomass: the biomass was boiled for 15 min in 500 ml of 15% (vol/vol) Extran detergent solution.

After each pretreatment the biomass was washed with a generous amount of deionised water till the pH of the wash solution was in near neutral range (pH

6.8–7.2). All chemicals used were of analytical grade procured from Merck, sd fine (India) and Glaxo.

2.2. Batch studies

A stock solution of 1000 mg dm^{-3} Cr(VI) was prepared by dissolving 2.8289 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in double distilled water and made up to 1000 cm^3 in a flask. To determine the effect of agitation time and adsorbate concentration on removal of Cr(VI), 1000 mg of the adsorbent was added to 50 cm^3 of 4, 8, 12, 16 and 20 mg dm^{-3} solutions of Cr(VI) and agitated in a rotary shaker at 150 rpm for predetermined time intervals at 30°C . The adsorbate and adsorbent were separated by centrifugation at 10000 rpm for 20 min. Cr(VI) in the adsorbate were analyzed spectrometrically (APHA, 1995) (Elico model SL 171). The equilibrium time was determined from these experiments.

A study was carried out with different dosages of adsorbent ($250\text{--}2250\text{ ml}^{-1}$) for the equilibrium time to determine the effect of adsorbent dose on Cr(VI) removal. The effect of pH on Cr(VI) removal was studied by using 50 cm^3 of 12 mg dm^{-3} solution of Cr(VI), adjusted to an initial pH of 2–10 mixed with optimum dosage of adsorbent and agitated for the equilibrium time. Control experiments were carried out in the absence of the adsorbent in order to find out whether there is any adsorption on the container walls.

From the data, the Langmuir plot was drawn and adsorption constant (Q_0) was calculated from the slope of the curve.

2.3. Column studies

Only the pretreated biomass with maximum adsorption capacity was used as an adsorbent in column studies. 2.5 cm bed height of the adsorbent was packed in a glass column ($45 \times 2.2\text{ cm}$) and the 12 mg dm^{-3} Cr(VI) solution was adjusted to a flow rate of 2.5, 5.0, 7.5 and 10 ml min^{-1} . Fractions were collected at regular intervals and analysed for Cr(VI). The study was then repeated with the best flow rate and bed height and with different concentrations of Cr(VI) (4, 8, 12, 16 and 20 mg dm^{-3}) to determine the effect of metal ion concentration on removal of Cr(VI). Data obtained were used to plot BDST curves and adsorption rate constant (N_0) was calculated from the plot. Bed-depth-service-time model (BDST), proposed by Hutchins (1973) is a simple method to correlate the service time, t , with process variables in fixed bed adsorber.

$$C_0 t = N_0 / uH - [1/k_a \times \ln(C_0/C_t - 1)] \quad (1)$$

where t is service time to breakthrough; min, N_0 is the adsorption capacity, mg dm^{-3} , of the adsorbent bed, C_0 is the influent concentration; mg dm^{-3} , u is linear flow rate; mg min^{-1} , H is the depth of bed; cm, k_a is

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