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The Adsorption of Chromium from Aqueous Solution Using Dead Biomass

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Abstract: Dead biomass was treated with NaOH 0.1N for chromium removal from aqueous solution. MEB and FTIR analysis show that the dead biomass is clearly porous and contain complexing functional groups in their cellular wall. The adsorption isotherm and kinetics experiments of chromium onto dead biomass were then carried out to investigate the adsorption property. It shows that the adsorption capacity of chromium is about 65 mg g^{-1}. The adsorption isotherm was fitted by the Langmuir, Freundlich and Dubinin-Radushkevich (D-R), which reveals that the Langmuir model is the best one. Two kinetics models, pseudo-first-order and pseudo-second-order, were rearranged for expediently investigating the adsorption mechanisms. Fitting results show that the pseudo-second order is better in describing the adsorption process.

Key words: Adsorption, uptake, chromium, kinetic, biosorption

INTRODUCTION

Understanding the sorption of metal ions from aqueous solution is important in water pollution control. 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 (Krishna and Philip, 2005). These industries contain Cr(III) and Cr (VI) at concentration ranging from 10-100 mg L^{-1} (Park *et al*., 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). Several International Environmental Agencies have introduced strict regulations with regard to metal discharge, especially from industrial activities. According to USEPA, the discharge of Cr (VI) into surface water is 0.5 mg L^{-1}, while total Cr including Cr (III), Cr (VI) and its other forms is regulated to below 2 mg L^{-1} (Vishwanatham, 1997). The conventional chemical processes are often restricted because of technical or economical constraints and generate large amount of toxic sludge. Thus the biosorption of heavy metals is relatively new technology. Several researchers found microorganisms, e.g. fungi (Huang and Huang, 1996; Volesky and Holan, 1995), seaweed and seaweed derivatives (Cossich *et al*., 2004; Vijayaraghvan *et al*., 2005) and fresh water algae (Bishnoi *et al*., 2005; Gupta *et al*., 2006), capable of efficiently accumulating heavy metals. Physical pretreatment methods such as heating, autoclaving and freeze-drying, boiling and chemical pretreatment such as using acids, alkali and organic chemical showed enhancement or reduction in metal biosorption depending upon the biomass and treatment procedures used (Huang *et al*., 1988; Kuyucak and Volesky, 1989; Kapoor and Viraraghvan, 1998). Most efforts were focused on the research of adsorption properties of biomass; an application of biomass on the waste-water treatment depends mightily on its origin and a few more efforts should be attempted to enhance its adsorption capability.

In this study, raw biomass was treated with NaOH to improve its adsorption capability and the effects of activation by NaOH and chromium adsorption were investigated. Meanwhile, the adsorption mechanism was studied via the adsorption isotherms and kinetics of chromium onto treated biomass.

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MATERIALS AND METHODS

Biomass preparation and characterisation: 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), λ = 35907 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_O and C_f : Are the initial and final concentration (mg L^{-1}), respectively.

All experiments were conducted at a constant temperature of 20±1°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: The zeta potential of biomass particles was measured using a Zeta Potential Analyser (model 1200 MICROMERITICS) (T=20°C; sample density 1 g cm^{-3}; Test duration 150s; Conductivity cell constant: 0.803 cm^{-1}; Intensity I = 7mA; 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 : The sorbent mass suspended in the test solution.
- d_p : Particle size diameter.
- ρ_{app} : The apparent density of the sorbent
- V : The solution volume.

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

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

SEM micrographs were obtained using JEOL 840 LGS. FTIR spectra were obtained using a Nicolet 560 spectrometer.

RESULTS AND DISCUSSION

Characteristics of adsorbent: The physical properties of the biosorbent are shown in Table 1.

SEM and FTIR analysis: To investigate the variation of the raw biomass after activated by NaOH,.SEM and FTIR analysis were carried out. Figure 1 contrast the SEM photograph of a raw biomass and treated biomass with NaOH.

On the Fig. 1 (a) and (b) are presented, respectively raw biomass and biomass treated with NaOH 0.1 N. (a) shows the raw biomass at x 2000. The structure is fibrous. Where as (b) shows the treated biomass with 0.1 N of NaOH, the structure is clearly porous with a large surface area and is compatible with good metal uptake characteristics (Tobin and Roux, 1998; Fourest *et al*., 2006; Fourest and Roux, 1992).

Table 1: The physical characteristic of the biomass

State of the biomass	Raw biomass	NaOH treated biomass
Particle size d_p (μm)	50-160	50-160
Humidity (%)	3.21	4.4
ρ_{app} (g cm^{-3})	1.05	0.41
S (m^{-1}) a	390	418
S_p (m^2 g^{-1}) a	0.131	0.14
Zeta potential (Volt)	-0.062	-0.072

*An average value of was used for calculation

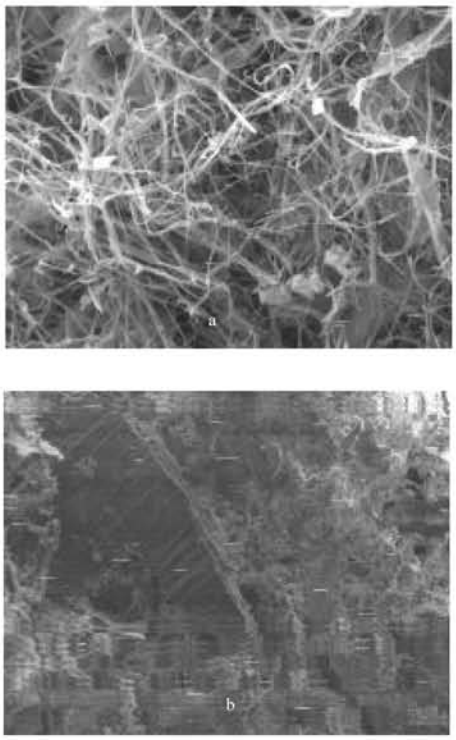

Fig. 1: SEM of (a) raw biomass (b) treated biomass with NaOH

Figure 2 shows the IR spectra obtained for a raw and NaOH-treated biomass samples. The frequencies of vibrations and their corresponding groups are presented in Table 2. According to Fig.2, no significant change was induced by treatment with NaOH in the main functional groups (carboxyl, amino, phosphate, amide and hydroxyl) likely to contribute to metal ion biosorption. Alkaline treatment has been reported to disrupt microbial cells walls, exposing additional functional groups and also to solubilize certain cell constituents such as lipids, which do not possess extensive metal binding capabilities (Glombitza and Iske, 1989).

A treatment for the partial or total removal of non-adsorbent molecules should increase the amounts of metal taken up (Glombitza and Iske, 1989). However, the most important effect of NaOH pre-treatment should be the high degree of deprotonation of the binding groups

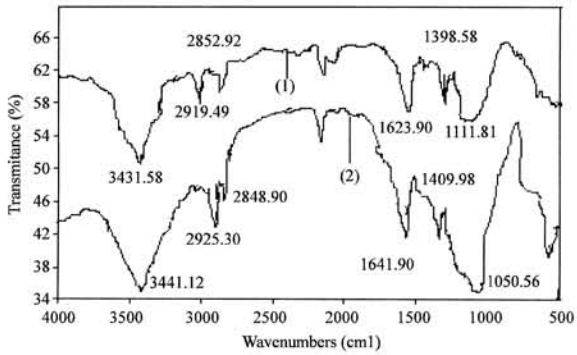

Fig. 2: FTIR spectra of raw biomass (1) and NaOH-treated biomass (2)

Table 2: IR absorption bands and corresponding possible groups

Functional groups	Raw biomass	NaOH treated biomass
-OH, -NH	3431	3441
-CH	2915	2925
-CH	2832	2848
-COO-, -C=O	1623	1640
-COO-	1398	1409
-C-O, -C-N, -P = O, P-OH, -P-O-C	1111	1050

(Fourest *et al*., 1994; Tobin *et al*., 1984; Siegel *et al*., 1983), increasing the number of available sites for metal ions. 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 (Hughes and Poole, 1989; Hancock, 1986). Due to this high fixed anionic content of the cell forms which are obviously present in *Streptomyces rimosus.* They may exhibit large sorption capacities; which could be of an important aspect for its industrial application as biosorbent especially for the transition metal cations that have high affinity not only to the surface ligands, such as phosphoryl, RNH_2 but also to carbonyl (COO^-) groups too.

Chromium adsorption isotherm: NaOH treated biomass was taken as example for investigating the adsorption isotherm. Figure 3 shows the amount of chromium uptake against the equilibrium concentration at a constant temperature 20°C. It reveals that the chromium uptake increases with the chromium concentration increasing from 0-2400 mg L^{-1} to reach an adsorption capacity of about 65 mg g^{-1}. The adsorption isotherm is essential for the research of an adsorption process. Numerous isotherm equations have been reported and 3 major isotherms, the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms (Vijayaraghavan *et al*., 2006) are tested to fit the experimental data in Figure 3.

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir isotherm is represented in the following equation:

$$q_e = q_{max}\frac{bC_e}{1+bC_e} \quad (4)$$

Where,

q_{max} : Is the adsorption capacity corresponding to form a complete monolayer.

b : Is the Langmuir constant related to the energy of biosorption.

The Freundlich isotherm is a non linear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules. The general form of this model is:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

Where,

K_F : Is the extent of the adsorption.

n : The degree of non-linearity between chromium concentration and adsorption.

The logarithmic form of Eq. (5) is

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (6)$$

The Dubinin-Radushkevich (D-R) adsorption isotherm has also used to describe the adsorption of chromium on biomass. The D-R equation has:

$$q_e = q_d \exp\left(-\beta_D \varepsilon_D^2\right) \quad (7)$$

Where,

q_e : The amount of chromium adsorbed per unit weight of adsorbent (mg g^{-1}).

q_m : The maximum adsorption capacity.

B_D : The capacity coefficient related to mean adsorption energy.

ϵ_D : The Polanyi potential, which is equal to:

$$\varepsilon_D = RT\ln\left(1+\frac{1}{C_e}\right) \quad (8)$$

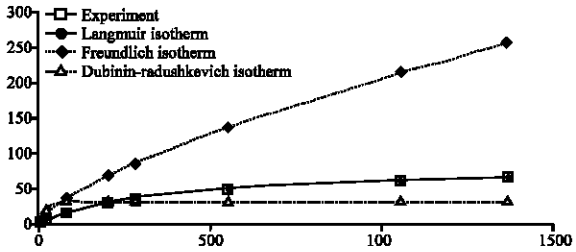

Fig. 3: Fitting the adsorption equilibrium data by the Langmuir, Freundlich and Dubinin-Radushkevich. Experimental condition: masse of biosorbent 0.3 g, initial chromium concentration 10-2400 mg L^{-1}. Solution volume 100 mL and agitation speed 300 rpm and equilibrium time 5 h

Where,

R : The gaz constant (J/mol°K).

T : The temperature (°K).

The saturation limit q_d may be represent the total specific micropore volume of the adsorbent. The adsorption potential is independent of the temperature but varies according to the nature of adsorbent (Khan *et al*., 1995). The slope of the plot of lnq versus ϵ_D gives β ($mol^2\ J^{-2}$) and the intercept yields the adsorption capacity, q_d (mg g^{-1}). The adsorption space in the vicinity of a biomass surface is characterised by a series of equipotential surfaces having the same adsorption potential. This adsorption potential is independent of the temperature but varies according to the nature of adsorbent and adsorbate.

Figure 3 displays a comparison of the non linear fitting of the experimental data with the above-mentioned 3 adsorption isotherms. Obtained parameters of all the models are given in Table 3. As can be seen that, the correlation coefficient (R^2) of Freundlich is higher than the Dubinin-Radushkevich while, the Langmuir model is the highest in the 3 models, indicating that the Langmuir model is the best one in simulating the adsorption isotherms of chromium onto biomass, which suggests that adsorption, occurs in homogeneous sites in the adsorbent.

In order, to predict whether the adsorption process by biomass is favourable or unfavourable for the Langmuir type adsorption process. The isotherm shape can be classified by a term R_L, a dimensionless constant separation factor, which is defined below (Altindogân *et al*., 2000; Rao *et al*., 2002):

$$R_L = \frac{1}{1+bC_0} \quad (9)$$

Where,

R_L : Dimensionless separation factor.

C_0 : The highest initial concentration of the metal cation (mg L^{-1}) in the investigated concentration range.

b : The Langmuir constant (l mg^{-1}).

The parameter RL indicates the shape of the isotherm accordingly Table 4.

It was found that the calculated R_L value for Cr^{3+} adsorption onto biomass was 0.13. This value indicates that the Cr^{3+} biosorption process is highly favourable at the highest initial metal concentration of 2400 mg L^{-1}, 20°C at pH 4.8.

Chromium adsorption kinetics: Kinetic study is important to an adsorption process because it depicts the uptake rate of adsorbate and controls the residual time of the whole process.

Time course: Time course of Cr uptake is presented in Fig. 4. It is obvious that Cr uptake is rapid; equilibrium can approximately be established within 60 min between absorbed Cr ions on the biomass and unabsorbed metal ions in solution. The process can be mainly divided into 2 stages rapid increases at the very beginning of the accumulation (e.g., 30 min) followed by slow uptake. In the second period, Cr uptake takes place slowly. The time course of Cr uptake is in agreement with the result of other metal ions uptaken by biomass (Fourest and Roux, 1992; Selatnia *et al.*, 2004).

Various kinetic models are available for describing the adsorption process and 2-known models are selected in this study.

The pseudo-first-order kinetic model, proposed by Lagergren (Lagergren, 1989) for adsorption analysis, is in the form:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \quad (10)$$

Where,

k_1 : The rate constant of pseudo-first order model.

q_t : The amount of solute adsorbed on the adsorbent at time.

Table 3: Comparison of three adsorption isotherm model

Langmuir model	Freundlich model	Dubinin-radushkevich model
q_{max} = 83,33 (mg g^{-1})	K_F=1.724 (l g^{-1})	q_d= 31,449 (mg g^{-1})
b= 0.0028 (l mg^{-1})	1/n =0.6930	β_D=0,00003 (mol^2J^{-2})
R_2 =0.992	R_2 =0.957	R_2 =0,739

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

t : Integrating this for the boundary condition.

q_t = 0 q_t = q_t at t= t and rearranging yields the linear time-dependent function:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303} \quad (11)$$

The intercept of the straight-line plots of $(q_e\text{-}q_t)^2$ against t should equal q_e. However, if the intercept does not equal q_e, then the reaction is not likely to be first-order, irrespective of the magnitude of the correlation coefficient.

The pseudo-second-order (Ho, 2006) developed by equation is expressed as:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \quad (12)$$

where, k_2 is the rate constant of pseudo second order adsorption (g $mg^{-1}min^{-1}$). Taking into account, the boundary conditions t=0 to t=t and q_t = 0 to q_t = q_t.

The integrated form of Eq. (12) can be rearranged to obtain Eq. (13):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (13)$$

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

$$h = k_2 q_e^2 \quad (14)$$

The plot of (t/q_t) and t of Eq. (6) should give a linear relation ship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

Since, metal uptake is one of the most intelligible parameters in an adsorption system. The chromium uptake

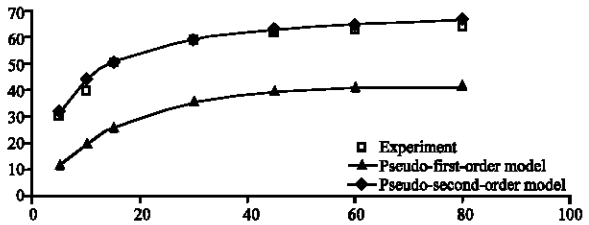

Fig. 4: Fitting adsorption kinetics data for chromium onto treated biomass using two models. Experimental condition, mass of biosorbent 0.3 g, initial chromium, Concentration 2400 mg L^{-1}, solution volume; 100 mL, agitation speed, 300 rpm

Table 5: Pseudo-first-order and pseudo-second order Kinetics parameters of chromium biosorption onto Streptomyces rimosus

Pseudo-first-ordermodel	Pseudo-second-order model
q_e= 41.51 (mg g^{-1})	q_e= 71.43 (mg g^{-1})
k_1= 0.064 (min^{-1})	k_2= 2.2 10-3 (g $mg^{-1}.min^{-1}$)
R_2= 0.989	R_2=0.999

form of pseudo-first-order and pseudo-second-order equation obtained by us was then employed for non-linear-fitting of the experimental results. As shown in Fig. 4 and their model parameters obtained from non-linear regression are listed in Table 5. As can be seen from the correlation coefficient, the pseudo-second-order is better than the pseudo-first-order, suggesting that the biosorption process of chromium onto treated biomass follows the pseudo-second-order process.

CONCLUSION

In this study, biosorption of Cr (III) on dead Streptomyces rimosus in treated and untreated forms has been investigated. Treated biomass with NaOH 0.1N indicates good biosorbent compatible with good metal uptake characteristic. The adsorption isotherm of chromium onto treated biomass was fitted by Freundlich, Dubinin-Radushkevich and Langmuir models. It is found that the Langmuir is the best one, indicating that adsorption, occurs in homogeneous sites in the adsorbent. The kinetic study of chromium onto treated biomass reveals that the adsorption behaviour is better described by the pseudo-second-order model than the pseudo-first-order model.

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