

Kinetic and Equilibrium Models for the Biosorption of Cr (III) on *Streptomyces rimosus*

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Abstract: The biosorption data of trivalent chromium by *Streptomyces rimosus* has been used for kinetic studies based on fractional power, Elovich, pseudo-first order and pseudo-second order rate expressions. The time-dependent Cr (III) biosorption data were well-described by pseudo-second-order kinetic model. The intraparticle diffusion is not the rate-limiting step for the whole reaction. The Temkin, Freundlich, Dubinin-Radushkevich and Langmuir biosorption models were used for the mathematical description of the biosorption equilibrium of Cr (III) ions to *S. rimosus*. It was found that the biosorption equilibrium data fitted well to the Langmuir.

Key words: Trivalent chromium, *Streptomyces rimosus*, kinetics, intraparticle diffusion, equilibrium models

INTRODUCTION

The accumulation of heavy metals on the environment is a serious problem that needs to be solved. The conventional methods for heavy metal removal from industrial effluents are precipitation, coagulation, ion exchange, cementation, electro-dialysis, electro-winning, electro-coagulation and reverse osmosis (Ahluwalia and Goyal, 2007). Certain drawbacks of these methods have been noticed, such as high cost, low efficiency, operational complexity and other difficulties Patterson (1985) and Aksu *et al.* (1991) which has urged for an alternative process.

The use of biological materials, including living and non-living micro-organisms, in the removal and possibly recovery of toxic metals from industrial wastes, has gained important credibility during recent years, because of the good performance and low cost of these materials. The natural affinity of biological compounds for metallic elements could contribute to the purification of metal-loaded wastewater, a fact which has been already proved in many cases and by many researchers (Volesky, 1990; Donmez and Aksu, 2001).

Chromium is released into the environment by a large number of industries such as mining, iron sheet cleaning, chrome plating, leather tanning and wood preservation (Krishan and Philip, 2005). Chromium exists in several oxidation states (-2 to +6), the most stable and common

forms are the hexavalent Cr (VI) and trivalent Cr(III) (Baral and Engelken, 2002). Cr (III) is selected instead of Cr (VI) because of following facts Cr (III) is toxic if excess quantity is taken and cause abnormalities in organisms. Chromium (III) sulphate salts are mainly used in tanning (Mant *et al.*, 2005).

Streptomyces rimosus, mycelial bacteria is classified Gram-positive. In general, Gram-positive bacteria have a greater sorptive capacity due to their thicker layer of peptidoglycan which contains numerous sorptive sites (Van Hullebusch *et al.*, 2003).

Numerous kinetic models have been investigated for the biosorption of metal ions from wastewater by biosorbents. Fractional power (Dalal, 1974), pseudo-first-order (Ho and McKay, 1998; Ho, 2004) Elovich (Ho, 2006; Zeldowitsch, 1936), pseudo-second-order 'Ho (2006a) and Ho (2006b) and intraparticle diffusion (Weber and Morris, 1963) rate equations have been used for modeling the kinetics of adsorption.

Modeling of biosorption isotherm data is important for predicting and comparing biosorption performance. Two, three and even four-parameter isotherm models are available for modeling biosorption data (Vijayaraghavan *et al.*, 2006). Freundlich (1906) and Langmuir (1916, 1917) models (2-parameter models) are the most commonly used isotherms. Further, other two-parameter models such Temkin (Temkin and Pyzhev, 1940), Dubinin (1960) were also used. The present

research is aimed to test the various kinetic and isotherm models to describe the sorption data generated from chromium (III) biosorption using *Streptomyces rimosus*.

MATERIALS AND METHODS

Dead *Streptomyces rimosus* biomass was obtained from oxytetracycline antibiotic production after fermentation. The biomass was washed with deionised water, dried at 50°C for 24 h in a drying oven, then the activated biomass was prepared by treating the raw biomass with 0.1 N NaOH solution for 30 min at ambient temperature., at once again washed, dried and then screened through a set of sieves to get geometrical size 50-160 µm. The effluent used in the experiment was the effluent of tannery, which is stored at 4°C without pre-treatment for 2 months before use. No pH or colour change or precipitation occurred during storage.

Samples were withdrawn at suitable time intervals and were separated from the sorbent by filtration, through 0.45 µm pore size and their chromium concentration determined by atomic absorption spectrometer (Perkin Elmer 2380), $\lambda = 359.7$ nm

The sorption capacity of chromium is the concentration of chromium on the bacterial biomass and can be calculated based on the balance principle where:

$$q = \frac{V(C_0 - C_f)}{m} \quad (1)$$

Where, q represents the amount of chromium uptaken per unit mass of the biomass (mg g^{-1}); V the volume of the solution (l); m the dry mass of the biosorbent (g); C_0 and C_f are the initial and final concentration (mg L^{-1}), respectively.

All experiments were conducted at a constant temperature of $20 \pm 1^\circ\text{C}$ to be representative of environmentally relevant conditions. Kinetic experiments were conducted on a rotary shaker with constant agitation speed of 300 rpm; using conical flasks (250 mL) containing 100 mL of solution and 0.3 g of biomass and an initial pH 4.8 with initial concentration of 2400 mg L^{-1} for 80 min. The pH of the solution was monitored continuously with a pH electrode and adjusted with HCl or NaOH solution.

Batch equilibrium biosorption experiments were carried out in 250 ml Erlenmeyer flasks containing effluent of tannery (100 mL) of known concentrations, which varied from 10-2400 mg L^{-1} . Weighed amounts of biomass were added to each flask and the mixtures were agitated on the rotary shaker. The solution pH was adjusted to the required value. After 5 h of agitation (300 rpm), the

solution was separated from the biomass by membrane filtration (Millipore 0.45 mm pore size. Samples were taken periodically to analyse the chromium concentration.

Physical properties of biomass: The zeta potential of biomass particles was measured using a Zeta Potential Analyser (model 1200 MICROMERITICS) ($T = 20^\circ\text{C}$; sample density 1 g cm^{-3} ; Test duration 150s; Conductivity cell constant: 0.803 cm^{-1} ; Intensity $I = 7 \text{ mA}$; pH = 4.8 for the NaOH-treated biomass).

The effective surface area of the biosorbent was approximated as the external surface of biomass particles. Assuming biomass particles are spherical, their external surface per unit volume of test solution is:

$$S = \frac{6m}{d_p \rho_{app} V} \quad (2)$$

Where, m is the sorbent mass suspended in the test solution, d_p is particle size diameter, ρ_{app} is the apparent density of the sorbent and V is the solution volume.

The specific surface area of the biomass S_p was calculated from the following expression:

$$S_p = \frac{6}{d_p \rho_{app}} \quad (3)$$

The physical properties of biomass *Streptomyces rimosus* are given in Table 1.

Adsorption dynamics: The study of adsorption dynamics describes the solute uptake rate. This rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of chromium biosorption on dead biomass were analysed using Fractional power, pseudo-first-order, Elovich, pseudo-second-order and intraparticle diffusion kinetics models (Table 2). The model predicted values are validated by the correlation r^2 that should be close or equal to 1.

Equilibrium modelling: Equilibrium data, commonly known as adsorption isotherms, are the basic requirement for the design of adsorption systems. Classical adsorption models, such Langmuir and Freundlich models were used to describe the equilibrium between adsorbed chromium on the biomass and chromium in solution (C_e) at constant temperature, further, other two-parameter models Temkin, Dubinin-Radushkevich were also used (Table 3).

The essential characteristic of the Langmuir isotherm can be expressed in terms of dimension less constant separation factor or equilibrium parameter R_L .

Table 1: The physical characteristics of the biomass

	NaOH-treated biomass
Particle size d_p (μm)	50-160
Humidity (%)	4.4
ρ_{app} (g cm^{-3})	0.41
S (m^{-1}) ^a	418
S_p ($\text{m}^2 \text{g}^{-1}$) ^a	0.14
Zeta potential (Volt)	-0.072

An average value of d_p was used for calculation

Table 2: Kinetic biosorption model

N ^o	Kinetic model	Equation
1	Fractional power	$q_t = kt^v$
2	Pseudo-first-order	$q_t = q_e [1 - \exp(-k_1 t)]$
3	Elovich	$q_t = \ln(\alpha_1 \beta_1 t)^{1/\beta_1}$
4	Pseudo-second-order	$q_t = k_2 q_e^2 t / (1 + k_2 q_e t)$
5	Intraparticle diffusion	$q_t = K_p t^{0.5}$

Table 3: Biosorption isotherm model

N ^o	Isotherm model	Equation
1	Freundlich	$q_e = K_F C_e^{1/n}$
2	Temkin	$q_e = \frac{RT}{b_t} \ln(a_t C_e)$
3	Dubinin-Radushkevich	$q_e = q_d \exp(-\beta_D \varepsilon_D^2)$ $\varepsilon_D = RT \ln \left(1 + \frac{1}{C_e} \right)$
4	Langmuir	$q_e = \frac{b C_e q_{\text{max}}}{1 + b C_e}$ $R_L = \frac{1}{1 + b C_0}$

Hall and Vermeylem (1966) show, using mathematical calculation, that the parameter R_L indicates the shape of isotherm as follows (Table 4).

Non-linear regression analysis: All the model parameters were evaluated by non-linear regression using Excel 2007[®] software. 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 Ho *et al.* (2002) and Kundu and Gupta (2006). Apart from the correlation coefficient (R^2), the residual Root Mean Square Error (RMSE) and the chi-square test were also used to measure the goodness-of-fit. RMSE can be defined as:

$$RMSE = \sqrt{\frac{1}{m-2} \sum_{i=1}^m (q_i - q_{ie})^2} \quad (4)$$

where, q_i is the observation from the batch experiment, q_{ie} is the estimate from the isotherm for corresponding q_i and m is the number of observations in the experimental isotherm. The smaller RMSE value indicates the better curve fitting (Tsai and Juang, 2000).

Table 4: Constant parameter R_L

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

The chi-square test can be defined as:

$$\chi^2 = \sum_{i=1}^m \frac{(q_i - q_{ie})^2}{q_{ie}} \quad (5)$$

If data from model are similar to the experimental data, χ^2 will be a small number (Ho *et al.*, 2005)

RESULTS AND DISCUSSION

Effect on pH on chromium uptake: The pH of the metal solution usually plays an important role in the biosorption of metals (Vijayaraghavan *et al.*, 2005).

As can be seen in Fig. 1, the uptake of Cr^{3+} by *Streptomyces rimosus* biomass was obtained by varying the initial concentration of chromium. When the pH value was raised from 1-4.8, the adsorption capacity was enhanced significantly from 27-64 mg g^{-1} biomass. Uptake was enhanced, probably because of proton competition to Cr^{3+} binding (Yun and Volesky, 2003). Adsorption at pH 5.5 and 7.0 marked precipitation effects augmented the biosorption removal of chromium. From solution resulting in apparent sequestration levels of in excess of 93 and 133 mg g^{-1} , respectively illustrated in Fig. 1.

As can be seen in the Fig. 1, when the precipitation component is subtracted the net biosorption values are in good agreement with each other and those observed at pH 4.8 (Tobin and Roux, 1998).

If the biosorption takes place under conditions that chromium may precipitate, a chemical sludge is generated which should be treated via appropriate solid waste management methods. From a practical point of view, therefore, chromium biosorption process is better operated at pH 4.8.

The batch experimental data, shown in Fig. 2 and Fig. 3 on kinetic and equilibrium studies for the biosorption of Cr (III) on *Streptomyces rimosus* were tested to fit the various kinetic and equilibrium models, respectively.

As shown in Fig. 2 the removal of chromium increases rapidly in the beginning (first 30 min) and then more slowly until the equilibrium.

As seen in Fig. 3, it readily appears that, isotherm is somewhat curved and the equilibrium is established between chromium ions and the biomass.

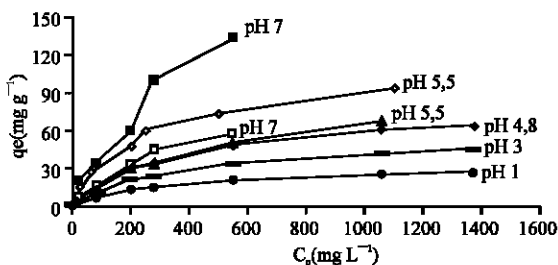


Fig. 1: Effect of pH and influence of precipitation on uptake (** indicate where precipitation effects have been subtracted)

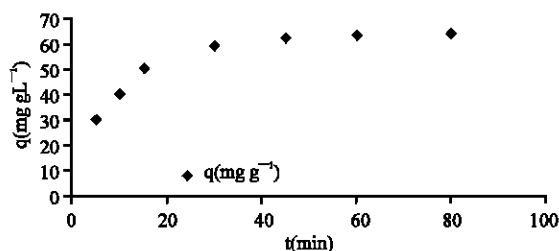


Fig. 2: Kinetic (biosorption capacity vs. Time) of Cr (III) on *Streptomyces*

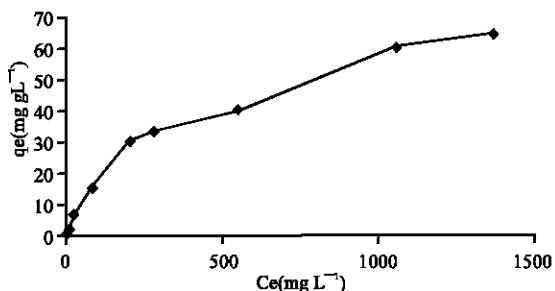


Fig. 3: Biosorption isotherm for Cr (III) on *Streptomyces rimosus*

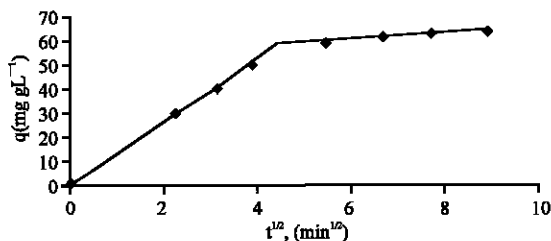


Fig. 4: Intraparticle diffusion plots for the biosorption of Cr (III) on *Streptomyces rimosus*

The metal-binding properties of Gram-positive bacteria are largely due to the existence of specific anionic polymers in the cell wall structure, consisting mainly of peptidoglycan, teichoic acids (Hancock, 1986; Hughes and Poole, 1989; Remacle *et al.*, 1992).

Table 5: Kinetic model parameters for Cr (III) biosorption on *Streptomyces rimosus*

Models	Parameters	
Fractional power	v (min^{-1})	0.271
	k (mg g^{-1})	21.434
	R^2	0.916
	RMSE	4.7284
	χ^2	2.109
Pseudo-first-order	q_e (mg g^{-1})	41.512
	R^2	0.989
	RMSE	27.083
	χ^2	116
	α_E ($\text{mg g}^{-1}\text{min}^{-1}$)	33.212
Elovich	β_E (g mg^{-1})	0.079
	R^2	0.950
	RMSE	3.224
	χ^2	1026
	K_2 ($\text{mg g}^{-1}\text{min}^{-1}$)	2.210^3
Pseudo-second-order	Q_e (mg g^{-1})	71.43
	h (mg g^{-1})	11.11
	SR_{30} (mg g^{-1})	2.778
	SR_{90} (mg g^{-1})	0.111
	$t_{1/2}$ (min)	6.43
	R^2	0.999
	RMSE	2.035
	χ^2	0.436

Due to this high fixed anionic content of the cell forms which are obviously present in streptomyces rimosus, they may exhibit high sorption capacities that would be very important aspect in future because of its industrial application as biosorbent for the metal cations.

Kinetic models: A simple kinetic analysis of biosorption of Cr (III) on *Streptomyces rimosus* has been tested according to fractional power model (Dlal, 1974) and Table 5 shows the estimated parameters of the model. The results indicate that the power function model described the time-dependent Cr (III) on sorbent as the value of constant v was less than 1 (Shaik and Murthy, 2007). The chromium biosorption data do not correlate well with fractional power model and this confirmed by high RMSE and chi-square values (Table 5).

The kinetic constant, k_1 , of the pseudo-first-order equation (Ho and Mckay, 1998; Ho, 2004) for the biosorption of Cr (III) on to biomass is given in Table 5. The results demonstrated that Lagergren model (Ho and Mckay, 1998; Ho, 2004) is not applicable in the present case as high RMSE and chi-square values were observed.

The kinetic constants obtained from the Elovich equation (Zeldowitsch, 1936) are listed in Table 5. The results demonstrate a significant relationship between Cr(III) sorbed, q_t and t in this study with acceptable regression coefficient 0.95 and low values of RMSE and chi-square. The low values of standard error reflect agreement between the sets of data studied. In other words, the data also show satisfactory compliance with the Elovich equation.

The results in Table 5 show the biosorption rate constant, k_2 , initial biosorption rate, h and equilibrium

Table 6: Isotherm constants for Cr (III) biosorption on *Streptomyces rimosus*

Equilibrium models	Parameters	
Freundlich	$K_F(Lg^{-1})$	1.724
	n	1.443
	R^2	0.957
	RMSE	10.659
	χ^2	11.69
Temkin	$\alpha_T(Lg^{-1})$	0.086
	$b_T(jmol^{-1})$	197.27
	R^2	0.933
	RMSE	6.607
	χ^2	15.97
Dubinin-Radushkevich	Q_D	31.449
	B_D	0.00003
	$E(Kj mol^{-1})$	0.13
	R^2	0.739
	RMSE	38.005
Langmuir	χ^2	134
	$q_{max}(mg g^{-1})$	83.33
	$b(L mg^{-1})$	0.0028
	R_L	0.13
	R^2	0.992
	RMSE	2.009
	γ^2	1.067

biosorption capacity, q_e , of the pseudo-second-order model Ho (2006a) and Ho (2006b). These results show a very good compliance with the pseudo-second-order equation with high regression coefficients (>0.99).

The pseudo second order kinetic rate expression is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

where, k_2 is the rate constant of pseudo second order adsorption ($g\ mg^{-1}\ min^{-1}$). Taking into account the boundary condition, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Equation 6 can be rearranged to obtain Eq. 7.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (7)$$

The initial adsorption rate h ($mg\ g^{-1}.min^{-1}$), is expressed as:

$$h = k_2 q_e^2 \quad (8)$$

The initial biosorption rate, h , has been widely used for evaluation of the biosorption rates (Ho and McKay, 2000, 1999, 1998). According to the pseudo-second-order kinetic model (Ho, 2006a, b), the rate of a biosorption reaction nonlinearly decreased with time. For example, the instantaneous rates at 50 and 90% of Cr (III) biosorption (SR_{50} and SR_{90} , respectively) can be calculated from pseudo-second order rate equation as follows:

$$SR_{50} = k_2 [q_e - (0.5q_e)]^2 = \frac{k_2 q_e^2}{4} = \frac{h}{4} \quad (9)$$

$$SR_{90} = k_2 [q_e - (0.9q_e)]^2 = \frac{k_2 q_e^2}{100} = \frac{h}{100} \quad (10)$$

Therefore, SR_{50} and SR_{90} values are one-fourth and one-hundredth of initial biosorption rate, h , respectively (Table 5) and comparisons reported here based on h values can be extended to the entire experiment duration. Based on the pseudo-second-order kinetic model the half-life of Cr (III) biosorption (the time at which half of the biosorption process is completed) directly depends on the biosorption capacity of the biosorbent and inversely relates to the initial biosorption rate:

$$t_{\frac{1}{2}} = \frac{1}{k_2 q_e} = \frac{q_e}{h} \quad (11)$$

Biosorption capacity of the biosorbent determined from the fitted pseudo-second-order kinetic model was comparable to the maximum biosorption capacity calculated from the Langmuir isotherm as can be seen later.

The intraparticle diffusion coefficient for the biosorption of Cr(III) was calculated from the slope of the plot between the amount of Cr(III) sorbed, q_t ($mg\ g^{-1}$) vs. $t^{1/2}$ ($min^{1/2}$).

Based on these plot (Fig. 4), the biosorption process of the Cr(III) is comprised by two phases, suggesting that the intraparticle diffusion is not the rate-limiting step for the whole reaction (Ho and Ofomaja, 2005). The initial portion of the plot indicated an external mass transfer whereas the second linear portion is due to intraparticle or pore diffusion. Similar results were reported by Aguilar-Carrillo *et al.* (2006). The intercept of the plot provides an estimation of the thickness of the boundary layer (Oubagaranadin *et al.*, 2007). The slope of the second linear portion of the plot has been identified as the intraparticle diffusion rate constant ($K_p = 12,90\ mg\ g^{-1}\ min^{-1/2}$). The high value of K_p corresponded to low value of pseudo-second order rate constant, k_2 (Table 5), indicating that the intraparticle diffusion retards the biosorption process. This also indicates, the biosorption process is rather complex and involves more than one diffusive mechanism.

Equilibrium isotherm models: Analysis of equilibrium data is important for developing an equation that can be used to design and optimize an operating procedure. To examine the relationship between biosorption and aqueous concentration at equilibrium, various biosorption isotherm models are widely employed for fitting the data.

The Freundlich isotherm is originally empirical in nature (Freundlich, 1996), but was later interpreted as

biosorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data (Oubagaranadin *et al.*, 2007). The value of n , of this model, falling in the range of 1-10 indicates favourable biosorption (Aksu and Kutsal, 1991). The present study results indicate that the Freundlich model does not fit the experimental data well. It is not the suitable model for describing these biosorption processes, as RMSE and χ^2 values are higher than 10.

Isotherm of Temkin was first developed by Temkin and Pyzhev (Ho *et al.*, 2002) and it is based on the assumption that the heat of adsorption would decrease linearly with the increase of coverage of adsorbent, due to sorbate/sorbent interactions (Yu and Ya-Juan, 2008). Temkin model is unable to describe the data, as low correlation coefficients and high RMSE and chi-square values were observed.

Another popular equation for the analysis of isotherms of a high degree of regularity is that proposed by Dubinin (1960). They have reported that the characteristic sorption curve is related to the porous structure of the sorbent. In this study Dubinin-Radushkevich model could not satisfactorily fit the data of Cr (III) biosorption by *Streptomyces rimosus* as low regression coefficients and high χ^2 and RMSE values were observed.

The Langmuir model (Langmuir, 1916, 1917) served to estimate the maximum metal uptake values where they could not be reached in the experiments and it contains the two important parameters of the biosorption system (q_{\max} and b) (Nelson *et al.*, 2001; Tian *et al.*, 2002).

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \quad (12)$$

q_{\max} is attributable to the maximum metal uptake upon complete saturation of the sorbent and b is a coefficient attributed to the affinity between the sorbent and sorbate.

q_{\max} and b can be determined from the linear plot C_e/q_e versus C_e .

The adsorption data provided an excellent fit to the Langmuir isotherm with high values of the R^2 (Table 6). The separation factor (R_L) value indicates that Cr (III) biosorption of biosorbent in this study is favourable.

CONCLUSION

Biosorption performances of *Streptomyces rimosus* was studied in terms of kinetic and biosorption isotherms for the removal of trivalent chromium from aqueous

solutions. The kinetic experiments show that the biosorption on the sorbent is rapid and maximum biosorption capacities achieved in 80 min. Kinetic models evaluated included the fractional power, the Elovich, the pseudo-first-order and the pseudo-second-order. The kinetic data were well-described by pseudo-second-order model for the biosorption of Cr (III) on the biosorbent due to their high regression coefficient, low RMSE and chi-square values. Equilibrium isotherm data were fitted using different models. Among the different models, Langmuir model is in good agreement with all the experimental data with high R^2 and low standard error.

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