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RESEARCH ARTICLE

STUDIES ON ADSORPTION OF HEXAVALENT CHROMIUM USING *ASPERGILLUS NIGER*

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ABSTRACT

Adsorption has shown a promising solution for treating heavy metal contaminated water. The biosorption of Cr (VI) ions from synthetic aqueous solutions using dead and dried fungal biomass of *Aspergillusniger*, was studied under batch conditions. These experiments were performed to optimize the parameters: equilibrium time, initial pH of the solution (range: pH 2.52–12.1), biosorbent concentration (range: 1–20g/L) and adsorbate concentration (range: 10-500mg/L).From all these batch studies it was found that, the optimum parameters for this biosorption process were 360mins of contact time to reach equilibrium, initial solution pH 8, 1g/L of *A.niger* biomass concentration and 500mg/L of Cr(VI)concentration of the solution. With all these optimum factors, *A.niger* biosorption capacity of 198.21mg/g could be achieved. Langmuir and Freundlich isotherm models were studied for the biosorption process. Freundlich isotherm fitted best for the biosorption process followed by the Langmuir isotherm. Adsorption kinetic studies using pseudo-first order and pseudo-second order kinetic models were performed. The biosorption kinetics followed pseudo-second order kinetic model better than pseudo-first order kinetic model. These results indicate the potential use of *Aspergillusniger* biomass for removal of high Cr(VI) ion concentrations from industrial effluents.

INTRODUCTION

Advances in industrialization have contributed to the alarming increase in the discharge of metal pollutants into the environment directly or indirectly, especially into the aqueous environment. The most toxic heavy metal pollutants in water bodies are Hg, Pb, Cd, As and Cr (Vieira *et al*, 2000).Due to the serious health risks associated with drinking this metal contaminated water, it becomes imperative to treat heavy metals in industrial effluents before they are discharged into freshwater bodies. A number of physico-chemical conventional treatment methods have been developed over the years for their removal from aqueous solutions (Narayana Rao and Amal Dutta, 1995; Fenglian Fu *et al,* 2011). There is still a search for highly efficient yet economically attractive and environment friendly treatment methods for heavy metal removal.

Recently, adsorption has been proved to be an economical method for heavy metals' removal. Various natural materials of biological origin including microorganisms (living or non-living) can be utilized for adsorption; this form of adsorption is known as 'biosorption'. Biosorption is thus a metabolism–independent process. Metal ions being positively charged, could be adsorbed by complexing with negatively charged reactions sites on the cell surface. Due to its high surface area filamentous fungus is considered as better biosorbent than other microorganisms (Gadd, 1990; Paknikar *et al*, 1993; Rosenberger, 1975). Fungal biomass can be cheaply and easily procured as a by-product from various industrial fermentation processes. Strains of *Aspergillus* are being used in various industries such as, production of ferrichrome, kojic acid, gallic acid, itaconic acid, citric acid and enzymes like amylases, glucose isomerase, pectinase, lipases and glucanases (Gadd, 1993).

The heavy metal 'chromium', is a fourth period and sixth group chemical element. Among its several oxidation states, trivalent (Cr^{3+} and $CrOH^{2+}$) and hexavalent ($HCrO_4^-$ and $Cr_2O_7^{2-}$) species of chromium are mainly found in industrial effluents (Park *et al*, 2005). Cr(III) has relatively low toxicity than Cr(VI), seldom found in potable waters and would be a concern in drinking water only at very high levels of contamination (Anderson, 1997). Cr(VI) is a very strong oxidizing agent, therefore very fast in reacting and likely to form complexes. Thus, high concentrations of Cr(VI) are toxic and carcinogenic (Browning E., 1969; Kaufaman *et al*, 1970). Indian Standards (2012) has set 0.05mg/L to be the maximum contamination limit (MCL) for Cr(VI) ions in drinking water. The objective of the present work was to investigate and understand the factors influencing the biosorption of Cr(VI) ions onto dead and dried fungal biomass of *Aspergillus niger* and to analyze the best fit

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equilibrium adsorption isotherm model and adsorption kinetic model for the process.

MATERIALS AND METHODS

The materials used in this research work were Orbital Shaker, Autoclave, Laminar air flow, Hot air oven, UV-Visible Spectrophotometer (Optizen 3220U), pH meter, Table top centrifuge, Potassium Dichromate ($K_2Cr_2O_7$), Potato Dextrose Broth (PDB), Acetone, 1,5-diphenylcarbazide (DiPC), Concentrated Sulphuric acid (H_2SO_4), 250mL conical flasks, Mortar and pestle, sieve (0.25mm diameter pore size, No.60). The fungus, *Aspergillus niger* (NCIM No. 773) was procured from National Collection of Industrial Microorganisms (NCIM), NCL, Pune.

Preparation of biosorbent

The fungus was cultured in conical flasks containing PDB media, which were maintained at 28°C and 150rpm of orbital shaking. After the culture growth of 5-6 days (Figure 1), the fungus was filtered and then autoclaved at 121°C and 15lb pressure for 15mins. This dead fungus was then dried in hot air oven at 80°C for overnight. The dried fungus was then ground finely and sieved using a sieve of No.60. These fungal particles (Figure 2) were used as adsorbent in the biosorption process.

***Aspergillus niger* biomass**

Figure 1 Live *Aspergillus niger fungal* biomass cultured in PDB media for5-6 days in orbital shaker maintained at 28°C and 150rpm of orbital shaking.

Biosorbent particles

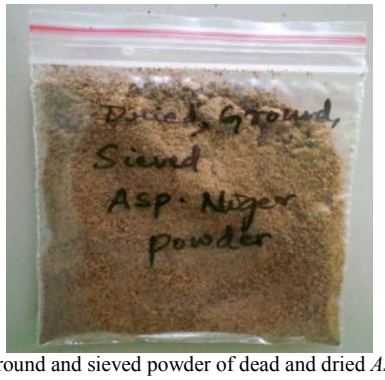


Figure 2 Ground and sieved powder of dead and dried *Aspergillus niger* biomass which were used as biosorbent particles in the present

Preparation of adsorbate solution

Synthetic solution of Cr(VI)ions of desired concentration (as adsorbate solution), was prepared by dissolving a calculated amount of potassium dichromate ($K_2Cr_2O_7$) in deionised water.

Batch biosorption studies

Laboratory batch mode biosorption studies were conducted to optimize the parameters namely contact time to reach equilibrium, initial pH of the solution, biosorbent concentration and adsorbate concentration. These studies were performed at constant temperature of 30°C and orbital shaking of 150rpm. All experiments were conducted in duplicates and their average readings were taken for the analysis purpose.

Optimization of contact time to reach equilibrium

This experiment was performed using 100ml of 100mg/l and 200mg/l Cr (VI) ion solutions, each having initial pH of 5.8. To each of these solutions, 0.3gm of *Aspergillus niger* biomass was added and then they were agitated for 420mins. Nearly 3ml of sample was drawn from each study solution in certain time intervals as shown in graphs and taken into different eppendorf tubes. Samples were collected frequently in the initial stage of the experiment.

Optimization of initial pH of the solution

100ml of Cr (VI) concentration solutions of 100mg/L and 200mg/L were taken in different flasks, adjusted to desired initial pH values (over the range 2.5-12.1), 0.3gm of *A.niger* adsorbent added and then agitated till the equilibrium time of 360mins. After the study,3ml of solution from each study flask was taken in different eppendorf tubes.

Optimization of biosorbent (A.niger biomass) concentration

600ml of 200mg/l Cr(VI) solution with initial pH of 7, was divided into flasks each containing 100 ml of the solution and to this, *A.niger* biomass in varied dosage range of 1 – 20g/L was added. The above process was repeated for Cr (VI) solutions with initial pH of 8. The study was performed for 360mins after which 3ml of the solution from each study flask was taken in different eppendorf tubes.

Optimization of adsorbate (Cr (VI) ion) concentration

The study was performed using various Cr(VI)concentrations ranging from 10 - 500mg/L with initial solution pH of 8. Each concentration was studied using biomass of 1g/L and 3g/L, separately. The study was performed for 360mins after which 3ml of the solution from each study flask was taken in different eppendorf tubes.

Analysis of concentration of Cr (VI) adsorbed

Solution depletion analysis was used to determine the amounts of each metal adsorbed by comparing the initial and final solution concentrations. The residual Cr(VI) ions were complexed with 1,5-diphenylcarbazide (DiPC) and then Cr(VI) ion concentration in the solution was determined colorimetrically at 540nm (Shateesh Kumar, 2011). A 0.25% w/v solution of DiPC was prepared in 50% acetone. The study

samples taken in the eppendorf tubes were centrifuged soon after they were collected. From the supernatant liquid, 1mL of the liquid was taken into a test tube to which 0.7mL of 6N H_2SO_4 was added followed by 0.2mL of 0.25% DiPC and the total volume was made to 10mL using deionised water. The solution was then left for 10mins to develop its color into red-violet. This coloured complex solution was then analyzed in a UV-Visible Spectrophotometer at a wavelength of 540nm.

Analysis of the biosorption process

Batch biosorption studies

Biosorption capacity of the biosorbent was calculated for each sample and the parameter was then optimized by plotting biosorption capacity vs. the parameter. Biosorption capacity, $C_i=\frac{(C_o-C_i)*V}{m}$…. (Equation 1) Where, C_o is the initial adsorbate concentration (mg/L) and C_i is the biosorption capacity of the adsorbent i.e. the mass of adsorbate adsorbed per unit mass of adsorbent (mg/g dry weight) at every equilibrium concentration of C_i.

Equilibrium data (Adsorption isotherms)

The equilibrium data of the biosorption process was obtained by studying the adsorption isotherms using the results obtained from adsorbate concentration variation studies. Langmuir isotherm and Freundlich isotherm were plotted using their respective linear equations. Based on the fitting of the straight line in both these plots, the best fit isotherm model was found. The equations developed from these isotherm models can be used to represent the equilibrium pattern of the biosorption process.

The linear Langmuir isotherm equation can be represented as (Langmuir, 1916):

$$\frac{C_i}{Q_i} = \frac{C_i}{Q_{max}} + \frac{1}{(Q_{max} * k_L)} \quad \text{….(Equation 2)}$$

Where, Q_{max} is the maximum biosorption capacity (monolayer capacity) and k_L is the Langmuir equilibrium constant of the system, related to the bonding energy(affinity) of the binding sites (L/mg). A plot of C_i/Q_i vs. C_i is the Langmuir isotherm. Langmuir isotherm indicates homogenous adsorption surface and monolayer coverage on it. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter 'R_L', which is defined by

$$R_L = \frac{1}{[1+ (k_L * C_o)]} \quad \text{… (Equation 3)}$$

R_L indicates the shape of the isotherm as in Table 1

The linear Freundlich equation is in logarithmic form, as (Freundlich, 1906)

$$\mathbf{Ln(Q_i) = Ln(k_F) + (1/n)\ Ln(C_i)}$$. (Equation 4)

Table 1 Type of Isotherm for various R_L

R_L	Type of Biosorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Where, k_F is the Freundlich adsorption equilibrium constant, indicative of adsorption capacity [(mg/g)(l/mg)$^{1/n}$]. 'n' is a Freundlich constant, indicative of biosorption intensity. A plot of $Ln(Q_i)$ vs. $Ln(C_i)$ is the Freundlich isotherm. Freundlich isotherm model is an empirical equation used to describe sorption on a heterogeneous surface. It is a multisite adsorption isotherm for rough surfaces.

Kinetic data (Adsorption kinetics)

The kinetic data of the biosorption process was studied through adsorption kinetic models using the results obtained from contact time variation studies. Pseudo-first order and pseudo-second order kinetic models were plotted using their respective linear equations. Based on the fitting of the straight line in both these plots, the best fit kinetic model was found. The equations developed from these kinetic models can be used to represent the kinetics of the biosorption process.

The pseudo-first order kinetic model expression was given by Lagergren and Svenska, which can be written as (Lagergren, 1898):

$$\mathbf{Ln(Q_{eq,exp} - Q_i) = Ln(Q_{eq,cal}) - (k_1 * t)} \quad \text{…. (Equation 5)}$$

Where, $Q_{eq,exp}$ is the experimental value of maximum equilibrium biosorption capacity observed from the graph Q_i vs. time (mg/g); $Q_{eq,cal}$ is the calculated value of maximum equilibrium biosorption capacity calculated from the intercept of pseudo-first order kinetic graph (mg/g) and k_1 is the pseudo-first order equilibrium rate constant (1/min).

The plot $Ln(Q_{eq,exp} - Q_i)$ vs. t gives the pseudo-first order kinetic graph. The pseudo-first order kinetic equation can be applied only for the rapid initial stage and is not appropriate for the entire process. The pseudo-second order kinetic rate equation is given by Ho and McKay and is expressed as (Ho and McKay, 1999):

$$\frac{t}{Q_i} = \frac{1}{(k_2 * Q_{eq,cal}^2)} + \frac{t}{Q_{eq,cal}} \quad \text{…. (Equation 6)}$$

Where k_2, is pseudo-second order equilibrium rate constant (g/mg.min). The plot t/Q_i vs. t gives the pseudo-second order kinetic graph. The pseudo-second order rate equation is based on chemical adsorption, especially chemical bonding among divalent metal ions and polar functional groups on biomass (Ho, 2006).This kinetic equation can be applied to the entire adsorption process.

RESULTS AND DISCUSSION

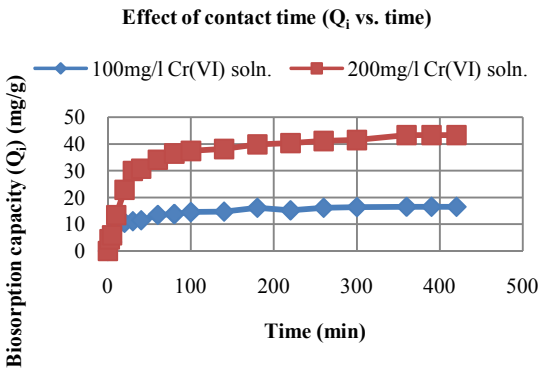
Batch Biosorption Studies

The optical density values (OD) of the samples were deduced from the calibration graph drawn using the standard Cr(VI) solutions.

Effect of contact time to reach equilibrium

The result of effect of contact time is as shown in Graph 1.

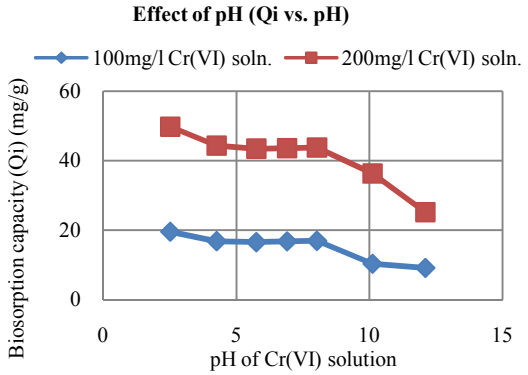
The biosorption capacity increases sharply in the initial stages and then slowly reaches to a plateau stage. The initial rapid stages are attributed to the abundant availability of active binding sites on the particles of *A.niger* biomass. With gradual occupancy of these sites, the biosorption becomes less efficient in the later stages. In both the Cr (VI) solutions the equilibrium was found to reach at 360mins. Thus, the next studies were carried out for 360mins. The Cr (VI) solution of 200mg/L took longer time to attain equilibrium than for 100mg/L, due to the presence of proportionally high amount of metal ions. The maximum biosorption capacity of the biomass in 100mg/L Cr(VI) solution was found to be 16.57mg/g and 43.36mg/g in 200mg/L Cr(VI) solution.



Graph 1 Effect of contact time variation on biosorption capacity (Q_i) of *A.niger* biomass.

Effect of initial pH of the solution

The result of effect of initial pH of the Cr(VI)solution is as shown in Graph 2. The pH of the heavy metal solution not only influences the solution chemistry but also the activity of the functional groups on the biomass surface.



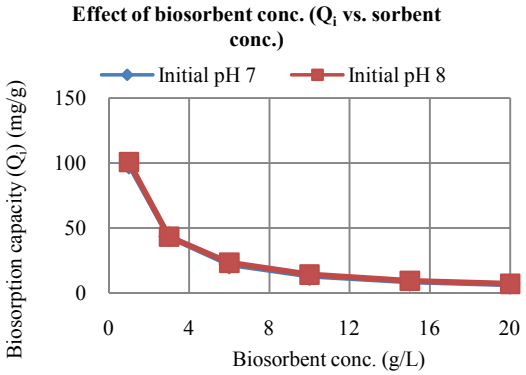
Graph2 Effect of initial pH variation on biosorption capacity (Q_i) of *A.niger* biomass.

The biosorption capacity decreases slowly as the pH of the solution increases, except in the solutions of pH range 5.75 – 8.03 where a slight increase in the biosorption capacity was found. As reported by Nikola Stanic (2010), chromium species form (complexed) compounds depending on the pH of the solution. In the pH range 2-6, $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions are in equilibrium. At still lower pH values (pH < 2.0) values, $Cr_3O_{10}^-$ and $Cr_4O_{13}^{2-}$ species are formed (Hunt, 1965). The only species that can exist in solution above pH 8 is $(CrO_4)^{2-}$. In the biosorption process, the adsorbent surfaces are highly protonated and thus favor the uptake of the anionic forms of Cr(VI). Thus, higher the pH of the solution, lesser is the protonation and thus less is the biosorption of the anionic forms of chromium (Tunali *et al,* 2005).

The biosorption capacity of the biomass was found to be the maximum in the solution with initial pH 2.52. But the pH of the industrial effluents containing chromium ions was observed to be in the range of pH 7 – 12 (Narayana Rao and Amal Dutta, 1995). Thus, considering the pH range 6.91 – 12.1 from the study (which includes the range of pH 7-12) (for biosorption process in large scale), it was found that the maximum biosorption capacity of the biomass was attained when the initial pH of the solution was 8.03 (16.86mg/g and 43.72mg/g biosorption capacity for 100mg/L and 200mg/L Cr(VI) solution, respectively), followed by solution with initial pH of 6.91 (16.71mg/g and 43.58mg/g biosorption capacity for 100mg/L and 200mg/L Cr(VI) solution, respectively). The biosorption capacities at all the pHswere found to be higher for 200mg/L initial Cr(VI) solution rather than for 100mg/L initial Cr(VI) solution. Thus, the next studies were conducted with 200mg/L Cr(VI) solution having its initial solution pH as 7 and 8 which were found to be optimum for the biosorption process.

Effect of biosorbent (A.niger biomass) concentration

The result of effect of *A.niger* biomass concentration on the biosorption of Cr (VI)ions is as shown in Graph 3. In this study, the biosorption capacity of the biosorbent decreased with increase in biomass concentration. Gadd and White (1993) explained this phenomenon by hypothesizing that an increase in biomass concentrations leads to interference between binding sites. The biosorption capacities were found to be approximately equal for both the Cr(VI) solutions with initial pH 7 and 8. The highest metal uptake was found to be at biosorbent concentration of 1g/L (99.98mg/g and 100.9mg/g at initial solution pH of 7 and 8, respectively), followed by 3g/L biosorbent concentration (43.49mg/g and 43.4mg/g at initial solution pH of 7 and 8, respectively). Thus, 1g/l and 3g/l were considered to be the optimum biomass concentration for the biosorption process and these concentrations were used in the next studies.

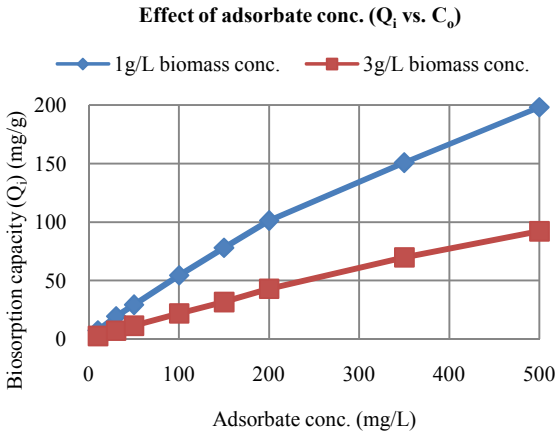


Graph 3 Effect of biomass concentration variation on biosorption capacity (Q_i) of *A.niger* biomass.

Effect of adsorbate (Cr(VI)) concentration

The result of effect of Cr (VI) concentration on the biosorption of Cr (VI) ions is as shown in Graph4. The biosorption capacity of the biomass increased steeply with an increase in Cr (VI) concentration in the solution. The maximum biosorption

capacity of *A.niger* was found to be at 500mg/L of initial Cr(VI) concentration of the solution for both the biosorbent concentrations (198.21mg/g for 1g/L and 92.1mg/g for 3g/L biosorbent concentrations). This is probably due to higher interaction between the metal ions and metal sequestering sites of biosorbent, in higher Cr(VI) concentration solutions. Thus the optimum adsorbate concentration was considered to be 500mg/L. At every initial Cr(VI) concentration, 1g/L biomass concentration showed more uptake capacity than 3g/L biomass concentration. Thus the biosorbent concentration of 1g/L was considered to be the optimum for the biosorption process.



Graph 4 Effect of adsorbate concentration variationon biosorption capacity (Q_i) of *A.niger* biomass.

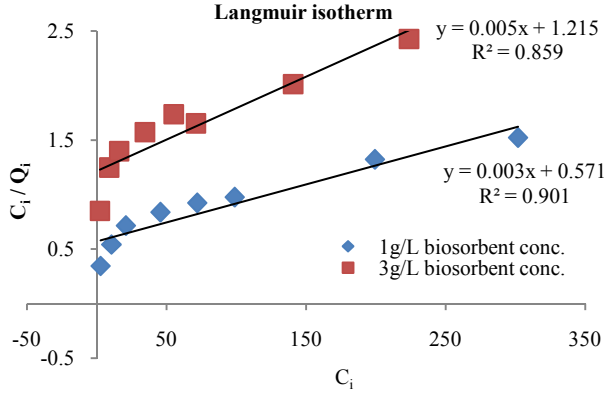
Equilibrium data (Adsorption isotherms)

Equilibrium isotherm experiments of Langmuir and Freundlich models were conducted and the results are as shown in Graphs5 and 6. The equilibrium parameters determined by the two isotherm models and their corresponding correlation coefficients (R^2) are listed in Table 2.According to the literature, high k_L values and high Q_{max} values of Langmuir isotherm and high k_F values of Freundlich isotherm are favourable for any biosorption process (Kratochvil and Volesky, 1998). If the value of 1/n lies between 0 and 1, it indicates beneficial adsorption (Yadava *et. al.*, 1991). From Table 2, it was seen that the solution containing 1g/L biomass concentration had high k_L value, high Q_{max} value and high k_F value, thus indicating 1g/L concentration to be the most optimum biomass concentration for the biosorption process. Biosorption studies also indicated 1g/L biomass concentration to be optimum for the process. Thus, the batch studies and the equilibrium studies satisfy each other. For both the biosorbent concentrations, '1/n' values were found to be between 0 and 1 under the studied conditions, indicating beneficial adsorption.

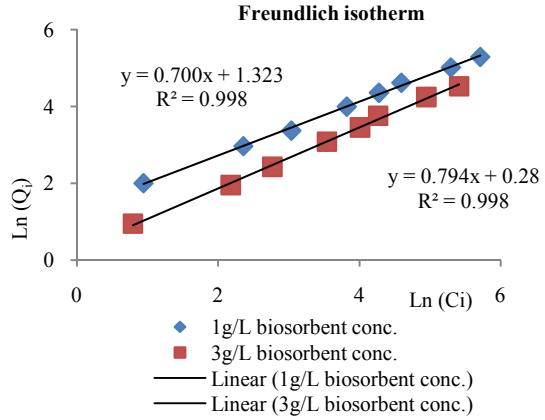
Freundlich isotherm was found to have a higher correlation coefficient than that of the Langmuir isotherm. Thus, Freundlich isotherm could be considered more suitable to the biosorption process. The obedience of the biosorption process to Langmuir isotherm was examined using another characteristic of Langmuir isotherm, i.e. equilibrium factor, 'R_L', presented as in Equation 3. R_L values for different initial concentrations of Cr(VI)were plotted against the initial Cr(VI) concentrations (C_o) as shown in Graph 7.

Table 2 The Langmuir and Freundlich constants of the biosorption process

Isotherm models	Langmuir constants			Freundlich constants		
	Q_{max}	k_L	R^2	n	k_F	R^2
For 1 g/L conc. of biosorbent	333.3333	0.0053	0.9013	1.4280	3.7576	0.9982
For 3 g/L conc. of biosorbent	149.2537	0.0047	0.8593	1.2588	1.3231	0.9980



Graph 5 Langmuir Isotherm model for Cr(VI) biosorption using *A.niger* biomass.



Graph 6 Freundlich isotherm model for Cr (VI) biosorption using *A.niger* biomass

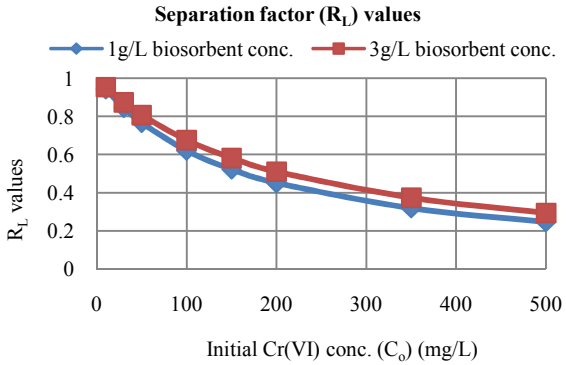
Freundlich isotherm was found to have a higher correlation coefficient than that of the Langmuir isotherm. Thus, Freundlich isotherm could be considered more suitable to the biosorption process. The obedience of the biosorption process to Langmuir isotherm was examined using another characteristic of Langmuir isotherm, i.e. equilibrium factor, 'R_L', presented as in Equation 3. R_L values for different initial concentrations of Cr (VI) were plotted against the initial Cr(VI) concentrations (C_o) as shown in Graph 7.

Considering Table 1, as the R_L values were between 0 and 1 for all the initial concentrations of chromium, Langmuir isotherm could be considered to be favorable for biosorption of Cr(VI) ions using dried biomass of *A.niger*. But as the correlation coefficients of Langmuir isotherm were lesser than that of Freundlich isotherm, it appeared that the Freundlich isotherm fitted the biosorption model better than Langmuir isotherm. The fit of Freundlich isotherm model indicates that the biosorption of Cr(VI) onto *A.niger* is multilayer or heterogeneous surface biosorption.

The Langmuir and Freundlich equations for the present study can be represented as following:

Langmuir isotherm equations:

For 1g/L biosorbent concentration
$(C_i/Q_i) = 0.003\ C_i + 0.5714$

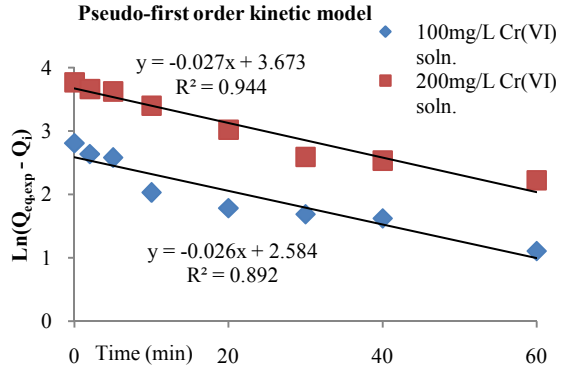


Graph 7 R_L values at different initial concentrations of adsorbate (C_o) plotted against C_o.

For 3g/L biosorbent concentration
$(C_i/Q_i) = 0.0058C_i + 1.2156$
Freundlich isotherm equations:
For 1g/L biosorbent concentration
$Ln(Q_i) = 0.7003\ Ln(C_i) + 1.3238$
For 3g/L biosorbent concentration:
$Ln(Q_i) = 0.7944\ Ln(C_i) + 0.28$

Kinetic data (Adsorption kinetics)

Kinetic experiments of pseudo-first order and pseudo-second order were conducted and the results are as shown in Graphs8 and 9. The kinetic parameters determined by the two models and their corresponding correlation coefficients (R^2) are as listed in Table 3.

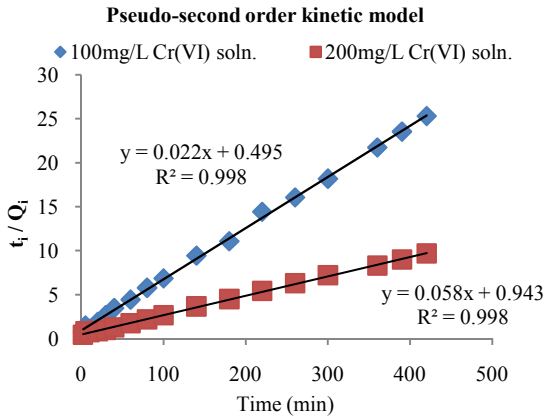


Graph 8 Pseudo-first order kinetic model for Cr(VI) biosorption using *A.niger* biomass.

Table3 Kinetic parameters of the two kinetic models

Kinetic models	Pseudo - first order constants			Pseudo - second order constants		
	$Q_{eq,cal}$	k_1	R^2	$Q_{eq,cal}$	k_2	R^2
100 mg/L of Cr(VI) soln.	13.2579	0.0265	0.8922	17.2117	0.0036	0.9989
200 mg/L. of Cr(VI) soln.	39.3817	0.0273	0.9449	45.4545	0.0098	0.9989

According to the literature, high k_1 and k_2 values are favorable for the biosorption process. The closeness betweenQ_{max} (i.e. $Q_{eq,exp}$) from the contact time studies and $Q_{eq,cal}$from kinetic studies determines favorability of the biosorption process.



Graph 9 Pseudo-second order kinetic model for Cr (VI) biosorption using *A.niger* biomass.

The k_1 and k_2 values of 200mg/L Cr(VI) solution were found to be higher than that of 100mg/L Cr(VI) solution, indicating 200mg/L Cr(VI) to be the optimum adsorbate concentration than 100mg/L. Thus, the kinetic studies satisfied the batch biosorption studies. From the contact time studies, it was observed that the Q_{max} (i.e. $Q_{eq,exp}$) values were 16.57mg/g and 43.36mg/g for 100mg/L and 200mg/L concentration of Cr(VI) solution concentration, respectively. $Q_{eq,cal}$ values from Table 3 were found to be approximately equal to their respective $Q_{eq,exp}$ values. Comparing, $Q_{eq,cal}$ values of pseudo-first order kinetics and $Q_{eq,cal}$values of pseudo-second order kinetics, it was observed that $Q_{eq,cal}$ values of pseudo-second order kinetics were more near to $Q_{eq,exp}$ values. On the basis of the higher R^2 values, the pseudo-second order kinetic model was considered to be a better fit to the biosorption data followed by the pseudo-first order model. This result demonstrated that the rate-limiting step for biosorption may be chemical biosorption involving covalent forces through sharing or the exchange of electrons between *A.niger* biomass and Cr(VI) metal ions. The pseudo-first order and pseudo-second order equations for the present study can be given as:
Pseudo-first order kinetic equation:

For 100mg/L Cr(VI)concentration solution:
$Ln(Q_{eq,exp} - Q_i) = -0.0265\ t + 2.5846$
For 200 mg/L concentration of Cr(VI) solution:
$Ln(Q_{eq,exp} - Q_i) = -0.0273\ t + 3.6733$
Pseudo-second order kinetic equations:
For 100 mg/L Cr(VI)concentration solution:
$(t / Q_i) = 0.0581\ t + 0.943$
For 200 mg/L Cr(VI)concentration solution:
$(t / Q_i) = 0.022\ t + 0.495$

CONCLUSIONS

Batch experiments on biosorption of Cr(VI) ions from the aqueous solution using dead and dried biomass of *Aspergillus niger* biomass, were performed to optimize the parameters: equilibrium time, initial pH of the solution (range: pH 2.52–12.1), biosorbent concentration (range: 1–20g/L) and adsorbate concentration (range: 10-500mg/L). From all these equilibrium batch studies it was concluded that, the optimum parameters for the present biosorption process were 360mins of contact time to reach equilibrium, initial solution pH 8, 1g/L of *A.niger*

biomass and 500mg/L of Cr(VI)concentration of the solution. With all these optimum factors *A.niger* biosorption capacity of 198.21mg/g could be achieved. Freundlich isotherm model fitted best for the biosorption of Cr(VI) ions followed by the Langmuir isotherm model, indicating that the biosorption of Cr(VI) ions onto *A.niger,* is multilayer and a heterogeneous surface biosorption. The biosorption kinetics of Cr(VI) onto *A.niger* biomass followed pseudo-second order kinetic model (which was based on chemical biosorption) more than pseudo-first order kinetic model and that the kinetic data fitted the equilibrium data. Thus, dried *Aspergillus niger* biomass can be used as potential low-cost and eco-friendly biosorbent for the effective removal of Cr(VI) ions from the aqueous solutions and thus from industrial effluents too.

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