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Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*

Yasmin Khambhaty, Kalpana Mody*, Shaik Basha, Bhavanath Jha

Discipline of Marine Biotechnology and Ecology, Central Salt and Marine Chemicals Research Institute (Council of Scientific and Industrial Research), GB Marg, Bhavnagar-364002, Gujarat, India

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ABSTRACT

Quite a number of reports are available on metal binding capacity of different groups of microorganisms. However, reports on the equilibrium studies on biosorption by marine fungi are quite inadequate. The present study was carried out in a batch system using dead biomass of marine *Aspergillus niger* for the sorption of Cr(VI). The removal rate of Cr(VI) was increased with a decrease in pH and an increase in Cr(VI) and biomass concentration. *A. niger* exhibited the highest Cr(VI) uptake of 117.33 mg g^{-1} of biomass at pH 1.0 in the presence of 400 mg l^{-1} Cr at 50 °C. Kinetics studies based on fractional power, zero order, first order, pseudo-first order, Elovich, second order and pseudo-second order rate expressions have also been carried out. The experimental data were analyzed using five, two-parameter isotherms (Langmuir, Freundlich, Dubinin–Radushkevich, Temkin and Halsey). It was observed that Langmuir model exhibited the best fit to experimental data. Thermodynamic parameters of the biosorption (ΔG°, ΔH° and ΔS°) were also determined.

1. Introduction

Wastewater and effluents contaminated with heavy metals is a serious environmental problem. Current treatment processes, for metal containing wastewaters are reported to exhibit reduced efficiency at low concentrations. Increasing interest is observed in the application of biological materials for heavy metal removal from diluted, large volume solutions. Biosorption has become a method of choice as compared to traditional methods of wastewaters treatment such as precipitation, adsorption, coagulation, etc. as it is economically and environmentally more viable [1–4].

Chromium is one of the major contaminant in the wastewaters of dyes and pigments, film and photography, galvanometric and electric, plating and electroplating, leather and mining industries [5]. Chromium exists in several oxidation states out of which Cr(III) and Cr(VI) are the most stable forms. Because of its high toxicity and potential carcinogenicity Cr(VI) is of special concern [6]. The US EPA has set the discharge limit of Cr(VI) to surface water below 0.05 mg l^{-1} while the total Cr including Cr(III), Cr(VI) and its other forms to below 2 mg l^{-1} [7].

Reports on marine fungi as potential biosorbents of hexavalent chromium are very scanty. Babich and Stotzky [8] revealed that the growth of some marine fungi exposed to nickel was less depressed in the presence of magnesium as compared to that of in the presence of nickel alone. Hicks and Newell [9] found that exposing *Phaeospharia typharum*, a salt marsh fungus, to mercury at metal concentration of 0.74 mg l^{-1} resulted in no significant change in glucosamine content or growth as compared to the cultures grown in the absence of mercury. In another study, Vala et al. [10] have performed a preliminary study on the tolerance and accumulation of hexavalent chromium by two seaweed associated *Aspergilli* where luxuriant growth was observed in the presence of 100 mg l^{-1} Cr(VI) concentration. Taboski et al. [11] revealed the effect of lead and cadmium on the growth of two species of marine fungi, *Corollospora lacera* and *Monodictys pelagica*.

In the present study, dead biomass of a marine fungus, *Aspergillus niger* was used as biosorbent for the removal of Cr(VI). The aim of the present investigation was to study the sorption kinetics, to establish the kinetic rate coefficients for sorption of Cr(VI) by *A. niger*, biosorption equilibrium employing different two-parameter isotherm models as well as thermodynamic studies.

2. Experimental

2.1. Preparation of dead fungal biomass

A. niger was cultivated in the medium containing (per liter of seawater) boiled and smashed potato 250 g and dextrose 20 g and incubated at 30 ± 2 °C. After 7 days of incubation, the live

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* Corresponding author. Tel.: +91 278 2561354; fax: +91 278 2570885/67562.
E-mail address: khmody@csmcri.org (K. Mody).

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Nomenclature

b_{Te}	constant in Temkin adsorption isotherm (J mol^{-1})
B	constant in D–R adsorption model (mol^2 kJ^{-2})
C_{e}	equilibrium concentration of adsorbate in solution (mg l^{-1})
C_{i}	initial concentration of adsorbate in solution (mg l^{-1})
d	parameter in Temkin isotherm
e	Polanyi potential (kJ mol^{-1})
E	mean free energy (kJ mol^{-1})
ΔG°	change in Gibbs free energy (J mol^{-1})
h	initial sorption rate in pseudo-second model (mg g^{-1} min^{-1})
ΔH°	enthalpy change (kJ mol^{-1})
k	fractional power model constant
k_1	Lagergren's sorption isotherm rate constant (min^{-1})
k_2	second order sorption rate constant (g mg^{-1} min^{-1})
$k_{2\mathrm{p}}$	pseudo-second order sorption rate constant (g mg^{-1} min^{-1})
k_{p}	initial rate of the intraparticle diffusion (mg g^{-1} min$^{-0.5}$)
K_{F}	Freundlich isotherm constant (l g^{-1})
K_{H}	Halsey isotherm constant
K_{L}	Langmuir isotherm equilibrium binding constant (l mg^{-1})
K_{T}	Temkin isotherm constant (l mg^{-1})
m	number of experimental data points
n	exponent in Freundlich isotherm
n_{H}	Halsey isotherm constant
p	number of parameters in the adsorption isotherm
q_{e}	amount of adsorbate adsorbed at equilibrium (mg g^{-1})
q_i	observed sorption capacity of batch experiment i
q_{m}	maximum sorption capacity (mg g^{-1})
q_t	amount of sorbate sorbed at time t (mg g^{-1})
Q_i	estimated sorption capacity of batch experiment i
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
R_{L}	Langmuir separation factor
R^2	correlation coefficient
ΔS°	entropy change (kJ mol^{-1} K^{-1})
S.E.	standard error
SSE	sum of squares error
t	time (min)
T	absolute temperature (K)
v	fractional power model constant
V	volume of metal solution (l)
W	mass of sorbent (g)

Greek symbols

α_{E}	initial sorption rate in Elovich model (mg g^{-1} min^{-1})
β_{E}	desorption constant in Elovich model (g mg^{-1})

fungi was harvested and killed by boiling in 0.5N NaOH solution for 15 min and then washed repeatedly with deionized water till neutrality. After washing, the biomass was dried at 50 °C for 24 h and powdered in a mortar and pestle [12]. The dried biomass was stored in a desiccator and used for the following experiments. The surface area, pore volume and pore size of *A. niger* were measured by surface area analyzer (Micromeritics, ASAP 2010) and is given in Table 1.

Table 1
Characteristics of marine fungi *Aspergillus niger*

Parameter	Fungal biomass
Surface area	
Single point surface area (m^2 g^{-1})	3.4037
BET surface area (m^2 g^{-1})	3.9506 ± 0.0375
BJH adsorption cumulative surface area of pores between 17.000000 and 150.000000 Å diameter (m^2 g^{-1})	4.0368
BJH desorption cumulative surface area of pores between 17.000000 and 150.000000 Å diameter (m^2 g^{-1})	4.1242
Pore volume	
Single point adsorption total pore volume of pores (cm^3 g^{-1})	0.005713
Pore size	
Adsorption average pore diameter (4 V/A by single point) (Å)	57.8417
BJH adsorption average pore diameter (4 V/A by single point) (Å)	91.1765
BJH desorption average pore diameter (4 V/A by single point) (Å)	82.8620

2.2. Sorption experiments and analytical method

Experiments were conducted at a various temperatures (22–50 °C) in continuously stirred (180 rpm) conical flasks containing 25 ml of solution with initial Cr(VI) concentration ranging from 25 to 400 mg l^{-1} with biomass of 4 g l^{-1} and pH 1.0 for 48 h. Preliminary results on Cr(VI) biosorption revealed that *A. niger* could biosorb maximally at pH 1.0 and biomass of 4 g l^{-1}. Samples were drawn from the mixture at pre-determined time intervals for analysis. After the sorption equilibrium was reached, the solution was separated from the biomass by membrane filtration (Millipore 0.45 μm pore size). The change in Cr(VI) concentration in the filtrate due to sorption was determined colorimetrically using Shimadzu (UV-1201, UV–vis) spectrophotometer according to standard methods [13]. A purple-violet colored complex was developed due to reaction between Cr(VI) and 1,5-diphenylcarbazide in acidic condition. Absorbance was measured at 540 nm.

Kinetic experiments were conducted under similar conditions mentioned above at temperature 37 ± 2 °C and samples were drawn at regular time intervals for analysis. The pH of the solution was monitored continuously with a pH electrode and adjusted with HCl or NaOH solution, if deviations were observed. All the experiments were repeated twice to confirm the results.

2.3. Chromium uptake capacities

The amount of Cr(VI) sorbed at equilibrium, q (mg g^{-1}), which represents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after adsorption, according to the following equation:

$$q = \frac{V(C_{\mathrm{i}} - C_{\mathrm{e}})}{W} \tag{1}$$

where V is the volume of Cr(VI) solution (L), C_{i} and C_{e} are the initial and equilibrium concentration of Cr(VI) in solution (mg l^{-1}), respectively, and W is the mass of dry seaweed (g).

2.4. Kinetic and equilibrium studies

Fractional power, zero order, first order, pseudo-first order, Elovich, second order and pseudo-second order rate equations have been used for modeling the kinetics of Cr(VI) sorption (Table 2). To examine the relationship between sorbed and aqueous concentration at equilibrium, various two-parameter sorption isotherm models like Langmuir, Freundlich, Dubinin–Radushkevich (D–R),

Table 2
Kinetic sorption models

Sr. no.	Kinetic model	Equation	Reference
1	Fractional power	$q_t = kt^v$	[40–42]
2	Zero order	$q_t = q_e - k_0 t$	[43]
3	First order	$q_t = q_e - \exp(k_1 t)$	[44,45]
4	Pseudo-first order	$q_t = q_e[1 - \exp(-k_1 t)]$	[46,47]
5	Elovich	$q_t = (1/\beta_E)\ln(1 + \alpha_E \beta_E t)$	[48]
6	Second order	$q_t = \frac{q_e}{1+q_e k_2 t}$	[49]
7	Pseudo-second order	$q_t = \frac{k_{2p} q_e^2 t}{1+k_{2p} q_e t}$	[50]
8	Intraparticle diffusion	$q_t = k_p t^{0.5}$	[51–53]

Table 3
Two-parameter sorption isotherm models

Sr. no.	Model	Equation	Reference
1	Langmuir	$qe = \frac{q_m K_L C_e}{1+K_L C_e}$	[54–56]
		$R_L = \frac{1}{1+K_L C_i}$	[57]
2	Freundlich	$qe = K_F C_e^{1/n}$	[58]
3	Dubinin–Radushkevich	$qe = q_m \exp(-Be^2)$	[59]
		$e = RT \ln\left(1 + \frac{1}{C_e}\right)$	
		$E = \frac{1}{\sqrt{2B}}$	
4	Temkin	$q_e = B_1 \ln(K_T C_e)$	[60]
5	Halsey	$qe = \left(\frac{k_H}{C_e}\right)^{1/n_H}$	[61]

Temkin and Halsey isotherms were used for fitting the data (Table 3).

2.5. Thermodynamics

2.5.1. Gibbs free energy change (ΔG°)

ΔG° is the fundamental criterion of spontaneity. Reaction occurs spontaneously at given temperature if the value of ΔG° is negative [14,15]. Value of ΔG° can be determined from the following equation:

$$\Delta G^\circ = -RT \ln K_L \tag{2}$$

where R is gas constant (8.314 J mol^{-1} K^{-1}), K_L is Langmuir constant and T is absolute temperature.

2.5.2. Enthalpy (ΔH°) and entropy (ΔS°) change

Relation between ΔG°, ΔH° and ΔS° can be expressed by the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{3}$$

Eq. (3) can be written as

$$-RT \ln K_L = \Delta H^\circ - T\,\Delta S^\circ \tag{4}$$

or

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{5}$$

where values of ΔH° and ΔS° can be determined from the slope and the intercept of the plot between $\ln K_L$ vs. $1/T$ [14,15].

2.6. Non-linear regression analysis

All the model parameters were evaluated by non-linear regression using DATAFIT® software (Oakdale Engineering, USA). The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data [16]. Apart from the correlation coefficient (r^2), the residual or sum of squares error (SSE) and the standard error (S.E.) of the estimate were also used to measure the goodness-of-fit. SSE can be defined as

$$\mathrm{SSE} = \sum_{i=1}^{m} (Q_i - q_i)^2 \tag{6}$$

Standard error (S.E.) of the estimate can be defined as

$$\mathrm{S.E.} = \sqrt{\frac{1}{m-p}\sum_{i=1}^{m} (Q_i - q_i)^2} \tag{7}$$

where q_i is the observation from the batch experiment i, Q_i is the estimate from the isotherm for corresponding q_i, m is the number of observations in the experimental isotherm and p is the number of parameters in the regression model. The smaller S.E. value indicates the better curve fitting [17].

3. Results and discussion

3.1. Kinetic studies

Table 4 presents the values of constants of kinetic models like fractional power, zero order, first order, pseudo-first order, Elovich, second order and pseudo-second order for sorption of Cr(VI) on *A. niger*.

A simple kinetic analysis for sorption of Cr(VI) on to *A. niger* has been tested according to fractional power model and Table 4 shows the estimated parameters of the model. The results indicate that this model was unable to describe the time-dependent Cr(VI) sorption by *A. niger* as the value of the correlation coefficient was 0.829 and constant 'v' was greater than 1, though the correlation coefficient was 0.986 and the values of SSE and S.E. were low.

The kinetic constants, k_0, k_1, k_{1p}, α_E and β_E, and k_2 of zero order, first order, pseudo-first order, Elovich and second order equations, respectively, for the sorption of Cr(VI) by *A. niger* are also presented in Table 4. The results demonstrated that there is no significant relationship between the kinetic data (figures are not shown) with

Table 4
Kinetic parameters for the sorption of Cr(VI) on *Aspergillus niger*

Models	r^2	SSE	S.E.	Constants
Fractional power	0.986	0.0124	0.0353	$k = 1.3619$, $v = 1.6441$, $kv = 2.2391$ (mg g^{-1} min^{-1})
Zero order	0.939	80.2018	2.8319	$k_0 = -0.0152$ (mg ml^{-1} min^{-1}), $q_e = 26.6279$ (mg g^{-1})
First order	0.869	0.0227	0.0476	$k_1 = -0.000384$ (min^{-1}), $q_e = 27.4595$ (mg g^{-1})
Pseudo-first order	0.952	0.00003	0.0018	$k_{1p} = 190.8355$ (min^{-1}), $q_e = 54.7948$ (mg g^{-1})
Elovich	0.983	23.028	1.5175	$\alpha_E = 0.5793$ (mg g^{-1} min^{-1}), $\beta_E = 0.0851$ (g mg^{-1})
Second order	0.764	0.0002	0.0041	$k_2 = -0.000010$ (g mg^{-1} min^{-1}), $q_e = 27.726$ (mg g^{-1})
Pseudo-second order	0.991	0.869	0.0894	$q_e = 61.69$ (mg g^{-1}), $k_{2p} = 0.000053$ (g mg^{-1} min^{-1}), $h = 0.2009$ (mg g^{-1} min^{-1})
Intraparticle diffusion	0.666	5.7418	1.3834	$k_p = 0.9768$ (mg g^{-1} min$^{-1/2}$)

S.E.: standard error of the estimate; SSE: residual or sum of squares error.

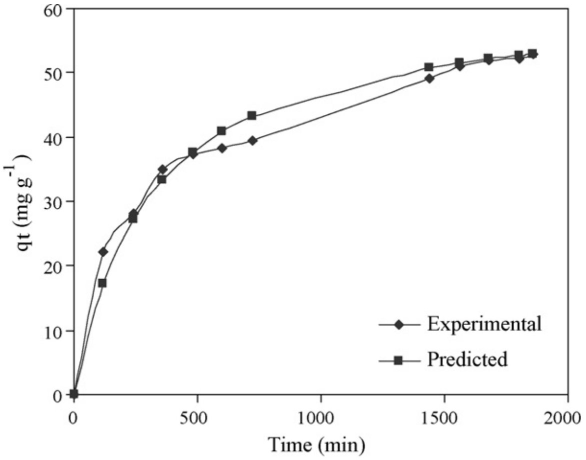

Fig. 1. Predicted kinetics from pseudo-second order model for the sorption of Cr(VI) on *A. niger*.

low correlation coefficients (<0.982) indicating that these models are not applicable in the present case.

The sorption rate constant, k_{2p}, initial sorption rate, h, and equilibrium sorption capacity, q_e, of the pseudo-second order model are depicted in Table 4 (Fig. 1). These results show a very good compliance with the pseudo-second order equation with high correlation coefficient (0.991) and standard error <1. The equilibrium concentration, q_e, obtained from this model is closely in line with the experimental value. The pseudo-second order model has been widely used to describe non-chemical equilibrium [18–20] and non-physical equilibrium [21,22]. This model assumes that two reactions are occurring, the first one is fast and reaches equilibrium quickly and the second is a slower reaction that can continue for long time periods. The reactions can occur either in series or in parallel [23]. The initial sorption rate, h, has been widely used for evaluation of the sorption rates [24]. In the present study the value of "h" is 0.2009. Tewari et al. [6] observed h values ranging from 0.99 to 6.72 mg g^{-1} min^{-1} for the sorption of Cr(VI) on *Mucor hiemalis*. Some studies published in the literature also report pseudo-second order kinetics as suitable for sorption of Cr(VI) by peat, leaf mould, corncob and granular activated carbon [25–28].

The intraparticle diffusion coefficient for the sorption of Cr(VI) was calculated from the slope of the plot between the amount of Cr(VI) sorbed, q_t (mg g^{-1}) vs. $t^{1/2}$ (min$^{1/2}$). Based on this plot (Fig. 2), it was concluded that the sorption process of Cr(VI) is comprised of two phases, suggesting that the intraparticle diffusion is not the rate-limiting step for the whole reaction [29]. The initial portion of the plot indicated an external mass transfer whereas the second linear portion is due to intraparticle or pore diffusion. The intercept of the plot provides an estimation of the thickness of the boundary layer, i.e. the larger the intercept value the greater is the boundary layer effect [30]. The slope of second linear portion of the plot has been identified as intraparticle diffusion rate constant k_p (mg g^{-1} min$^{-1/2}$).

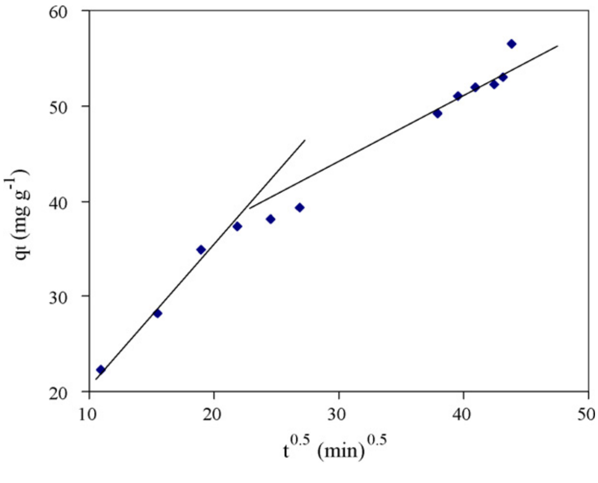

Fig. 2. Intraparticle diffusion plot for the sorption of Cr(VI) on *A. niger*.

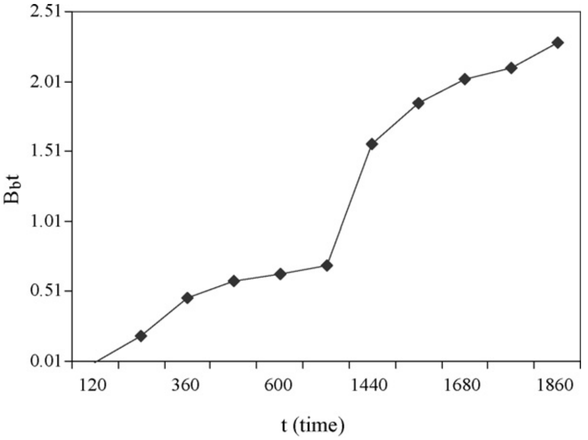

Fig. 3. Boyd plot for the sorption of Cr(VI) on *A. niger*.

The kinetic data were further analyzed using the kinetic expression given by Boyd et al. [31] to check whether sorption proceeds via external diffusion or intraparticle diffusion mechanism, which is expressed as follows:

$$F = 1 - \frac{6}{\Pi^2}\exp(-B_b t) \tag{8}$$

where B_b is a constant and F is the fractional attainment of equilibrium at time t given by

$$F = \frac{q_t}{q_e} \tag{9}$$

where q_e and q_t represent the amount of Cr(VI) sorbed (mg g^{-1}) at equilibrium and any time t, respectively. To compute $B_b t$, Eq. (9) is substituted into Eq. (8) and the kinetic expression becomes

$$B_b t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \tag{10}$$

Thus, the value of $B_b t$ can be computed for each value of F, and then plotted against time (Fig. 3) to configure the so-called Boyd plots [32]. Linearity of this plot is employed to distinguish between external-transport- (film diffusion) and intraparticle-transport-controlled rates of sorption [33]. A straight line passing through the origin is indicative of sorption processes governed by particle-diffusion mechanisms; otherwise they are governed by film diffusion [34]. In the present case, the plots were neither linear nor passed through the origin (Fig. 3). This indicates that, in all the sorbents, film diffusion is the rate-limiting sorption process for Cr(VI). However, further studies are needed to establish the same. Similar results were obtained by Refs. [33,35].

3.2. Equilibrium isotherm models

The analysis of equilibrium data is essential to develop an equation that can be used to compare different biosorbents under different operational conditions and to design and optimize an operating procedure. To examine the relationship between sorption and aqueous concentration at equilibrium, various sorption

Table 5
Isotherm constants of two-parameter models for Cr(VI) sorption on *Aspergillus niger* at different temperatures

Parameters	Temperature (°C)		
	22	37	50
Langmuir			
r^2	0.780	0.960	1.0
SSE	8.263	0.254	0.002
S.E.	0.866	0.152	0.016
q_m (mg g^{-1})	54.348	74.074	117.647
K_L (l mg^{-1})	0.015	0.138	0.368
R_L	0.302	0.059	0.024
Freundlich			
r^2	0.945	0.805	0.103
SSE	0.059	0.300	1.817
S.E.	0.074	0.165	0.406
n	2.448	2.789	2.846
K_F (l g^{-1})	0.646	1.129	1.594
D–R			
r^2	0.208	0.005	0.103
S.E.	0.643	0.859	0.936
SSE	4.542	8.129	9.635
q_m (mg g^{-1})	26.568	35.527	39.275
B (kJ^2 mol^{-2})	−9.038	2.357	81.363
E (kJ mol^{-1})	−0.111	0.424	0.012
Temkin			
r^2	0.723	0.931	0.255
SSE	789.676	479.488	11,345.25
S.E.	8.521	6.602	32.115
b_{Te} (J mol^{-1})	8.009	11.259	20.811
K_T (l g^{-1})	0.577	3.582	12.545
Halsey			
r^2	0.945	0.805	0.103
SSE	0.318	1.591	9.635
S.E.	0.169	0.380	0.936
n_H	−2.448	−2.789	−2.824
K_H (l g^{-1})	−0.275	−0.138	−0.096

S.E.: standard error of the estimate; SSE: residual or sum of squares error.

Table 6
Sorption capacities for Cr(VI) using various biosorbents

Biosorbent	Sorption capacity (mg g^{-1})	Reference
Padina sp.	54.60	[62]
Pilayella littoralis	4.68	[63]
Sargassum siliquosum	66.4	[64]
Turbinaria ornate	31.0	[65]
Sargassum sp.	31.72	[62]
Aspergillus sp.	1.20	[66]
Rhizopus	4.33	
Rhizopus arrhizus	78.0	[67]
A. niger	2.39	[68]
A. sydoni	1.76	
P. jenthinellum	1.77	
Mucor hiemalis	53.5	[6]
Lentinus sajor caju	191.24	[69]
A. niger	117.33	Present study

isotherm models are widely employed for fitting the data. In the present work, two-parameter models, i.e. Langmuir, Freundlich, Dubinin–Radushkevich (D–R), Temkin and Halsey isotherms were used to describe the equilibrium between the Cr(VI) sorbed onto the dead biomass of *A. niger* and Cr(VI) in the solution. The isotherm constants, correlation coefficient (r^2), the residual or sum of squares error (SSE) and the standard error of the estimate (S.E.) of these models for sorption of Cr(VI) on *A. niger* at different temperatures are presented in Table 5.

The Langmuir model served to estimate the maximum metal uptake values where they could not be reached in the experiments and it contains two important parameters of the sorption system, i.e. q_m and K_L [35,36]. The Langmuir isotherm model exhibited good fit to the experimental sorption data at temperatures 37 and 50 °C since the r^2 values were 0.960 and 1.0, respectively. However, comparatively low r^2 value (0.866) was observed at temperature 22 °C. The q_m for Cr(VI) on *A. niger* was increased from 54.3 to 117.6 mg g^{-1} with the increase in temperature from 22 to 50 °C while the experimental data indicate that the amount of Cr(VI) sorbed increased from 58.79 to 117.55 mg g^{-1}. Similar results have been observed by Tewari et al. [6], Sag and Kutsal [37] and Bai and Abraham [38] where sorption capacity of the respective biosorbents increased with the rise in temperature. The rise in sorption capacity with temperature is because of rise in the kinetic energy of sorbent particles. Thus, the collision frequency between sorbent and sorbate increases, which results in the enhanced sorption on to the surface of the sorbent. Due to bond rupture at high temperature, there may be an increase in number of active sorption sites, which may lead to enhanced sorption [39]. All these results showed that Langmuir isotherm model fitted the results quite well suggesting that the surface of the sorbent is homogenous. Each binding site accepts only one Cr(VI) molecule, as well as the sorbed molecules are organized as a monolayer and all sites are energetically equivalent and there is no interaction between sorbed molecules.

The Freundlich isotherm equation describes the sorption of solute from liquid to solid surface and assumes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. The results of present study indicate that the Freundlich model does not fit the experimental data since the r^2 values were 0.944, 0.805 and 0.103, respectively, for 22, 37 and 50 °C with low S.E. and SSE values. Similarly, the Dubinin–Radushkevich, Temkin and Halsey isotherm models were unable to fit the experimental data as low correlation coefficients and high SSE and S.E. values were observed.

Table 6 lists some reported sorption capacity values for Cr(VI) uptake by various biosorbents. In general, *A. niger* tested in this study exhibited sorption capacity higher than most of the reported biosorbent except *Lentinus sajor caju*.

3.3. *Thermodynamics*

3.3.1. *Effect of temperature*

The results on effect of temperature indicated that the maximum uptake of Cr(VI) was observed at 50 °C. The increase in temperature increased the Cr(VI) biosorption rate and decreased the contact time required for complete Cr(VI) removal. The rise in sorption capacity is due to the increase in collision frequency between sorbent and sorbate, which results in the enhanced sorption on to the surface of the sorbent.

The value of ΔG° for the sorption of Cr(VI) on *A. niger* at different temperature is given in Table 7. The magnitude of ΔG° increased with the rise in temperature. The negative value confirms the feasibility of the process and the spontaneous nature of sorption of Cr(VI) on *A. niger*. The values of ΔH° and ΔS° were determined from slope and intercept of the plot of $\ln K_L$ vs. $1/T$ as shown in Fig. 4. ΔH° for the sorption of Cr(VI) on *A. niger* was found to be 7.366×10^{-4} kJ mol^{-1} while ΔS° was 0.0251 kJ mol^{-1}. The value of ΔH° was positive, indicating that the sorption reaction is endother-

Table 7
Gibbs free energy change for the sorption of Cr(VI) on *A. niger*

Temperature (°C)	ΔG° (J mol^{-1})
22	−7.403
37	−7.780
50	−8.106

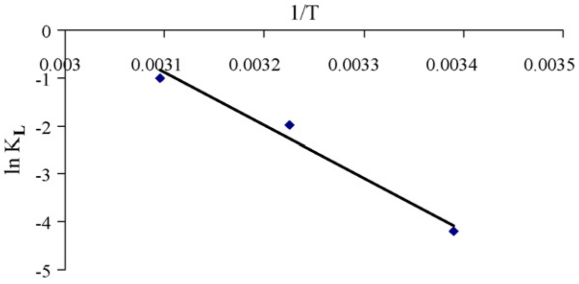

Fig. 4. Plot of $\ln K_L$ vs. $1/T$ for the sorption of Cr(VI) on *A. niger*.

mic. This is also supported by the increase in value of uptake capacity of all the sorbent with the rise in temperature up to 50 °C. The positive value of ΔS° reflects the affinity of Cr(VI) for sorbent used. In addition, positive value of ΔS° shows the increasing randomness at the solid/liquid interface during the sorption of Cr(VI) on selected sorbent.

4. Conclusions

Kinetic studies on sorption of Cr(VI) on *A. niger* revealed that pseudo-second order model showed the best fit to the experimental data and film diffusion might be involved in the sorption process. The study on equilibrium sorption revealed that Langmuir isotherm model gave the best fit to experimental data. Further, from the value of ΔH° it was revealed that the biosorption process is endothermic. Thus, it may be concluded that *A. niger* exhibited the potential for application in treatment of aqueous solutions containing Cr(VI). However, further research is needed to establish the process with specific attention to the regeneration of the sorbent and the recovery of the sorbed metal.

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References

[1] H.S. Regime, F. Viera, B. Volesky, Biosorption: a solution to pollution, Int. Microbiol. 3 (2000) 17–24.
[2] S.K. Mehta, J.P. Gaur, Use of algae for removing heavy metal ions from wastewater: progress and prospects, Crit. Rev. Biotechnol. 25 (2005) 113–152.
[3] S. Basha, Z.V.P. Murthy, Seaweeds for engineering metal biosorption: a review, in: L.G. Mason (Ed.), Focus on Hazardous Materials Research, Nova Science Publishers, Hauppauge, New York, 2007, pp. 165–210.
[4] S.M. Nomanbhay, K. Palanisamy, Removal of heavy metals from industrial wastewater using chitosan coated oil palm shell charcoal, Electron. J. Biotechnol. 8 (2005) 43–53.
[5] M. Costa, Potential hazards of hexavalent chromate in our drinking water, Toxicol. Appl. Pharmacol. 188 (2003) 1–5.
[6] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, Biochem. Eng. J. 23 (2005) 185–192.
[7] A. Baral, R.D. Engelken, Chromium-based regulations and greening in metal finishing industries in the USA, Environ. Sci. Policy 5 (2002) 121–133.
[8] H. Babich, G. Stotzky, Nickel toxicity to estuarine/marine fungi and its amelioration by magnesium in sea water, Water Air Soil Pollut. 19 (1983) 193–202.
[9] R.E. Hicks, S.Y. Newell, The growth of bacteria and fungus *Phaeospharia typharum* (Desm.) Holm (*Eumycota*: *Ascomycotina*) in salt-marsh microcosms in the presence and absence of mercury, J. Exp. Mar. Biol. Ecol. 78 (1984) 143–155.
[10] A.K. Vala, N. Anand, P.N. Bhatt, H.V. Joshi, Tolerance and accumulation of hexavalent chromium by two seaweed associated *Aspergilli*, Mar. Pollut. Bull. 48 (2004) 983–985.
[11] M.A.S. Taboski, T.G. Rand, A. Piorko, Lead and cadmium uptake in the marine fungi *Corollospora lacera* and *Monodictys pelagica*, FEMS Microbiol. Ecol. 53 (2005) 445–453.
[12] D. Karunasagar, J. Arunachalam, K. Rashmi, J.N.L. Latha, P.M. Mohan, Biosorption of inorganic and methyl mercury by a biosorbent from *Aspergillus niger*, World J. Microbiol. Biotechnol. 19 (2003) 291–295.
[13] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, American Water Work Association, and Water Environment Federation, Washington, DC, 1998, pp. 366–368.
[14] Y.S. Ho, A.E. Ofomaja, Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent, Biochem. Eng. J. 30 (2006) 117–123.
[15] J.M. Smith, H.C. Van Ness, Introduction to Chemical Engineering Thermodynamics, 4th ed., McGraw-Hill, Singapore, 1987.
[16] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol. 96 (2005) 1285–1291.
[17] S.C. Tsai, K.W. Juang, Comparison of linear and non-linear forms of isotherm models for strontium sorption on a sodium bentonite, J. Radioanal. Nucl. Chem. 243 (2000) 741–746.
[18] J.W. Hamaker, J.M. Thompson, Adsorption, in: C.A.I. Goring, J.W. Hamaker (Eds.), Organic Chemicals in the Environment, Dekker, New York, 1972, pp. 49–143.
[19] S.W. Karickhoff, Sorption kinetics of hydrophobic pollutants in natural sediments, in: R.A.R.A. Baker (Ed.), Contaminant and Sediments, Ann Arbor Sci., Ann Arbor, MI, 1980, pp. 193–205.
[20] P.J. McCall, G.L. Agin, Desorption of picloram as affected by residence time in the soil, Environ. Toxicol. Chem. 4 (1985) 37–44.
[21] L.S. Lee, P.S.C. Rao, M.L. Brusseau, R.A. Ogwada, Non-equilibrium sorption of organic contaminants during flow through columns of aquifer materials, Environ. Toxicol. Chem. 7 (1988) 779–793.
[22] M.Th. van Genuchten, R.J. Wagenet, Two-site/two-region models for pesticide transport and degradation: theoretical development and analytical solutions, Soil Sci. Soc. Am. J. 53 (1958) 1303–1310.
[23] M.L. Brusseau, P.S.C. Rao, Sorption non-ideality during organic contaminant transport in porous media, CRC Crit. Rev. Environ. Control 19 (1984) 33–99.
[24] A. Benhammou, A. Yaacoubi, L. Nibou, B. Tanouti, Study of the removal of mercury(II) and chromium (VI) from aqueous solutions by Moroccan stevensite, J. Hazard. Mater. 117 (2005) 243–249.
[25] D.C. Sharma, C.F. Forster, Removal of hexavalent chromium using sphagnum moss peat, Water Res. 27 (1993) 1201–1208.
[26] D.C. Sharma, C.F. Forster, The treatment of chromium wastewaters using the sorptive potential of leaf mold, Bioresour. Technol. 49 (1994) 31–40.
[27] D.C. Sharma, C.F. Forster, Removal of hexavalent chromium from aqueous solutions by granular activated carbon, Water SA 22 (1996) 153–160.
[28] S. Bosinco, J. Roussy, E. Guibal, P. Le Cloirec, Interaction mechanisms between hexavalent chromium and corncob, Environ. Technol. 17 (1996) 55–62.
[29] Y.S. Ho, A.E. Ofomaja, Kinetics and thermodynamics of lead ion sorption on palm kernel fibre from aqueous solution, Process Biochem. 40 (2005) 3455–3461.
[30] J.U.K. Oubagaranadin, N. Sathyamurthy, Z.V.P. Murthy, Evaluation of Fuller's earth for the adsorption of mercury from aqueous solutions: a comparative study with activated carbon, J. Hazard. Mater. 142 (2007) 165–174.
[31] G.E. Boyd, A.W. Adamson, L.S. Myers, The exchange adsorption of ions from aqueous solutions by organic zeolites, J. Am. Chem. Soc. 69 (1947) 2836–2848.
[32] X.S. Wang, Y. Qin, Z.F. Li, Biosorption of zinc from aqueous solutions by rice bran: kinetics and equilibrium studies, Sep. Sci. Technol. 41 (2006) 747–756.
[33] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, Water Res. 36 (2006) 2304–2318.
[34] A.M. El-Kamash, A.A. Zaki, M. Abed-El-Geleel, Modeling batch kinetics and thermodynamics of zinc and cadmium removal from waste solutions using synthetic zeolite, J. Hazard. Mater. 127 (2005) 211–220.
[35] B.P. Nelson, T.E. Grimsrud, M.R. Liles, R.M. Goodman, R.M. Corn, Surface plasmon resonance imaging measurements of DNA and RNA hybridization adsorption onto DNA microarrays, Anal. Chem. 73 (2001) 1–7.
[36] Z.Q. Tian, B. Ren, D.Y. Wu, Surface-enhanced Raman scattering: from noble to transition metals and from rough surfaces to ordered nanostructures, J. Phys. Chem. 106 (2002) 9463–9483.
[37] Y. Sag, T. Kutsal, Determination of biosorption activation energies of heavy metal ions on *Zoogloea ramigera* and *Rhizopus arrhizus*, Process Biochem. 35 (2002) 801–807.
[38] R.T. Bai, E. Abraham, Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*, Bioresour. Technol. 79 (2001) 73–81.
[39] Y. Nuhoglu, E. Oguz, Removal of copper(II) from the aqueous solution by biosorption on the cone biomass of *Thuja orientalis*, Process Biochem. 38 (2003) 1627–1631.
[40] C. Aharoni, D.L. Sparks, S. Levinson, I. Ravina, Kinetics of soil chemical reactions: relationships between empirical equations and diffusion models, Soil Sci. Soc. Am. J. 55 (1991) 1307–1312.
[41] R.C. Dalal, Desorption of phosphate by anion exchange resin, Commun. Soil Sci. Plant Anal. 5 (1974) 531–538.
[42] Y.S. Ho, G. McKay, Sorption of dyes and copper ions onto biosorbents, Process Biochem. 38 (2003) 1047–1061.
[43] E.F. Covelo, M.L. Andrade, F.A. Vega, Heavy metal adsorption by humic umbrisols: selectivity sequences an competitive sorption kinetics, J. Colloid Interf. Sci. 280 (2004) 1–8.
[44] V.K. Gupta, M. Gupta, S. Sharma, Process development for the removal of lead and chromium from aqueous solutions using red mudan aluminium industry waste, Water Res. 35 (2001) 1125–1134.

[45] C. Namasivayam, K. Kadirvelu, Uptake of mercury (II) from wastewater by activated carbon from an unwanted agricultural solid byproduct: coirpith, Carbon 37 (1999) 79–84.

[46] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, K. Sven. Vetenskapsakad Handl. 24 (1898) 1–39.

[47] Y.S. Ho, Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometrics 59 (2004) 171–177.

[48] M.J.D. Low, Kinetics of chemisorption of gases on solids, Chem. Rev. 60 (1960) 267–312.

[49] C.W. Cheung, J.F. Porter, G. McKay, Sorption kinetic analysis for the removal of cadmium ions from the effluent using bone char, Water Res. 35 (2001) 605–612.

[50] Y.S. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, Water Res. 40 (2006) 119–125.

[51] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[52] G. McKay, M.S. Otterburn, J.A. Aga, Intraparticle diffusion process occurring during adsorption of dyestuffs, Water Air Soil Pollut. 36 (1987) 381–390.

[53] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanitary Eng. Div.: Am. Soc. Civil Eng. 89 (1963) 31–60.

[54] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[55] I. Langmuir, The constitution and fundamental properties of solids and liquids. II. Liquids, J. Am. Chem. Soc. 39 (1917) 1848–1906.

[56] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[57] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, Ind. Eng. Chem. Res. 5 (1966) 212–223.

[58] H.M.F. Freundlich, Uber die adsorption in lasugen, J. Phys. Chem. 57 (1906) 385–470.

[59] J.P. Hobson, Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure, J. Phys. Chem. 73 (1969) 2720–2727.

[60] M.J. Temkin, V. Pyzhev, Recent modifications to Langmuir isotherms, Acta Physchim. USSR 12 (1940) 217.

[61] G. Halsey, Physical adsorption on non-uniform surfaces, J. Chem. Phys. 16 (1948) 931–937.

[62] P.X. Sheng, L.H. Tan, J.P. Chen, Y.P. Ting, Biosorption performance of two brown marine algae for removal of chromium and cadmium, J. Dispers. Sci. Technol. 25 (2004) 679–686.

[63] E.N. Carrilho, T.R. Gilbert, Assessing metal sorption on the marine algae *Pilayella littoralis*, J. Environ. Monit. 2 (2000) 410–415.

[64] L.K. Cabatingan, R.C. Agapay, J.L.L. Rakels, M. Ottens, L.A.M. van der Wielen, Potential of biosorption for the recovery of chromate in industrial wastewaters, Ind. Eng. Chem. Res. 40 (2001) 2302–2309.

[65] R. Aravindhan, B. Madhan, J.R. Rao, B.U. Nair, Recovery and reuse of chromium from tannery wastewaters using *Turbinaria ornata* seaweed, J. Chem. Technol. Biotechnol. 79 (2004) 1251–1258.

[66] S. Zafar, F. Aqil, I. Ahmad, Metal tolerance and biosorption potential of filamentous fungi isolated from metal contaminated agricultural soil, Bioresour. Technol. 98 (2007) 2557–2561.

[67] Z. Aksu, E. Balibek, Chromium(VI) biosorption by dried *Rhizopus arrhizus*: effect of salt (NaCl) concentration on equilibrium and kinetic parameters, J. Hazard. Mater. 145 (2007) 210–220.

[68] R. Kumar, N.R. Bishnoi, K. Bishnoi, Biosorption of chromium(VI) from aqueous solution and electroplating wastewater using fungal biomass, Chem. Eng. J. 135 (2008) 202–208.

[69] G. Bayramoglu, G. Celik, E. Yalcın, M. Yılmaz, M.Y. Arıca, Modification of surface properties of *Lentinus sajor-caju* mycelia by physical and chemical methods: evaluation of their Cr^{6+} removal efficiencies from aqueous medium, J. Hazard. Mater. B 119 (2005) 219–229.