Kinetic modeling: Chromium(III) removal from aqueous solution by microbial waste biomass

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Received 05 September 2008; revised 27 March 2009; accepted 02 April 2009

This study presents removal of chromium (III) from aqueous solution by microbial waste biomass (MB2) obtained as a byproduct of pharmaceutical fermentation industry. Sorption kinetic behavior of Cr(III) was studied in a series of experiments in batch mode at different pH, adsorbent dosage and initial Cr concentration. Optimum Cr(III) removal (73.9%) from aqueous solution was at pH 4 by 1% biomass dosage. A comparison of kinetic models (Lagergren, Ho & McKay, Elovich & Morris-Weber) and correlation coefficient ($R^2$) indicated that Ho & McKay kinetic model correlates well with experimental kinetic data.

Keywords: Aqueous solution, Chromium (III), Kinetic modeling, Microbial waste biomass, Streptomyces sp., Tannery effluent

Introduction

Trivalent chromium [Cr(III)], widely used in industries (steel production, leather tanning, paints and pigments, metal plating) and other applications, is responsible for environmental pollution1,2. Cr(III) is relatively insoluble in water and less toxic than hexavalent chromium3. Conventional methods (precipitation, oxidation/reduction, ion exchange, filtration, membranes and evaporation) are extremely expensive or inefficient for metal removal and create sludge disposal problems4-6. Biosorption from industrial or natural sources may provide an efficient and competitive solution to treat wastewater. Biosorbents are prepared from bacteria, fungi and algae including waste biomass of fermentation and pharmaceutical industries7-8.

In this study, microbial waste biomass (MB2) from fermentation industry was used for Cr (III) removal from aqueous solution. Kinetics was studied at varying pH, adsorbent dosage and initial Cr(III) concentrations.

Materials and Methods

Microbial waste biomass of Streptomyces sp. (MB2) was obtained as a waste byproduct of pharmaceutical fermentation industry in fermentative production of antibiotics. Biomass collected from Ranbaxy (fermentation industry) Paonta Sahib, HP, India was grinded in a blender, sieved (size, 2.0 mm) and washed with distilled water before drying at 80°C for overnight or till moisture reduced to below 5%. Physico-chemical analysis of biomass was done as per reported9 method. Tannery effluent was collected from AV Tanneries, Kapurthala, Punjab, India and characterized10-11.

Preparation of Aqueous Solution

Aqueous solution of chromium was prepared by dissolving required quantity of $\text{Cr}_2\text{O}_3\cdot\text{S}_3$ in distilled water. Stock solution and tannery effluent were diluted with distilled water to obtain working solution (5-50 mg/l) for further experiments. Desired pH of solution was adjusted with 1N NaOH and 1N HCl.

Batch Kinetic Study

Batch experiments were conducted with MB2 in Erlenmeyer flask (250 ml) using different biomass dosage (0.25-2%) and aqueous solution (100 ml) of Cr(III) (25 mg/l). Suspension was shaken at 120 rpm, 28°C for 24 h. Similarly, experiments were conducted at different pH (2-5) and Cr(III) concentration (5-50 mg/l). Residual concentration of Cr(III) in aqueous solution was measured by atomic absorption spectrophotometer (AAS) with an air-acetylene flame using Cr-hollow cathode lamp having sensitivity limit of 0.05 ìg/ml. Working standard solution of Cr(III) was prepared from stock (1000 mg/l) procured from Acros Organic Ltd, New Jersey, USA. Triplicates of each sample were analyzed. Mean value and relative standard deviation as given by AAS were recorded. Cr(III) uptake ($q_e$) by biomass was calculated as
\[ q_e = \frac{(C_i - C_f)V}{m} \]  

where, \( C_i \) and \( C_f \), initial and final Cr(III) concentrations, mg/l; \( V \), Cr(III) solution volume, ml; \( m \), biomass wt, g.

Removed Cr(III) ions (\( R\% \)) was calculated as

\[ R(\%) = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \]

Results and Discussion

Physico-chemical parameters of MB2 are as follows:

\( pH, 6.50\pm0.43; \) bulk density, 0.70\pm0.21 g cm\(^{-3}\); ash, 45.77\pm1.20%; hydrogen, 6.79\pm0.22%; nitrogen, 8.53\pm0.34%; and calorific value (CV), 17.25\pm1.30 MJ/kg. CV (17.25 MJ/kg) of MB2 (\textit{Streptomyces} sp.) coincides with relative CV (17.5 MJ/kg) of biomass solid fuels, municipal waste, industrial waste, peat and brown coal\(^9\). Greenish tannery effluent [\( pH, 3.5; \) Cr(III), 1700.9 mg/l; total solids, 96,000 mg/l; total dissolved solids, 80,000 mg/l] had chemical oxygen demand (COD) of 332.8 mg/l and biochemical oxygen demand (BOD) of 290 mg/l. Traces of other metals (Fe, Pb Co, Cu, Cd), and secondary elements (Ca, Mg and Na) were also present.

Batch Kinetic Study

Batch sorption studies on Cr(III) removal from aqueous solution by MB2 was carried out to optimize adsorbent dosage, pH, contact time, Cr(III) concentration and removal of Cr(III) from tannery effluent.

Effect of Adsorbent Dosage

Effect of adsorbent dosage (0.25-2\%) on sorption of Cr(III) from aqueous solution (\( pH \) 4) containing Cr(III) (25 mg/l) with agitation rate of 120 rpm at ambient temperature was studied. Increasing adsorbent dosage (0.25-2\%), Cr(III) removal increased (45.84-54.89\%) by MB2 (\textit{Streptomyces} sp.). Similar observations were made with \textit{Aspergillus} sp\(^{15}\) and \textit{Streptomyces noursei}\(^{16}\), which showed 70-75\% removal of Cr(III) from aqueous solution and exhibited an adsorption capacity\(^{14}\) (1.8-2.0 mg/g) comparable with MB2 (2.24 mg/g) and commercial activated carbon\(^{1} \) (2.7 mg/g).

Effect of pH

Amount of Cr(III) adsorbed increased from 0.27 to 1.21 mg/g (72.38\%) by MB2 as \( pH \) increased from 2 to 5. Beyond \( pH \) 6.0, experiment was not done due to possibility of Cr(III) precipitation\(^{17}\). Maximum Cr(III) removal was achieved between \( pH \) 4-6, at which biomass surface is negatively charged\(^{12,13}\). Adsorption of Cr(III) is therefore an electrostatic interaction between biomass and Cr(III) cations. Ramos \textit{et al}\(^{18}\) reported that Cr(III) is not adsorbed at \( pH \) below 2 and Cr(III) is precipitated at \( pH \) above 6.4.

Effect of Chromium Concentration

Kinetics of Cr(III) removal by MB2 was studied at varying initial concentrations (5-50 mg/l) of Cr(III) in aqueous solution as well as from tannery effluent. Maximum Cr(III) removal capacities of MB2 from aqueous solution and tannery effluent were 24.9-68.2\% and 41.2-73.9\%, respectively in batch mode. Equilibrium uptake of Cr(III) increased in aqueous solution (0.08-2.89 mg/g) and tannery effluent (0.17-4.5 mg/g). Earlier reports\(^{16}\) also indicated that removal of Cr(III) was dependent on Cr(III) concentration because increase in initial Cr(III) concentration (50-300 mg/l) increased adsorbed amount of Cr(III).

Effect of Contact Time

With increase in contact time (0.08-4 h), Cr(III) removal increased from aqueous solution (40-70\%) and tannery effluent (11.5-57\%) by MB2. Maximum Cr(III) removal from aqueous solution (65\%) and tannery effluent (57.34\%) was observed within first 2 h. Lower removal rate in latter stage was due to difficulty faced by Cr ions to occupy remaining vacant surface sites because of forces between solute molecules of solid and liquid phase\(^{19}\). Therefore, adsorption is rapid and ultimate adsorption occurs within first hour of contact and saturation is reached within next 48 h\(^{1,8}\). Diminishing removal with increasing time may also be due to intraparticle diffusion process dominating over adsorption\(^{20}\).

Kinetic Modeling

Number of models have been developed to describe kinetics of metal biosorption in batch experiment\(^{1,2}\). Kinetic modelling of Cr(III) describes solute uptake rate, which controls residence time of adsorbate uptake at solid-solution interface. Conformity between experimental data and models predicted values was expressed by correlation coefficients (\( R^2 \), values close or equal to 1). A relatively high \( R^2 \) value indicates that model successfully described kinetics of Cr(III) adsorption.
Non-linear regression analysis was applied to each set of data. A correlation coefficient \( R^2 \) and a probability value (p) represent “goodness of fit” for models to the data obtained by linear as well non-linear regression.

Lagergren Equation (Pseudo-First-Order)

Sorption kinetic model\(^ {21} \) is expressed as

\[
\frac{dq_t}{dt} = k_l(q_e - q_t) \quad \ldots(3)
\]

where \( q_e \) and \( q_t \) (mg/g), adsorption capacity at equilibrium and at time \( t \), respectively; \( k_l \), rate constant of pseudo first-order adsorption process. After integration and applying initial conditions \( t = 0 \) to \( t = t \) and \( q_i = q_t \), integrated form of Eq. (3) becomes

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_l}{2.303} t \quad \ldots(4)
\]

Plot of \( \log (q_e - q_t) \) vs \( t \) should give a linear relation, from which \( k_l \) and \( q_e \) can be determined from slope and intercept of plot, respectively. \( R^2 \) of Cr(III) under different conditions were calculated from plots at different pH (Table 1), biomass dosage (Table 2) and Cr(III) concentration (Table 3). In most of the cases, first-order equation of Lagergren did not apply throughout the contact time and is generally applicable over initial (20-
30 min) sorption\textsuperscript{1,21}. A plot of log \((q_e - q_t)\) versus agitation time, gave a straight line with \(R^2\) of 0.94 for MB2 at pH 4 (Tables 1-3). Results showed that adsorption reaction can be approximated with pseudo first-order kinetic model. It was observed that \(k_1\) (0.03-0.88) and \(q_e\) (1.42-2.74) increased at different adsorbent dosage (0.25-2\%). Values of \(k_1\) (0.84-0.05) and \(q_e\) (1.83-0.95) decreased at different pH. In most of the cases, first-order equation of Lagergren did not apply throughout complete range of contact time and is generally applicable over initial (20-30 min) sorption process. Plots of log \((q_e - q_t)\) vs time \((t)\) (Fig. 1) deviated considerably from theoretical data after a short period. Slope and intercepts as calculated from plots were used to determine \(k_1\) (first-order rate constant) and equilibrium capacity \((q_e)\). Values of \(q_e\) are found lower than experimental one. Therefore, chromium-adsorbent systems do not follow a first-order rate equation\textsuperscript{1,22,23}.

**Ho and McKay Equation (Pseudo-Second-Order)**

Sorption kinetic model by Ho & McKay\textsuperscript{24,25} equation and adsorption kinetics rate is expressed as

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad \ldots(5)
\]

where \(k_2\) is rate constant of Ho & McKay equation (g/ mg/min). For boundary condition \((t = 0 \rightarrow t = t\) and \(q_t = 0\) to \(q_t = q_0\)), integrated form of Eq. (5) becomes

\[
\frac{l}{(q_e - q_t)} = \frac{l}{q_e} + kt \quad \ldots(6)
\]

This is integrated rate law for a pseudo second-order reaction. Eq. (6) can be rearranged as

\[
\frac{t}{q_t} = \frac{l}{k_2q_e} + \frac{l}{q_e} (t) \quad \ldots(7)
\]

If initial adsorption rate, \(h\) (mg/g/min) is \(h = k_2q_e^2\), then Eq. (7) becomes

\[
\frac{t}{q_t} = \frac{l}{h} \frac{l}{q_e} + \frac{l}{q_e} (t) \quad \ldots(8)
\]

Plot of \((t/q_t)\) and \(t\) of Eq. (7) should give a linear relationship, from which \(q_e\) and \(k_2\) can be determined from slop and intercept of plots, respectively (Fig. 2). \(R^2\) for linear plots are found superior (in most cases \(e^{0.99}\)) (Tables 1-3). It was observed that \(k_2\) (0.99-0.97) and \(h\) (6.32-25.38) increase with increase in biomass dosage. Values of \(k_2\) (0.29-2.94) and \(h\) (0.90-5.20) increased with increase in initial Cr(III) ions. Values of \(h\) and \(k_2\) were found higher for MB2 at different parameters [dosage, pH and Cr(III) concentration]. Experimental points shown together with theoretically generated values reflect extremely high correlation coefficients (Table 1-3). Data showed good compliance with pseudo-second order kinetic model\textsuperscript{1,16,17} \((R^2 > 0.99)\). However, these two models do not provide a definite mechanism. Therefore, another simplified model\textsuperscript{24,25} was tested, in which kinetic data is better fitted by second-order rate equation\textsuperscript{1,22,23}.
\[ y = 0.3401x + 0.1925 \]
\[ R^2 = 0.9985 \]

Fig. 2—Ho & Mckay equation for Cr(III) onto microbial waste biomass (MB2) \( C_i = 50 \text{ mg/l} \)

\[ y = 0.3507x + 1.8957 \]
\[ R^2 = 0.9859 \]

Fig. 3—Elovich equation for Cr(III) onto microbial waste biomass (MB2) \( C_i = 50 \text{ mg/l} \)

\[ y = 0.4031x + 1.3595 \]
\[ R^2 = 0.8309 \]

Fig. 4—Morris-Weber equation for Cr(III) onto microbial waste biomass (MB2) \( C_i = 50 \text{ mg/l} \)
(Fig. 2). Experimental \( q_e \) values were compared with \( q_e \) value determined by pseudo-first and second-order rate kinetic models, which suggests that sorption system is not a pseudo first-order reaction and that a pseudo-second-order model can be considered.

**Elovich Equation**

Elovich model equation is generally expressed as:

\[
\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)
\]  

\hspace{1cm}... (9)

where, \( \alpha \) initial adsorption rate (mg/g/min); \( \beta \), desorption constant (g/mg) during any one experiment. To simplify Elovich equation, Chien & Clayton assumed \( \alpha \beta >> t \) and by applying boundary conditions \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_e \) at \( t = t \), Eq. (9) becomes

\[
q_t = \frac{l}{\beta} \ln(\alpha \beta) + \ln(t)
\]  

\hspace{1cm}... (10)

If Cr(III) adsorption fits Elovich model, a plot of \( q_t \) vs \( ln(t) \) should yield a liner relationship with a slope of \( 1/(l/\beta) \) and an intercept of \( (l/\beta) \ln(\alpha \beta) \) (Fig. 3). \( R^2 \) were determined from plot between \( q_t \) and \( ln(t) \), respectively at different pH, biomass dosage and chromium concentration (Tables 1-3). Computed value of \( \alpha \) and \( \beta \) were calculated at biomass dosage [\( \alpha \) (18.18-0.26), \( \beta \) (9.42-34.13)], pH [\( \alpha \) (-3.69-94.32) \( \beta \) (-29.71-9.45)] and Cr(III) concentration [\( \alpha \) (7.55-78.07) \( \beta \) (26.25-2.85)]. Sorption kinetics of Cr(III) examined using Elovich model gave \( R^2 \) of 0.96 for MB2, which indicates that dynamics data fitted for biomass at pH 4.

**Morris-Weber Equation**

Intraparticle diffusion model of Cr(III) is expressed as by Weber & Morris and Srivastava et al. Sorption kinetics of Cr(III) was also examined by using Morris-Weber equation as

\[
q_t = R_{id} \sqrt{t}
\]  

\hspace{1cm}... (11)

where, \( q_e \), sorbed concentration at time \( t \); \( R_{id} \), rate constant of intraparticle transport. \( q_e \) was plotted against \( t^{1/2} \) (Fig. 4). Sorption follows linearity as per Eq (11) with \( R^2 \) (0.831). Value of \( R_{id} \) was computed from slope of plot. Value of \( R^2 \) was (Table 1-3): pH, 0.13-0.85; biomass dosage, 0.74-0.59; and Cr(III) concentration, 0.69-0.83. Values of \( R_{id} \) were calculated from slope of such plots (Fig. 4) and \( R^2 \) values led to the conclusion that intraparticle diffusion process is rate-limiting step. Higher values of \( R_{id} \) illustrate an enhancement in the rate of adsorption, whereas larger \( R_{id} \) values illustrate a better adsorption mechanism, which is related to an improved bonding between Cr(III) ions and adsorbent particles.

**Conclusions**

Microbial waste biomass comprising of Streptomyces sp. involved in fermentation process was effective in removal of Cr(III) from aqueous solution as well as tannery effluent. Maximum chromium removal capacities of Streptomyces sp. biomass (MB2) were 24.9-68.2 % from aqueous solution and 41.2-73.9% from tannery effluent at ambient temperature, rpm 120, and initial concentration (50 mg/l) of Cr(III). A comparison of kinetic models (Lagergren, Ho & McKay, Elovich & Morris-Weber) applied to MB2 indicates that adsorption of Cr(III) on MB2 follows a best Ho & McKay pseudo-second-order rate equation and correlation coefficient \( (R^2) \) correlated with experimental data. Removal of Cr(III) from aqueous solution was possible using MB2 from pharmaceutical fermentation industry. MB2 offers an alternative adsorbent for removal of Cr(III) from wastewater such as tannery effluent. This can provide means for using solid waste of one industry to treat chromium containing effluents from another industry for development of a suitable cost effective biosorbent.

**Acknowledgement**

Authors thank CSIR, New Delhi, for providing financial support, Ranbaxy Paonta Sahib, H P, India for providing microbial biomass and Director, Thapar University for providing infrastructural support.

**References**


8 Ahluwalia S S & Goyal D, Microbial and plant derived biomass for removal of heavy metals from wastewater, Biores Technol, 1165.


21 Lagergren S, About the theory of so-called adsorption of soluble substances, der Sogenanntensorption geloster stoffe Kungliga Svenska Vetenska psalka de Miens Handlingar, 24 (1898) 1-39.

22 Ho Y S, Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometrics, 59 (2004) 171-177.


