Adsorption-Desorption Studies on Cr(VI) Using Non-Living Fungal Biomass

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The present study was undertaken in batch bioreactor with an aim to examine the Cr(VI) adsorption potential of the non-living fungal biomass of *Aspergillus* sp. from aqueous solution and also to find out the possibility of recovering of Cr(VI) from the metal concentrated fungal biomass. The optimum pH for adsorption of Cr(VI) was found to be 2.0. The Cr(VI) adsorbed increased with increasing initial metal concentration upto 500 mg L^{-1}. A maximum removal of 27.5 mg g^{-1} was observed at pH 2.0 at 500 mg L^{-1} initial Cr(VI) concentration. The adsorption equilibrium constants were obtained from both Freundlich and Langmuir adsorption isotherms. Desorption studies carried out using a number of desorbing agents indicated a maximum of 76 % of Cr(VI) was recovered from the metal concentrated biomass using 0.1 N sodium hydroxide solution within 0.5 h of time period.

Key Words: Adsorption, *Aspergillus* sp., Cr(VI), Desorption, Freundlich and Langmuir adsorption isotherms.

INTRODUCTION

Chromium(VI) is one of the toxic heavy metals that are present as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) in aqueous waste streams[1] of many industries such as metal plating, metal cleaning and processing, manufacture of anticorrosive agents, wood preservation, wood processing, alloy preparation, pigment manufacture, leather tanning, manufacturing of dyes, printing, *etc*.[2-7]. This is of serious environmental concern as Cr(VI) persists indefinitely in the environment complicating its remediation. The persistant nature makes it accumulate in the food chain which with time reach harmful levels in living beings resulting in serious health hazards such as irritation in lungs and stomach, cancer in digestive tract, low growth rates in plants, death of animals *etc*. Therefore, removal of Cr(VI) from waste water prior to its discharge into natural water systems, adjoining landmasses, sewer systems, *etc*. requires serious and immediate attention. The conventional physico-chemical techniques used for the removal of Cr(VI) include chemical reduction followed by precipitation with caustic soda. This process requires a large excess of chemicals and produces voluminous sludges, disposal of which again create secondary pollution. Other available treatments include ion-exchange, electrolysis and reverse osmosis

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etc. which are not only expensive and high energy processes, but also are ineffective in removal of metal ions present at lower concentration in large volume of wastewaters[8]. Environmentally friendly processes, therefore, need to be developed to clean-up the environment without creating harmful waste by-products. Bioremediation involves potential application of microorganisms in removal of heavy metals and has been recognized as a potential alternative to the conventional methods for treatment of contaminated wastewaters[9]. The growing, resting and non-living cells of microorganisms are reported to remove Cr(VI) from aqueous solutions[10-12]. The use of non-living cells has advantages over growing and resting cells due to the absence of both toxicity limitations and requirements of growth media and nutrients. Moreover, adsorbed metal can be easily desorbed and regenerated biomass can be reused. Adsorption or ion-exchange on the cell surface is assumed to be the key mechanism involved in the metal removal by the non-living biomass.

In the present study, Cr(VI) adsorption was evaluated from the batch data at different initial Cr(VI) concentrations and at different pH values. The equilibrium adsorption data were tested with both the Freundlich and Langmuir adsorption isotherms and the nature of biosorption is discussed. The studies were also made to investigate the possibility of recovering Cr(VI) from the metal concentrated biomass, which assumes great importance from the point of resource recovery as the metals are non renewable.

EXPERIMENTAL

Microorganism and growth conditions: The fungus *Aspergillus* sp. was grown in 250 mL Erlenmeyer flasks in a shaking incubator at 30 ℃ and 180 rpm using media of the following composition (g L^{-1}): Glucose, 10.0; K_2HPO_4, 0.5; NaCl, 1.0; $MgSO_4$, 0.1; NH_4NO_3, 0.5 and yeast extract, 5.0. The pH of the media was 6.0. An inoculum of 10 % (v/v) of a 36 h old culture was used for the growth of the organism.

Preparation of biomass: The cells grown in 36 h (when sugar was completely utilized) were centrifuged at 5000 rpm for 5 min and then washed with distilled water and dried at 80 ℃ for 24 h. The dried biomass was then used for subsequent batch experiments.

Preparation of Cr(VI) solution: A stock solution (1000 mg L^{-1}) of Cr(VI) was prepared by dissolving the required quantities of potassium dichromate in distilled water. Chromium(VI) solutions of different concentrations (50-500 mg L^{-1}) were prepared by diluting the stock solution.

Adsorption studies: A weighed amount (4.5 g L^{-1}) of dried biomass was added to 100 mL of Cr(VI) solution of a known concentration in an Erlenmeyer flask. The pH of the solution was adjusted to the required value with 1 N H_2SO_4 solution before adding the biomass. The mixture was agitated in a shaker at 150 rpm for 8 h to reach the equilibrium. The samples were taken out at different time intervals and were centrifuged at 5000 rpm for 5 min. The separated supernatant liquid was analyzed for Cr(VI). The Cr(VI) adsorption studies were conducted to study the effect of pH in the range 2.0-6.0 and initial metal concentrations in the range of 0-500 mg L^{-1}.

Desorption studies: *Aspergillus* sp. (4.5 g L^{-1} on dry wt. basis) containing Cr(VI) solution harvested after the adsorption experiments was washed with distilled water and suspended in 100 mL of different concentrations of desorbing reagents taken in 250 mL Erlenmeyer flasks. The mixture was agitated in a shaker at 150 rpm for 2 h. The following desorbing reagents were used in the present study: sodium chloride solution: (0.01, 0.1, 0.5 N); EDTA: (0.01, 0.1, 0.5 N); sodium hydroxide solution: (0.01, 0.1, 0.5, 1.0 N); hydrochloric acid: (0.01, 0.1, 0.5 N); sulphuric acid: (0.01, 0.1, 0.5 N); nitric acid: (0.01, 0.1, 0.5 N). The liquid samples were periodically withdrawn, centrifuged and analyzed for Cr(VI).

Analysis of Cr(VI): The residual Cr(VI) concentrations in the aqueous solution was determined spectrophotometrically (Sytronics UV-VIS spectrophotometer 117) at 540 nm using diphenyl carbazide as the complexing agent[13].

RESULTS AND DISCUSSION

Fig. 1 shows the effect of pH on Cr(VI) adsorption percentage and weight of Cr(VI) adsorption mg/g of biomass, respectively, by the non living dry biomass (as an adsorbent) of the *Aspergillus* sp. at 50 mg L^{-1} initial Cr(VI) concentration. The figure indicates a sharp decrease in per cent adsorption of Cr(VI) with an increase in pH value from 2.0 to 3.0 beyond which a slow decrease was observed in the adsorption with further increase in pH upto 6.0. The Cr(VI) adsorption was 10 % at pH 6.0, whereas, a significant adsorption of 90 % was observed at pH 2.0. An increase in Cr(VI) removal with decreasing pH of the solution was also observed by Prakasham *et al.*[14] and Kapoor *et al.*[15] for fungal biomass, Nourbaksh *et al.*[16] for algal, fungal and bacterial biomass, Srinath *et al.*[12] for bacterial biomass and Gupta *et al.*[17] for green filamentous algal biomass. The decrease in adsorption with increase in pH is due to the decreased availability of hydrogen ions for the protonation of the cell wall functional groups, thus reducing the interaction between the metal ions and the available binding sites. The increased Cr(VI) removal at low pH is due to an interaction between the negatively charged dichromate ions and the positively charged cell protonated functional groups and also because of reduction of Cr(VI) to trivalent chromium[18]. A similar trend was observed in milligram of Cr(VI) adsorption/g of biomass at different pH values (2.0-6.0) and a maximum adsorption (10 mg g^{-1}) was obtained at pH 2.0.

The per cent Cr(VI) adsorption and Cr(VI) adsorption of mg/g of biomass at different initial Cr(VI) concentration ranging from 50 to 500 mg L^{-1} at pH 2.0 is shown in Fig. 2. The biomass concentration used for all the experiments was 4.5 g L^{-1}. The per cent Cr(VI) removal was decreased by increasing initial metal concentrations with 90 % removal at 50 mg L^{-1} and only 24.8 % removal at 500 mg L^{-1}. However, Cr(VI) adsorption of mg/g of biomass was increased with an increase in initial Cr(VI) concentration and a maximum adsorption (27.5 mg g^{-1}) was observed at 500 mg L^{-1}.
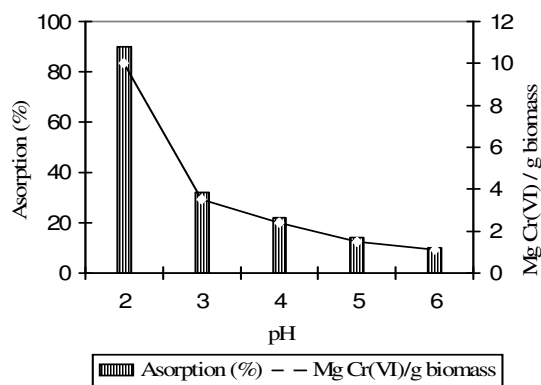
Fig. 1.   Effect of pH on Cr(VI) adsorption by *Aspergillus* sp. as an adsorbent at 50 mg L^{-1} Cr(VI) concentration
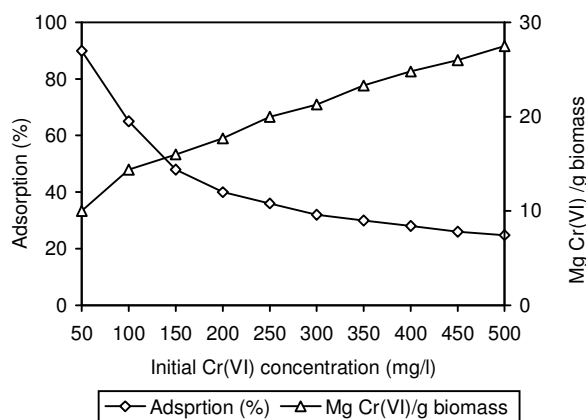

Fig. 2.   Effect of initial Cr(VI) concentration on % adsorption and Cr(VI) removal mg/g of biomass

The relation between the amount of metal adsorbed by the adsorbent and unadsorbed component in solution at a constant temperature can be represented by both Langmuir and Freundlich adsorption isotherms, which provide the equilibrium data required for the designing of the adsorption system. The Langmuir adsorption isotherm, which is applicable to monolayer sorption onto a surface having homogeneously distributed identical binding sites over the surface sorbent, is given by

$$q_e = \frac{Q^o b C_e}{1 + b C_e} \qquad (1)$$

or

$$\frac{1}{q_e} = \frac{1 + b C_e}{Q^o b C_e} \qquad (1a)$$

$$\text{or} \qquad \frac{C_e}{q_e} = \frac{1 + bC_e}{Q^o b} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \qquad (1b)$$

where q_e is the amount of metal adsorbed per gram of dried biomass at equilibrium [mg Cr(VI) g^{-1} of dried biomass] and C_e is the residual (equilibrium) metal concentration remaining in the solution after sorption [mg Cr(VI) L^{-1}]. The Langmuir constants, Q^o and b, indicating the maximum amount of metal ion bound per g of adsorbent to form a monolayer (mg g^{-1}) and the adsorption affinity (1 mg^{-1}) for binding of Cr(VI) on the adsorbent sites, respectively. The values of Q^o and b can be calculated[17,19] from the slope and intercept of the plot C_e/q_e against the residual concentration, C_e.

The Freundlich adsorption isotherm is applicable to adsorption of Cr(VI) on a heterogeneous surface and is expressed as

$$q_e = K_F C_e^{1/n} \qquad (2)$$

$$\text{or} \qquad \log q_e = \log K_F + \frac{1}{n} C_e \qquad (2a)$$

where K_F and n are the Freundlich constants and are related to the adsorption capacity and adsorption intensity of the adsorbent, respectively. Eqn. 2 can be linearized in logarithmic form and Freundlich constants n and K_F can be determined[16,19] from the slope and intercept which are equal to 1/n and K_F, respectively.

In the present study, both Langmuir and Freundlich adsorption isotherms were tested with the experimental data describing the adsorption equilibrium of Cr(VI) and to express the Cr(VI) adsorption potential of *Aspergillus* sp. Figs. 3-4 show the Langmuir and Freundlich adsorption isotherms constructed with Cr(VI) adsorption data obtained at different initial Cr(VI) concentrations (0-500 mg L^{-1}), pH 2.0 and at 30 ºC, respectively. The values of adsorption isotherm constants were calculated from the slopes and the intercepts of the straight lines shown in Fig. 3 (Langmuir isotherm) and Fig. 4 (Freundlich isotherm) along with the regression coefficients. The Langmuir adsorption constant 'Q^o' calculated in the present study indicates that the maximum amount of Cr(VI) adsorbed per gram of adsorbent (*Aspergillus* sp.) to form a complete monolayer on the surface was 29.2 mg and the adsorption affinity 'b' for binding of Cr(VI) on the adsorbent sites was 0.03 (L mg^{-1}). These results indicate strong binding of Cr(VI) on the adsorbent surface. The adsorption capacity (K_F) and adsorption intensity (n) obtained from the intercept and slope of the Freundlich adsorption isotherm were 6.8 and 4.5, respectively. With respect to the values of linear regression coefficient (R^2), both Langmuir and Freundlich models agreed well with the experimental data. However, Freundlich model exhibited a better fit of the adsorption data due to a higher value of R^2. Both the models can be applied for a monolayer adsorption. However, the Freundlich model provides a more realistic description of adsorption by the adsorbent with the different binding sites which are heterogeneously distributed over the adsorbent surface.
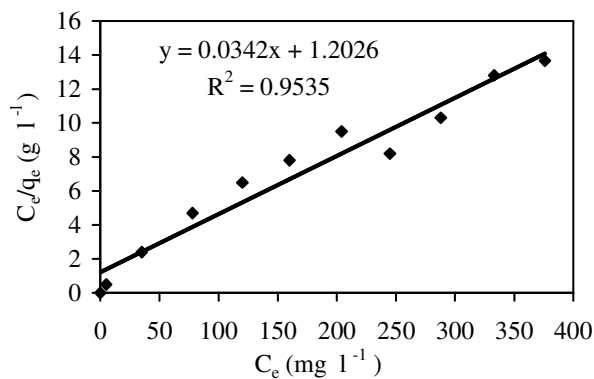
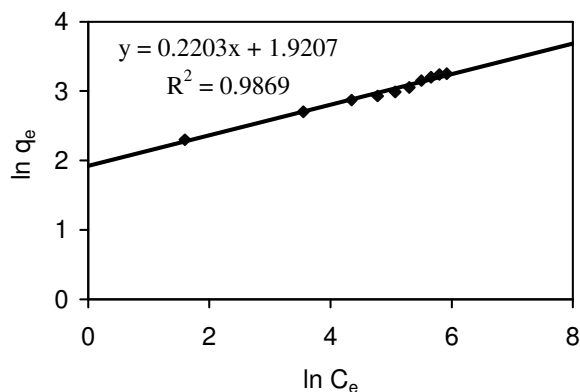Fig. 3. Langmuir adsorption isotherm of Cr(VI)

Fig. 4. Freundlich adsorption isotherm of Cr(VI)

On the other hand, Langmuir model describes the adsorption onto a surface with a finite number of identical sites homogeneously distributed over the adsorbent surface.

In many cases[20-22], both the models were reported to be fitted well with the experimental data of Cr(VI) adsorption. Chromium(VI) adsorption by *Aspergillus* sp. used in the present study appears to be a monolayer adsorption and higher value of R^2 found with Freundlich model is indicative of Cr(VI) adsorption also by the non-identical binding sites heterogeneously distributed on the adsorbent surface.

In order to explore the feasibility of recovering Cr contained in biomass (4.5 g L^{-1}, dry wt. basis) produced in the batch adsorption experiment conducted at 500 mg L^{-1} initial Cr(VI) concentration, the biomass (metal loaded biomass) was treated with different desorbing reagents as shown in Table-1. The time period required for the maximum release of bound Cr(VI) from the metal loaded biomass was monitored upto 120 min, by which the adsorbed Cr(VI) was almost completely desorbed into the desorbing reagents. Recovery of Cr assumes great importance from resource conservation point of view along with an added benefit of reusing the desorbed biomass for Cr(VI) removal. The table shows maximum desorption of Cr(VI)

TABLE-1
DESORPTION OF Cr(VI) FROM *Aspergillus* sp. CONTAINING Cr(VI) WITH TIME

Desorbing agents (Concentration)	Desorption of Cr(VI) (%)			
	5 min	30 min	60 min	120 min
Sodium chloride				
0.01 N	11.5	20.8	22.4	22.4
0.10 N	45.6	53.2	53.2	53.2
0.50 N	53.2	53.2	53.2	53.2
Sodium hydroxide				
0.01 N	15.6	25	25	25
0.10 N	51.9	76	76	76
0.50 N	76	76	76	76
1.00 N	76	76	76	76
EDTA				
0.01 N	0.76	1.9	1.9	1.9
0.10 N	1.9	1.9	3.8	3.8
0.50 N	1.9	1.9	3.8	3.8
Hydrochloric acid				
0.01 N	2	5	5	5
0.10 N	5	8	8	8
0.50 N	8	8	8	8
Sulphuric acid				
0.01 N	6	14	14	14
0.10 N	14	18	18	18
0.50 N	18	18	18	18
Nitric acid				
0.01 N	Nil	2	2	2
0.10 N	2	5	5	5
0.50 N	5	5	5	5

(94.2 mg) using 0.1 N sodium hydroxide solution within 0.5 h time period. This was 76 % of the total Cr(VI) (124 mg) adsorbed by the *Aspergillus* sp. Significant desorption of 65.9 mg of Cr(VI) was also observed in 0.5 h using 0.1 N sodium chloride solution. However, no significant desorption was obtained using other desorbing reagents. The above results indicate that the Cr(VI) desorption from the biomass was favoured by the alkaline desorbing reagent. It was expected that in the presence of alkaline solution the desorption of anionic dichromate from the biomass would follow an ion-exchange mechanism. Moreover, the optimum pH for the maximum adsorption of Cr(VI) was observed to be 2.0. In the alkaline region the Cr(VI) adsorption was decreased due to the reduced availability of H^+ ions, which had limited the protonation of cell wall functional groups and thus reduced the interaction with the negatively charged metal[18,19]. The above condition favors the desorption of bound Cr(VI) from the metal loaded biomass into the desorbing reagents.

Conclusion

The non-living fungal biomass of *Aspergillus* sp. was able to adsorbed Cr(VI) significantly from an aqueous solution. The adsorption process was dependent on pH and initial metal concentrations. The maximum adsorption (27.5 mg g^{-1}) was obtained at 500 mg L^{-1} initial Cr(VI) concentration at pH 2. The adsorption isotherm constants calculated from both the Langmuir and Freundlich adsorption isotherm indicated favorable adsorption capacity of the *Aspergillus* sp. for Cr(VI). 0.1 N solution of NaOH was identified as the potent desorbing reagent for effective recovery (76 %) of Cr(VI) from the metal loaded biomass.

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