

Biosorption of chromium(VI) from aqueous solution and electroplating wastewater using fungal biomass

Rajender Kumar, Narsi R. Bishnoi*, Garima, Kiran Bishnoi

Department of Environmental Science & Engineering, Guru Jambheshwar University of Science & Technology, Hisar 125001, India

Received 16 March 2006; received in revised form 27 February 2007; accepted 2 March 2007

Abstract

Biosorption of Cr(VI) ions from aqueous solution as well as from electroplating effluent with dead fungal biomass sp. *Aspergillus niger*, *Aspergillus sydoni* and *Penicillium janthinellum* was investigated in the batch mode. The influence of pH of the solution, biosorbents dose, concentration of ions and contact time on biosorption capacity of Cr(VI) ions was studied. The optimum pH for biosorption of Cr(VI) ions was found to be 2.0. The removal of Cr(VI) was 91.03% with *A. niger* at biosorbent dose 0.6 g/50 mL, whereas, 87.95% and 86.61% with *A. sydoni* and *P. janthinellum* at biosorbent dose 0.8 g/50 mL but uptake capacity (mg/g) of Cr(VI) ions decreased with increased biosorbent dose. Initially percent removal of Cr(VI) ions from solution was increased with increase in concentration from 10 to 30 mg/L and maximum percent removal was observed at concentration 30 mg/L after that percent removal decreased. Whereas, uptake capacity was increased with increase in concentration of Cr(VI) ions from 10 to 60 mg/L. Uptake rate of Cr(VI) increased from 1.72 to 2.39 mg/g with *A. niger*, 1.22 to 1.76 mg/g with *A. sydoni* and 1.18 to 1.77 mg/g with *P. janthinellum* with increases time from 15 to 120 min. Removal of Cr(VI) from electroplating wastewater was observed less than from synthetic solution. Higher value of correlation coefficient ($r^2 > 0.90$) indicates that adsorption data are best fitted in both Freundlich and Langmuir isotherms model. The high value of Freundlich constants K_f and n , i.e. 17.92 mg/g and 1.18 L/mg and Langmuir constants Q_0 and b 17.61 mg/g and 0.0026 L/mg for *A. niger* indicate its better adsorption capacity than *A. sydoni* and *P. janthinellum*.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Biosorption; Fungal biomass; Chromium(VI); Electroplating wastewater; Isotherms

1. Introduction

The presence of toxic heavy metal contaminants in aqueous streams, arising from the discharge of untreated metal containing effluents into water bodies, is one of the most important environmental issues. Cr(VI) in water bodies usually comes from several industrial processes such as electroplating, fertilizers, pigments, tanning, mining and metallurgical [1,2]. Chromium(Cr) naturally found in rocks, soil, plants, animals, volcanic dust and gases. Chromium exists primarily as the soluble, highly toxic Cr(VI) anions and the less soluble, less toxic Cr(III) species. A Cr(VI) salt showed higher mobility than Cr(III) and hence considered to be more toxic to human as well as animals and is associated with decreased plant growth and changes in plant morphology [3,4]. Conventional metal removal techniques such as reverse osmosis, solvent extraction, lime coagulation, ion

exchange and chemical precipitation are encountered with certain major disadvantages such as high energy requirements, incomplete metal removal and generation of a large quantity of toxic waste sludge due to various reagents used in a series of treatment such as reduction of Cr(VI), neutralization of acidic solution and precipitation [5,6]. Although investigations on effective remediation technologies of Cr(VI) from wastewater have been carried out from many years, successive applications are limited [7]. Biological method such as biosorption for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods [8]. Biosorption capacity of the heavy metals by inactivated cells might be greater, equivalent or less than that of living cells have been reported [9–11]. The use of dead microbial cells in biosorption is more advantageous for water treatment because they are not affected by toxic waste, and did not require a continuous supply of nutrient and can be regenerated and reuse for many cycles [12]. The use of dead fungal biomass has been preferred in numerous studies for biosorption of toxic metal ions from aqueous solution [13,14]. *Rhizopus* [5,15–17], *Aspergillus niger*, *Peni-*

* Corresponding author. Tel.: +91 9354312123; fax: +91 1662 276240.
E-mail address: nrbishnoi@gmail.com (N.R. Bishnoi).

cillium janthinellum [5,9,18] fungal biomass was selected by many researchers for bioremediation of Cr(VI) ions. Since their cell wall surface contained many functional groups of carboxyl, hydroxyl, sulfhydryl, amino groups, and phosphate group of lipids, proteins and polysaccharides having ability to bind metal ions [19,20]. The Cr(VI) was removed from aqueous solution through an “adsorption mechanisms” that the anionic chromate ion binds to positively charged groups such as amines of the dead fungal biomass [5]. Chromium exhibits different type of pH dependent equilibria in aqueous solution. As the pH shifted, the equilibrium will also be shifted. In the pH range 2.0–6.0, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions are in equilibrium. Above pH 8.0, CrO_4^{2-} is the only species that can exist in solution. At lower pH ($\text{pH} > 2.0$) values, $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ species are formed which results in decreased biosorption. Thus decrease in solution pH ($\text{pH} > 2.0$) causes the formation of more polymerized chromium oxide species [17,21,22]. The sorption capacity of biosorbent obtained from batch equilibrium experiments is useful in providing fundamental information about the effectiveness of metal biosorbent system. For industrial application, fungal biomass can be available in substantial quantities from variety of industrial fermentation processes, which could served as an economical and constant supply source of biomass for the removal of metal ions [19]. An attempt has been made in the present study (i) to determine the sorption capacity of dead fungal biomass of sp. *A. niger*, *A. sydoni* and *P. janthinellum* for Cr(VI) from aqueous and electroplating wastewater, (ii) to optimize various parameters, i.e. pH, biosorbent dose, initial metal ions concentrations, contact time and (iii) to evaluate the biosorption capacity of Cr(VI) using Freundlich and Langmuir isotherms.

2. Materials and methods

2.1. Preparation of synthetic solutions

0.2828 g of potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ (AR Grade) was dissolved in 1 L distilled water. This solution contains hexavalent chromium concentration of 100 mg/L used as stock solution.

2.2. Isolation of fungal strains

Metal resistant fungal strains were isolated from the soil samples of electroplating industry Luxmi Precision Screw Ltd., Rohtak, Haryana. The strains were maintained on solid Rose Bengal agar medium comprising (g/L): D-glucose, 10.0; bacteriological peptone, 5.0; potassium dihydrogen phosphate, 1.0; magnesium sulphate, 0.5; streptomycin, 0.03; Rose Bengal, 0.03; agar, 15.0 [23]. The fungal strains were identified from IARI, New Delhi.

2.3. Preparation of biomass

For experimental purpose, fungal species were cultivated in liquid phase using a rotating incubator. For *A. niger*, spores were transferred to 250 mL Erlenmeyer flasks filled with 100 mL of a culture medium composed of the following (g/L): bactodex-

trose, 20; bactopectone, 10; NaCl, 0.2; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.1; KCl, 0.1; K_2HPO_4 , 0.5; NaHCO_3 , 0.05; MgSO_4 , 0.25; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.005. The liquid phase pH was adjusted to 5.0 by the use of 1N HCl or 1N NaOH. Once inoculated, the flasks were shaken on a rotary shaker at 125 rpm for 5 days at 25 °C. *A. sydoni* and *P. janthinellum* were experimentally cultivated in broth Rose Bengal medium.

The biomass produced was collected by vacuum filtration and boiled in 0.5N NaOH solutions for 15 min. It was then washed with generous amounts of deionized water as long as the pH of the washing solution was in the near-neutral range (7.0–7.2). After washing, the biomass was dried at 60 °C for a period of 16 h and powdered to be used in biosorption tests in series. The moisture content of fungal biosorbent is 5%.

2.4. Characterization of wastewater sample

The characteristics of electroplating wastewater sample are listed in Table 1. They were determined according to APHA methods [24].

2.5. Batch experiment

The experiment was conducted for biosorption at concentration 30 mg/L of Cr(VI) ions, 0.5 g of biosorbent dose in 50 mL metal solution for 60 min with varying pH from 1.0 to 10.0. The pH value of the solution was adjusted using 1N HCl or 1N NaOH. Influence of biomass dose were studied ranging from 0.2 to 1.2 g for 50 mL of Cr(VI) solution in 250 mL of Erlenmeyer flask, while keeping the optimum pH from above experiments, temperature 25 °C and concentration of the Cr(VI) ions 30 mg/L. Effect of initial metal ions concentration on biosorption of Cr(VI) from 10 to 60 mg/L was studied. Effect of contact time was studied from 15 to 120 min at optimum conditions and samples were taken after an interval of 15 min. The optimum biomass dose and contact time observed from above experiments were applied for removal of Cr(VI) from electroplating industrial effluent whereas, concentration of Cr(VI) ions in the industrial effluent is 47 mg/L and pH of the wastewater is 2.2. The solutions were equilibrated for 1 h at 25 °C temperature on a mechanical

Table 1
Characteristics of the electroplating wastewater

Parameters	Characteristics
Colour	Dark green
Total dissolved solids	27,653 mg/L
Oil and grease	25 mg/L
pH	2.2
BOD	236 mg/L
COD	598 mg/L
Sulphate	450 mg/L
Phosphate	0.10 mg/L
Cr(VI)	47 mg/L
Copper	0.92 mg/L
Zinc	239 mg/L
Cyanide	16.0 mg/L
Iron	8.55 mg/L
Nickel	32 mg/L

shaker, then the filtrate was analyzed for residual Cr(VI) concentration using a spectrophotometer (ELICO SL-150) at 540 nm [24]. The amount of heavy metal ions adsorbed by the biomass was calculated using the following equation:

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q is the amount of heavy metal ions adsorbed by biomass (mg/g), C_0 the initial concentration of metal ions (mg/L), C_e the concentration of heavy metal ions at equilibrium (mg/L), V the volume of the metal solution (L) and W is the weight of adsorbent (g). All the experiments were conducted in triplicate and mean values were used in analyzing the data.

2.6. Adsorption isotherms

The adsorption isotherm is the initial experimental test step to determine feasibility of adsorption treatment and whether further test work should be conducted. It is a batch equilibrium test which provides data relating adsorbate adsorbed per unit weight to the amount of adsorbate remaining in the solution. Adsorption data for wide range of adsorbent concentration (0.2–1.2 g/50 mL) at 30 mg/L of Cr(VI) ions was described by the adsorption isotherms, such as Langmuir or Freundlich isotherms.

The Langmuir model can be described as [25,26]:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (2)$$

where q_e is the uptake of metal per unit weight of the adsorbent (mg/g), Q_0 the moles of solute sorbed per unit weight of adsorbent (mg/g), b the constant related to affinity between the biosorbents and biosorbate (L/mg) and C_e is the equilibrium (residual) concentration of ions (mg/L).

The constants, Q_0 and b are evaluated from the linear plot of the logarithmic equation:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{b Q_0 C_e} \quad (3)$$

The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecule is present on the adsorption surface, and the energy of adsorption is constant and that there is no migration of adsorbate molecule in the surface plane.

The Freundlich isotherm has the form [17,27]:

$$q = K_f C_e^{1/n} \quad (4)$$

The logarithmic form of the equation is given below:

$$\log q_e = \log K_f + \frac{1}{n \log C_e} \quad (5)$$

where q_e is the uptake of metal per unit weight of biosorbent (mg/g), C_e the equilibrium concentration of metal ions in solution (mg/L), K_f the Freundlich constants denoting adsorption capacity (mg/g) and n is the empirical constant, indicating of adsorption intensity (L/mg).

The value of K_f and $1/n$ were found by plotting the graph between $\log q_e$ and $\log C_e$, which is the residual chromium concentration and is calculated from the laboratory data. The value of $\log K_f$ is the intercept and value of $1/n$ is the slope of the plot. After finding the $\log K_f$, its antilog is found out to calculate K_f . A high ' K_f ' and ' n ' value is indication of high absorption through out the concentration range. A low ' K_f ' and high ' n ' indicates low adsorption through out the studied concentration range. A low ' n ' value indicates high adsorption at strong solute concentration [17,27].

The Freundlich model is basically empirical and was developed for heterogeneous surfaces. The model is a useful means of data description.

3. Results and discussion

3.1. Effect of pH

The removal of chromium by *A. niger*, *A. sydoni* and *P. janthinellum* at different pH of the test sample is shown in Fig. 1. The chromium concentration, adsorbent dose and time duration were kept constant (i.e. 30 mg/L, 0.5 g/50 mL and 60 min, respectively). The maximum percent removal of chromium(VI), i.e. $88.88 \pm 2.04\%$, $80.86 \pm 2.24\%$ and $78.53 \pm 2.28\%$ by *A. niger*, *A. sydoni* and *P. janthinellum* was observed at pH 2.0. In the pH range 2.0–6.0, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions are in equilibrium whereas, at lower pH ($\text{pH} > 2.0$), there is formation of more polymerized chromium oxide species such as $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ [17,21,22], which results in decrease in Cr(VI) removal. The optimum pH of the medium was also reported to be 2.0 for Cr(VI) adsorption using *S. equisimilis*, *S. cerevisiae* and *A. niger* [28,29]. As the pH of the system increases, the number of negatively charged sites increased and the number of positively charged sites decreased. A negatively charged surface site on the adsorbent does not favour the adsorption of anions due to the electrostatic repulsion [16]. This observation also agrees with the earlier reports on Cr(VI) removal by various

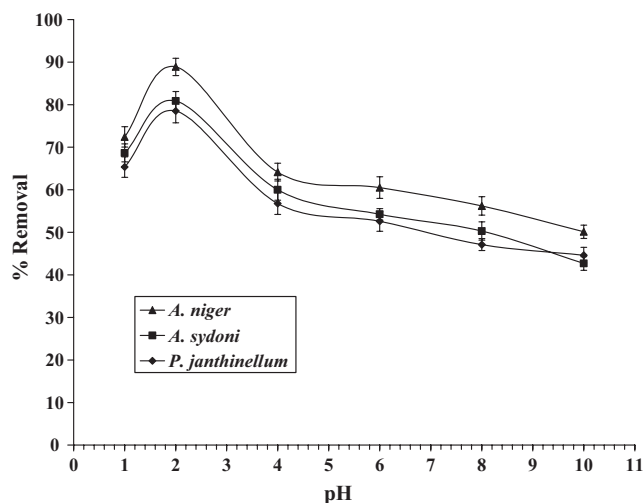


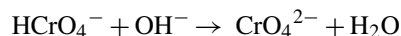
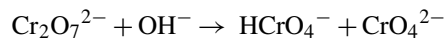
Fig. 1. Effect of pH on removal of Cr(VI) at initial Cr(VI) concentration 30 mg/L, fungal dose 0.5 g/50 mL, contact time 60 min, temperature 25 °C.

biosorbents [17,27,28,30]. The interaction between the metal ions and the microbial cell functional groups depend not only on the nature of the biosorbent used but also on the solution chemistry of the metal removal. The acquisition of charge by the biosorbent surface then facilitates interaction with species of opposite charges.

In acidic solution, the equilibrium is as follow:



The equilibrium in alkaline pH is given as:



It is apparent that for each mole of dichromate ion absorbed a maximum of 2 mol of hydroxyl ions are produced in the solution [17,31]. High adsorption capacity was observed at low pH 2.0; value may be attributed due to presence of large number of H^+ ions, which in turn neutralize the negatively charged adsorbent surface thereby, reducing hindrance to the diffusion of the dichromate ions at lower pH. The reduction in adsorption at higher pH may be possible due to the abundance of OH^- ions causing increased hindrance to diffusion of dichromate ions [32–34].

3.2. Effect of fungal dose

Cr(VI) removal by *A. niger*, *A. sydoni* and *P. janthinellum* as a function of adsorbent dose is shown in Fig. 2. The experiment was conducted with 30 mg/L test solution of Cr(VI), 60 min contact time, optimum pH 2.0 and fungal dose was varied from 0.2 to 1.2 g in 50 mL metal solution at 25 °C. Biosorption of Cr(VI) was observed to be $72.13 \pm 1.86\%$ at 0.2 g and $95.35 \pm 2.45\%$ at 1.2 g with fungal dose of *A. niger*, $66.60 \pm 2.36\%$ to $91.20 \pm 2.3\%$ with *A. sydoni* and in case of *P. janthinellum* it was observed

from $64.86 \pm 3.12\%$ to $91.09 \pm 2.8\%$ at 0.2–1.2 g in 50 mL of solution. As results showed that the removal of Cr(VI) was $91.03 \pm 2.27\%$ with *A. niger* at biosorbent dose 0.6 g/50 mL, whereas, $87.95 \pm 1.64\%$ and $86.61 \pm 1.62\%$ with *A. sydoni* and *P. janthinellum* at 0.8 g/50 mL and after that no appreciable amount of Cr(VI) ions removed from the solution. Actually a slow increase in Cr(VI) removal was observed after biomass dose of 0.6 g for *A. niger* and at 0.8 g/50 mL for *A. sydoni* and *P. janthinellum*. However a possible reason is that removal beyond an optimum dose may be attributed to the attainment of equilibrium between adsorbent and adsorbate at operating conditions. Before attainment of the equilibrium, the enhancement of metal sorption could be due to the increase in electrostatic interaction (relative to covalent interaction). After attainment of the equilibrium only marginal increase in adsorption rate of Cr(VI) was observed [35,36]. When an optimum amount has been sorbed, rate of adsorption decreased and desorption comes into play which considerably reduced the overall rate of removal. The adsorbed ions either blocked the access to the initial pores or caused particles to aggregate, thereby reducing the active site availability [37,38].

However, Cr(VI) uptake values showed a reverse trend, as it is a measure of the amount of Cr(VI) ions bound by unit weight of biomass and therefore, its magnitude decreased with increment in biomass dose 0.2–1.2 g/50 mL (Fig. 2). Adsorption capacity was decreased from 5.41 ± 0.14 to 1.19 ± 0.03 mg/g with *A. niger*, 4.99 ± 0.18 to 1.14 ± 0.029 mg/g and 4.86 ± 0.23 to 1.14 ± 0.35 mg/g with *A. sydoni* and *P. janthinellum*, respectively. The reason might be attributed to the fact that the high biomass concentration could make a “screen” effect on the dense outer layer protecting the binding sites from metal and thereby lowering the specific metal uptake at higher biomass loading [16]. Similarly, it has been reported that adsorption efficiency somewhat decreased with higher doses [39].

3.3. Effect of initial Cr(VI) ion concentrations

Cr(VI) removal by *A. niger*, *A. sydoni* and *P. janthinellum* as a function of initial metal ions concentration is shown in Fig. 3. The initial metal ions concentration was varied from 10 to 60 mg/L at temperature 25 °C. Therefore, the percentage of ions adsorbed at higher concentration level shows a decreasing trend, whereas uptake of ions displays opposite trend (Fig. 3). The percent removal was increased as the initial Cr(VI) concentration increased up to 30 mg/L but further increase in concentrations results in decrease in percent removal. Maximum percent removal of Cr(VI) was observed $90.88 \pm 2.9\%$, $87.28 \pm 1.48\%$ and $86.61 \pm 2.46\%$ with *A. niger*, *A. sydoni* and *P. janthinellum*, respectively, at 30 mg/L. This may be due to the saturation of the sorption sites and increase in the number of ions competing for the available binding sites in the biomass for complexation of Cr(VI) ions at higher concentration [6,17]. On the other hand, Cr(VI) uptake (mg/g) of the biomass increased with increase in concentration of Cr(VI) ions. Maximum adsorption capacity was observed 3.63 ± 0.13 mg/g with *A. niger*, whereas, 2.62 ± 0.06 and 2.43 ± 0.09 mg/g with *A. sydoni* and *P. janthinellum*, respectively, at higher concentration of 60 mg/L. The

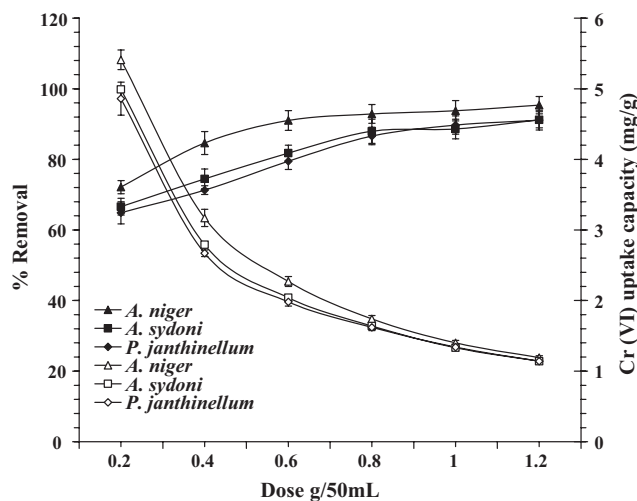


Fig. 2. Effect of fungal dose on the removal of Cr(VI) at initial Cr(VI) concentration 30 mg/L, pH 2.0, contact time 60 min, temperature 25 °C [(■) %removal; (□) uptake capacity (mg/g)].

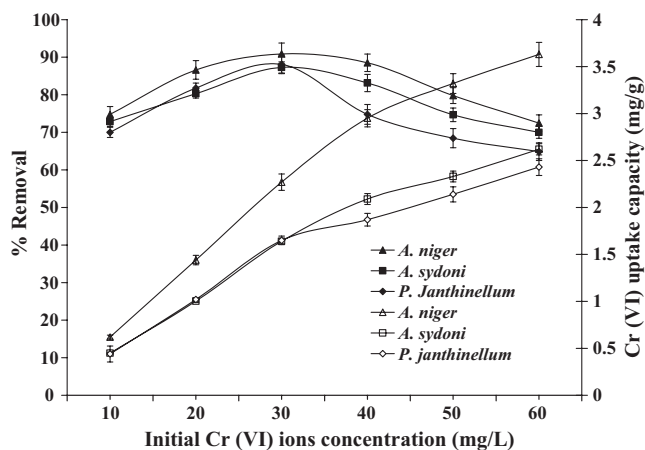


Fig. 3. Effect of initial metal ion concentration on removal of Cr(VI) at fungal dose 0.6 g/50 mL for *A. niger*, 0.8 g/50 mL for *A. sydoni* and *P. janthinellum*, time 60 min, temperature 25 °C [(■) %removal; (□) uptake capacity (mg/g)].

number of ions adsorbed from higher concentrations is more than that removed from less concentrated solutions. As higher ions concentration enhanced the mass transfer driving force, and increased the metal ions sorbed per unit weight of adsorbent at equilibrium [40]. In addition, increasing metal ions concentration increased the number of collisions between metal ions and sorbent, which enhanced the sorption process [17,40]. As the initial concentration of Cr(VI) increased from 25 to 250 mg/L loading capacity was also increased from 1.0 to 9.15 mg/g with *N. crassa* fungal biomass [41].

3.4. Effect of contact time

Chromium removal by various adsorbents as a function of contact time is shown in Fig. 4. The experiment was conducted at optimum initial chromium concentration of 30 mg/L, optimum dose were taken as 0.6 g for *A. niger* and 0.8 g for *A. sydoni* and *P. janthinellum* at optimum pH 2.0. It was observed

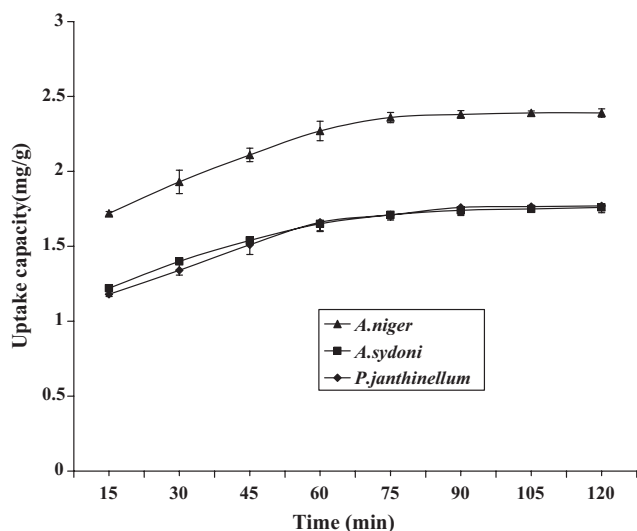


Fig. 4. Effect of contact time on removal of Cr(VI) at initial Cr(VI) concentration 30 mg/L, fungal dose 0.6 g/50 mL for *A. niger*, 0.8 g/50 mL for *A. sydoni* and *P. janthinellum*, temperature 25 °C.

from the results that uptake rate of Cr(VI) increased from 1.72 ± 0.012 to 2.39 ± 0.028 mg/g with *A. niger*, 1.22 ± 0.015 to 1.76 ± 0.036 mg/g with *A. sydoni* and 1.18 ± 0.015 to 1.77 ± 0.03 mg/g with *P. janthinellum* from 15 to 120 min. It showed that a major fraction of Cr(VI) gets sorbed onto biomass after 60 min and remained nearly constant afterwards. Similarly it was observed by Mohanty et al. [42], that the maximum removal of Cr(VI) was occurred in the initial stage, which gradually decreased and remains almost constant after an optimum period. It was also observed that the adsorption got slow down in later stages because initially a large number of vacant surface sites may be available for adsorption and after some time, the remaining vacant surface sites may be difficult to occupy due to repulsive forces between the solute molecules of the solid and bulk phase [43,44].

3.5. Adsorption isotherm of Cr(VI)

The Freundlich and Langmuir adsorption models were used for the mathematical description of the adsorption of Cr(VI) ions and isotherms constants were determined to compare the adsorption capacity of *A. niger*, *A. sydoni* and *P. janthinellum* for Cr(VI) ions. Fig. 5(a) and (b) shows typical sorption isotherms for chromium-adsorbent systems. For Freundlich isotherm, graph plotted between $\log q_e$ and $\log C_e$ yields a linear. A plot between $1/q_e$ and $1/C_e$ yields a linearized form of Langmuir isotherm.

The data have a high value of the correlation coefficient ($r^2 > 0.90$) (Table 2). In view of higher value of correlation coefficients indicate that adsorption data are best fitted in both Freundlich model and Langmuir model. The high value of Freundlich constants K_f and n , i.e. 17.92 mg/g and 1.18 L/mg for *A. niger* than *A. sydoni* and *P. janthinellum*, i.e. 8.06 mg/g and 0.95 L/mg, 9.05 mg/g and 1.10 L/mg, respectively, indicates better adsorption capacity of *A. niger*. The higher value of K_f indicates a high adsorption capacity. This is defined as the adsorbate adsorbed per unit weight of adsorbent. Higher the n ($n > 1$) value, higher is the intensity of adsorption [45]. The value of constants Q_0 and b were obtained by fitting the experimental data into Langmuir isotherm (Table 2). This data shows metal uptake Q_0 is higher 17.61 mg/g with *A. niger* than 9.07 mg/g with *A. sydoni* and 9.35 mg/g with *P. janthinellum* biomass and lower value of constant b indicate the high affinity of the biosorption of Cr(VI) with *A. niger*. The adsorption capacity of Cr(VI) is much higher than the biosorbents used by other workers, i.e. 2.66 mg/g for *A. niger* [46], 12.06 mg/g for *R. nigricans* [17], 11.10 mg/g for *R. arrhizus* free biomass and 9.00 mg/g for immobilized *R. arrhizus* fungal biomass [16], and 0.15 mg/g for *B. thuringiensis* [47].

Table 2
Freundlich and Langmuir constants for Cr(VI)

Biosorbents	Freundlich constants			Langmuir constants		
	r^2	K_f (mg/g)	n (L/mg)	r^2	Q_0 (mg/g)	b (L/mg)
<i>A. niger</i>	0.99	17.92	1.18	0.98	17.61	0.0026
<i>A. sydoni</i>	0.95	8.06	1.01	0.97	9.07	0.0022
<i>P. janthinellum</i>	0.91	9.05	1.10	0.95	9.35	0.0042

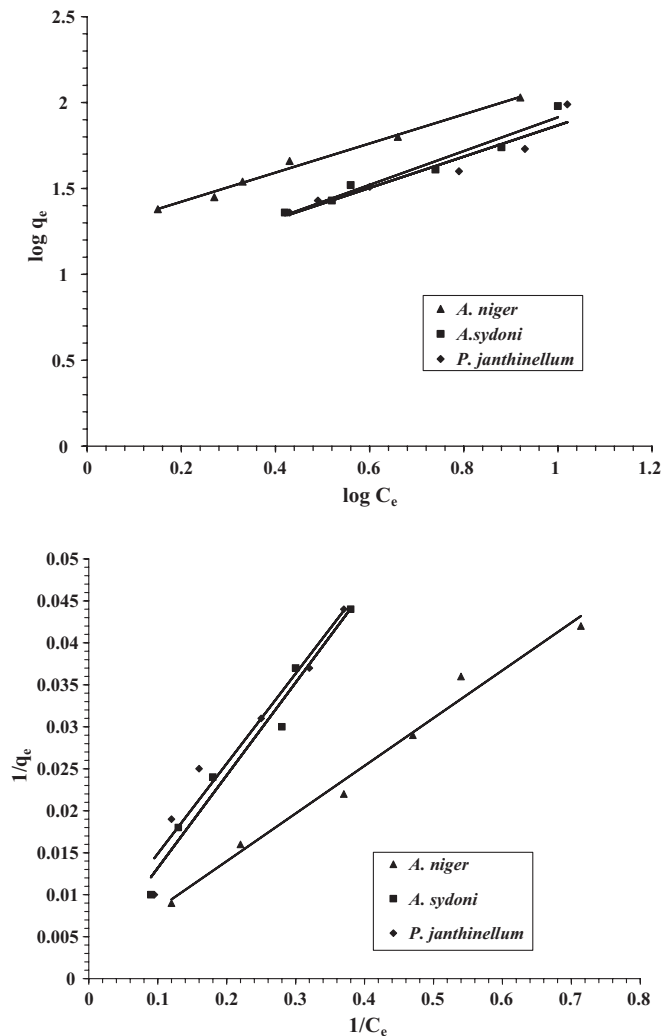


Fig. 5. (a) Freundlich isotherm for the adsorption of Cr(VI) at initial Cr(VI) concentration 30 mg/L, pH 2.0, time 60 min, temperature 25 °C. (b) Langmuir isotherm for the adsorption of Cr(VI) at initial Cr(VI) concentration 30 mg/L, pH 2.0, contact time 60 min, temperature 25 °C.

3.6. Sorption of Cr(VI) from electroplating wastewater

The results of percent removal of Cr(VI) by $71.18 \pm 2.86\%$ with *A. niger*, $65.32 \pm 2.10\%$ with *A. sydoni* and $62.59 \pm 1.34\%$ with *P. janthinellum*. There is some what less adsorption occurred in the wastewater sample as compared to synthetic sample. The decrease in percent removal may also be attributed due to presence of other metal ions like Cu, Zn, CN, Fe and Ni in wastewater as indicated in Table 1, which occupies the adsorption sites and therefore lesser Cr(VI) removal occurred. In the synthetic sample of potassium dichromate only Cr(VI) metal ions were present, so the binding sites on adsorbent surface were occupied by the single metal ions, so removal percent is greater than wastewater sample. It is also reported that there is a well-defined environment where only a single species of metal is present and byproduct adsorption in a complex industrial wastewater where more than one metal ion species are present [44,48].

4. Conclusions

The present study showed that fungal biosorbent can be considered as an alternative technology for sequestering Cr(VI) from electroplating effluent in batch process. Maximum biosorption of Cr(VI) were observed at pH 2.0, biomass dose 0.6 g/50 mL for *A. niger* and 0.8 g/50 mL for *A. sydoni* and *P. janthinellum*, metal ion concentration 30 mg/L in 60 min of contact time. Biosorption of Cr(VI) ions from electroplating wastewater was observed less than form aqueous solution, i.e. $71.18 \pm 2.86\%$ with *A. niger*, $65.32 \pm 2.10\%$ with *A. sydoni* and $62.59 \pm 1.34\%$ with *P. janthinellum* at optimum biosorbent dose and contact time. The adsorption equilibria data has been fitted very well to Langmuir as well as to Freundlich adsorption model. High value of Freundlich constants " K_f " 17.92 mg/g, " n " 1.18 L/mg for *A. niger*, than *A. sydoni* (8.06 mg/g, 1.01 L/mg) and *P. janthinellum* (9.05 mg/g, 1.10 L/mg) and Langmuir constants Q_0 17.61 mg/g, b 0.0026 L/mg for *A. niger* and 9.07 mg/g, 0.0022 L/mg and 9.35 mg/g, 0.0042 L/mg, respectively, for *A. sydoni* and *P. janthinellum* were indicated better adsorption intensity as well as better adsorption capacity of Cr(VI) by *A. niger*. The results showed that dead fungal biomass sp. *A. niger* is an efficient biosorbent for removal of Cr(VI) ions from aqueous solution and electroplating wastewater than *A. sydoni* and *P. janthinellum*. Further investigation is being made to prove the utility of these biosorbents for treating domestic and industrial effluent at pilot scale in continuous flow bioreactor system.

Acknowledgement

The authors are grateful to University Grants Commission, New Delhi for the financial grant supported for this investigation.

References

- [1] P. Kaewsarn, Q. Yu, Cadmium(II) removal from aqueous solution by pre-treated biomass of marine alga *padina* sp., Environ. Pollut. 112 (2001) 209–213.
- [2] A. Selatnia, M.Z. Bakhti, A. Madani, L. Kertous, Y. Mansouri, Biosorption of Cd(II) from aqueous solution by a NaOH-treated bacterial dead *Streptomyces rimosus* biomass, Hydrometallurgy 75 (2004) 11–24.
- [3] B.R. James, R.J. Bartlett, Plant–soil interaction of chromium, J. Environ. Qual. 13 (1984) 67–70.
- [4] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Chromium (update), US Department of Health and Human Services, 1998.
- [5] D. Park, Y.-S. Yun, J.M. Park, Use of dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics, Process Biochem. 40 (2005) 2559–2565.
- [6] S.R. Bai, T.E. Abraham, Studies on chromium(VI) adsorption–desorption using immobilized fungal biomass, Bioresour. Technol. 87 (2003) 17–26.
- [7] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250.
- [8] A. Kapoor, T. Viraraghavan, Fungal biosorption—an alternative treatment option for heavy metal bearing wastewater: a review, Bioresour. Technol. 53 (1995) 195–206.
- [9] N.R. Bishnoi, Garima, Fungus—an alternative for bioremediation of heavy metal containing wastewater: a review, J. Sci. Ind. Res. 65 (2005) 93–100.
- [10] F. Nuria, V. Isabel, M. Maria, M. Nuria, P. Jordi, S. Joan, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, Sep. Purif. Technol. 50 (2006) 132–140.

- [11] A. Kapoor, T. Viraraghavan, D. Roy Cullimore, Removal of heavy metals using the *Aspergillus niger*, *Bioresour. Technol.* 70 (1999) 95–104.
- [12] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the each biosorption of nickel(II) ions onto *Chlorella vulgaris*, *Process Biochem.* 1 (2002) 1–11.
- [13] A. Kapoor, T. Viraraghavan, Biosorption of heavy metals on *Aspergillus niger*, effect of pre-treatment, *Bioresour. Technol.* 63 (1998) 109–113.
- [14] A. Kapoor, T. Viraraghavan, Heavy metal biosorption sites in *Aspergillus niger*, *Bioresour. Technol.* 61 (1997) 221–227.
- [15] Y. Sag, B. Akcael, T. Kutsal, Evaluation, interpretation, and representation of three metal biosorption using a fungal biosorbent, *Process Biochem.* 37 (2001) 35–40.
- [16] S. Niyogi, T.E. Abraham, S.V. Ramakrishna, Removal of chromium(VI) ions from industrial effluents by immobilized biomass of *Rhizopus arrhizus*, *J. Sci. Ind. Res.* 57 (1998) 806–816.
- [17] S.R. Bai, T.E. Abraham, Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*, *Bioresour. Technol.* 79 (2001) 73–81.
- [18] H. Niu, S.X. Xu, J.H. Wang, B. Volesky, Removal of lead from aqueous solutions by *Penicillium* biomass, *Biotechnol. Bioeng.* 42 (1993) 785–787.
- [19] B. Volesky, Sorption Biosorption, BV Sorbex Inc., Montreal, St. Lambert, Quebec, Canada, 2003.
- [20] F. Vegilo, F. Beolchini, Removal of metals by biosorption—a review, *Hydrometallurgy* 44 (1997) 310–316.
- [21] C.L. Rollinson, Chromium, molybdenum and tungsten, in: Trotman-Dickenson (Ed.), *Comprehensive Inorganic Chemistry*, 3rd ed., Pergamon press, Oxford, 1973, pp. 691–694.
- [22] S. Mor, R. Khaiwal, N.R. Bishnoi, Adsorption of chromium from aqueous solution by activated alumina and activated charcoal, *Bioresour. Technol.* 8 (2006) 954–957.
- [23] J.P. Martin, Use of acid, Rose Bengal and streptomycin in the plate method for estimating soil fungi, *Soil Sci.* 69 (1950) 215–232.
- [24] A.D. Eaton, L.S. Clesceri, A.E. Greenberg, Standard methods for the examination of water and wastewater, American Public Health association (APHA), AWWA, WPCF, Washington, DC, 1995.
- [25] K.L. Shuttle-Worth, R.F. Unz, Sorption of heavy metals to the filamentous bacterium *Thiothrix* strain AI, *Appl. Environ. Microbiol.* 59 (1993) 1274–1282.
- [26] I. Langmuir, The adsorption of gases on plane surface of glass, mica, and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [27] S.R. Bai, T.E. Abraham, Studies on biosorption of chromium(VI) by dead fungal biomass, *J. Sci. Ind. Res.* 57 (1998) 821–824.
- [28] N. Goyal, S.C. Jain, U.C. Banerjee, Comparative studies on the microbial adsorption of heavy metals, *Adv. Environ. Res.* 7 (2003) 311–319.
- [29] D.C. Sharma, C.F. Forster, Continuous adsorption and desorption of chromium ions by sphagnum moss peat from acidic solution (pH 2), *Process Biochem.* 30 (1995) 293–298.
- [30] N.R. Bishnoi, M. Bajaj, N. Sharma, Adsorption of Cr(VI) from aqueous solution and electroplating wastewater, *Environ. Technol.* 25 (2004) 899–905.
- [31] M. Zhou, Y. Liu, G. Zeng, X. Li, W. Xu, T. Fan, Kinetics and equilibrium studies of Cr(VI) biosorption by dead *Bacillus licheniformis* biomass, *World J. Microbiol. Biotechnol.* 23 (2007) 43–48.
- [32] A. Bowers, C.P. Huang, Activated carbon processes for the treatment of chromium(VI) containing industrial wastewater, *Prog. Water Technol.* 12 (1980) 629–650.
- [33] J.S. Merrin, R. Sheela, N. Saswathi, R.S. Prakasham, S.V. Ramakrishna, Biosorption of chromium(VI) using *Rhizopus arrhizus*, *Indian J. Exp. Biol.* 36 (1998) 1052–1055.
- [34] Y.C. Sharma, Adsorption of Cr(VI) on wollastonite: effect of pH, *Indian J. Chem. Technol.* 8 (2001) 186–190.
- [35] N.R. Bishnoi, A. Pant, Garima, Biosorption of copper from aqueous solution using algal biomass, *J. Sci. Ind. Res.* 63 (2004) 813–816.
- [36] I.D. Mall, S.N. Upadhyay, Studies on treatment of basic dyes bearing wastewater by adsorptive treatment using flyash, *Indian J. Environ. Health* 40 (1998) 177–188.
- [37] B. Greene, Mcpherson, D.W. Darnall, Algal sorbents for selective metal ion recovery, in: J. Patterson, R. Pasino (Eds.), *Metal Speciation, Separation and Recovery*, Lewis, Michigan, 1987.
- [38] N. Kannan, T. Srinivasan, Natural adsorbents for water and wastewater treatment: a review, in: R.K. Trivedy (Ed.), *Eco Technologies for Pollution Control and Environmental Management*, Tata McGraw Hill Publ., New Delhi, 1997.
- [39] K.K. Pandey, G. Prasad, V.N. Singh, Removal of Cr(VI) from aqueous solutions by adsorption of flyash–wollastonite, *J. Chem. Technol. Biotechnol.* 34 (1984) 367–374.
- [40] Z. Aksu, Equilibrium and kinetic modeling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature, *Sep. Purif. Technol.* 21 (2002) 285–294.
- [41] S. Tunali, I. Kiran, T. Akar, Chromium(VI) biosorption characteristics of *Neurospora crassa* fungal biomass, *Miner. Eng.* 18 (2005) 681–689.
- [42] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Biosorption of Cr(VI) from aqueous solutions by *Eichhornia crassipes*, *Chem. Eng. J.* 117 (2006) 71–77.
- [43] M. Viswanadham, N. Sriramula, M.C. Adharvana, Removal of Zn(II) and Ni(II) ions by using a biopolymer chitin, *Indian J. Environ. Prot.* 20 (2000) 515–520.
- [44] R. Saravanane, T. Sundararajan, S. Sivamurthyreddy, Efficiency of chemically modified low cost adsorbents for the removal of heavy metals from wastewater: a comparative study, *Indian J. Environ. Health* 44 (2002) 78–81.
- [45] D.C. Sharma, C.F. Forster, A preliminary examination into the adsorption of hexavalent chromium using low cost adsorbents, *Bioresour. Technol.* 47 (1994) 257–264.
- [46] A. Kapoor, T. Viraraghavan, D.R. Cullimore, Removal of heavy metals using the fungus *Aspergillus niger*, *Bioresour. Technol.* 70 (1999) 95–104.
- [47] Y. Sahin, A. Ozturk, Biosorption of chromium(VI) ions from aqueous solution by the bacterium *Bacillus thuringiensis*, *Process Biochem.* 40 (2005) 1895–1901.
- [48] W.E. Marshall, E.T. Champagne, Agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater, *J. Environ. Sci. Health* 30 (1995) 241–261.