Research Article Biosorption of Hexavalent Chromium from Aqueous Medium with the Antibiotic Residue

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Abstract: The antibiotic residue was used as a biosorbent for Cr (VI) aqueous solution to investigate its Cr (VI) removal capacity. The effect of experimental parameters, such as pH, sorbent dosage, initial metal concentration and contact time were examined and the optimal experimental conditions were determined. The results showed that 88.61 and 95.07% of Cr (VI) was removed by using the raw and acid-treated antibiotic residue powder as biosorbent. Maximum removal of Cr (VI) ions in aqueous solution was observed at pH 1.0. Biosorption kinetic data were properly fitted with the pseudo-first order kinetic model. The adsorption process followed the Langmuir isotherm adsorption model. Thermodynamic parameters of the adsorption process, such as ΔG° , ΔH° and ΔS° , were calculated and the results indicated that the overall adsorption process were feasible, spontaneous in nature. Finally, the removal mechanism is discussed by deduction from the experimental results, FTIR and SEM images. The adsorption of Cr (VI) coexists with the redox process and the antibiotic residue powder is a potential biosorbent which could be used in treatment of chromium contaminated wastewater.

Keywords: Adsorption, Cr (VI), oxidation and reduction, the antibiotic residue, thermodynamics

INTRODUCTION

The recent rapid industrialization in China has lead to the release of huge amounts of industrial effluents into the environment and the heavy metals such as Cr, Cu, Pd, Ni, Zn and so forth, present in these effluents are more stable and persistent environmental contaminants; since they cannot be degraded or destroyed. Thus they tend to accumulate in ground water, the soil, seawater and sediments, which intensify environmental pollution. Chromium have been widely used in variety of industrial applications, such as leather tanning, steel production units, cement industries, mining, other metal alloys industries and so on (O'Dwyer and Hodnett, 1995; Gupta and Rastogi, 2009). The common forms that Chromium is present in the environment are chromium (0), chromium (III), chromium (VI). Chromium (VI) is mobile in the environment and is highly toxic. Cr (VI) can easily penetrate the cell wall and exert its noxious influence in the cell itself, being also a source of various cancer diseases. Cr (III) is less toxic than Cr (VI) and is nearly insoluble at neutral pH. It is poisonous only at high concentration (Mojdeh et al., 2009). The highest level of Cr (VI) ions permitted in a discharge into inland surface and potable waters, are 0.1 and 0.05 mg/L, respectively (EPA, 1990; Mojdeh et al., 2009). An increased risk of lung cancer is reported among workers exposed to chromate production environment (Gibb *et al.*, 2000). So there is a major concern for the elimination of such heavy metal from wastewater before disposal to the environment.

Different metal removal methods (chemical reduction and phytoremediation, reverse osmosis, precipitation, bioremediation, ion exchange, etc.) have been tested for detoxification of Chromium-laden waste waters in the recent years. However, they have high operating costs and problems in the disposal of the residual metal sludges. Biosorption techniques could use inexpensive sorbent materials as a feasible alternative for Chromium removal that features high efficiency, low operating costs with no adverse effects on the environment (Mohan and Pittman Jr., 2006). From the analysis of recent publications it was found that different inexpensive, locally and abundantly available biosorbents have been employed for removal of various heavy metals. For example, sugarcane bagasse (Ihsan et al., 2013), jatropha oil cake (Garg et al., 2007), mustard oil cake (Khan et al., 2012), sawdust, rice husk (Bansal et al., 2009), olive-stone (Blázquez et al., 2011), modified coconut coir pith (Namasivayam and Sureshkumar, 2008) and so forth.

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The biosorption with the mycelia (dead cells) from by-product of fermentation industry is of low cost, high selectivity as well as ready availability. Many fermentation processes, such as penicillin and citric acid production, produce a large quantity of biomass that has high metal ion adsorption capacity. Use of dead biomass from industries also helps solve the problem of waste biomass disposal. The microbial biomasses have been widely used for removal of metals like, Pb and Cr from aqueous solutions (Gupta and Rastogi, 2009; Gupta *et al.*, 2010).

The antibiotic resident are a good low-cost candidate for utilization as biosorbent. In this study, it was used as potential biosorbent for hexavalent chromium removal from aqueous solution. Parameters affecting the biosorption process are discussed. In addition, adsorption isotherms and kinetic models were tested in order to have a better understanding of the biosorption process.

MATERIALS AND METHODS

Reagent: All chemicals and reagents used were of analy-tical grade; 1, 5-Diphenylcarbazide (DPCI), CH_3 COCH₃, HCl, HNO₃, H₃PO₄, H₂SO₄, K₂CrO₇ and NaOH were obtained from Xilong Chemical Co., Ltd. (China). Stock solutions of Cr (VI) were prepared by dissolving salts of K₂Cr₂O₇ in double distilled water. The working solutions were obtained by diluting the stock solutions with double distilled water. All the glass-ware and plastic centrifuge tube were rinsed in 1 mol/L HNO₃ overnight to remove any metal that remained adsorbed on the glass wall and cleaned with deionized water before use.

Biomass collection and preparation: The antibiotic residue was collected from one Pharmaceutical Factory in Shaanxi Province, dried in sunlight followed by oven dried at 65°C for 72 h. The dried residue was filtered through a 0.15 mm size sieve and subsequently referred as raw biomass. The acid-treated antibiotic residue was prepared by transferring the raw antibiotic residue into 0.1 mol/L HCl and then stirring the mixture at 200 rpm for 24.0 h at room temperature. Following the acid treatment, the material was then centrifuged, washed several times with the deionized water until the pH value reached 7±0.5 and dried in an oven at 65°C. Subsequently, the fraction with 0.15 mm diameter was selected and used for sorption experiments. The sieved material was stored in airtight plastic containers until used.

Batch biosorption experiments: Adsorption of Cr (VI) by raw and acid-treated antibiotic residue was studied as a function of contact time, initial concentration of Cr (VI), biosorbent dose, pH and temperature. To study the adsorption as a function of pH, 1-9 pH for Cr (VI) were considered and biomass dose (0.5 g), For biosorption experiments, aqueous solutions of varying pH were prepared from the stock by adjusting the pH with 0.1

mol/L NaOH or 0.1 mol/L HCl using a pH meter. Contact times (0, 5, 10, 20, 30, 40, 50, 60, 90, 120, 180, 210, 240, 270 and 300 min, respectively) were used for dose effect studies, while additional contact times were employed for kinetic measurements and initial metal ions concentration (50 mg/L) were kept constant. To evaluate the initial metal concentration, 10-300 mg/L concentrations of Cr (VI) were used, while 0.5 g biomass dose, contact time 5 h were constant and pH of 1 were adjusted for Cr (VI). The contact time ranging from 5 to 300 min was used to evaluate kinetic study, while dose (0.5 g), initial concentration (50 mg/L) and pH of 1 were constant. The volume of solution (50 mL) and biosorbent particle size (0.15 mm), shaking (200 rpm) and temperature (25°C) were constant in all batches. The residual Cr (VI) ions present in the supernatant was determined by 1, 5-diphenylcarbazide method. And in acidic solutions, Cr (VI) reacted with 1, 5-diphenylcar-bazide to a red-violet-colored solution which was form spectrophotometrically measured at 540 nm (Shanmugaprakash et al., 2014). All the experiments were performed in triplicate.

The removal efficiency R (in percent) of metal ions was then calculated for each run as follow:

$$R (\%) = \frac{C_0 - C_e}{C_0} \times 100$$
 (1)

where,

C_0 and C_e : The initial and the final concentrations of the metal ions in milligrams per litre

The biosorption capacities of the antibiotic residue waste biomass of Cr (VI) were estimated using the amount of ions retained on unit mass of biomass (q_e , mg/g) (Manzoor *et al.*, 2013):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{2}$$

where,

 C_0 and C_e : The initial and the equilibrium concentration of chromium (mg/L)

V : The volume of solution (L) and m is the biosorbent mass (g)

Kinetic studies: Kinetics studies were performed at 298 K. Two kinetic models (the pseudo-first-order Eq. (3) and the pseudo-second-order Eq. (4) (Ihsan *et al.*, 2013) were applied to the adsorption data to better understand the effects of the antibiotic residue and time on the adsorption process:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$
(3)

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where,

- q_e and q_t (mg/g): The solid phase-concentrations of metal adsorbed on the adsorbent at equilibrium and any time t
- k₁ (min⁻¹) and k₂ (g/mg.min) : The rate constants of pseudo-first-order and pseudo-second-order adsorption

Adsorption isotherms:

Freundlich adsorption model: The Freundlich model (Shaik *et al.*, 2008; Zenggiang and Yiping, 1998) gives a better fit particularly for adsorption from liquids and can be expressed as:

$$Inq_e = InK_f = \frac{1}{n}InC_e \tag{5}$$

In this model, C_e is the equilibrium concentration of Cr (VI) in the solution (mg/L), q_e is the adsorption capacity of Cr (VI) at equilibrium (mg/g), K_f (L/mol) is a Langmuir binding constant related to the energy of adsorption.

Langmuir adsorption model: The Langmuir adsorption isotherm (Shaik *et al.*, 2008; Ronghua *et al.*, 2014) is given by the following equation:

$$q_e = \frac{q_m K_c C_e}{1 + K_c C_e}$$
(6)

In this model, q_m (mg/g) is the maximum adsorption capacity and K_c (L/mol) is the Langmuir constant.

 K_c values derived from the Langmuir modeling of isotherm data were used to estimate the thermodynamic parameters of changes in enthalpy (ΔH°), entropy (Δ S°) and free energy (Δ G°) according to the following equations (Ronghua *et al.*, 2014; Yasmin *et al.*, 2009):

$$\Delta G^{\circ} = -RT \ln K_c \tag{7}$$

$$\Delta H^{\circ} = RT_2T_1(T_2 - T_1)\ln\frac{Kc_2}{Kc_1}$$
(8)

$$\Delta S^{\circ} = \left(\Delta H^{\circ} - \Delta G^{\circ} \right) / T \tag{9}$$

where,

R : The universal gas constant (8.314 J/mol. K)

T : The absolute temperature (K)

K_c : Expressed in L/mol

RESULTS AND DISCUSSION

Characterization of the biosorbent: The physical and chemical properties of the raw and acid treated antibiotic residue were determined by the standard methods. The pore Diameters (D_{BJH}), the BET Surface area (S_{BET}) and the total pore Volumes (V_{total}) of the raw sample together with the acid treated sample were summarized in Table 1. The S_{BET} of Antibiotic residue was enhanced by the acid-treatment (S_{BET} (raw) = 0.39 m²/g, S_{BET} (acid-treated) = 4.87 m²/g).

Scanning Electron Microscopy (SEM) is a primary tool for characterizing the surface morphology. SEM micrographs of native antibiotic residue and the adsorbed residue with Cr (VI) are shown in Fig. 1. It is clearly seen the surfaces of particles after adsorption in Fig. 2 (right) that the pores and surfaces of adsorbent were covered and became smooth by adsorbate. This may be due to the significant possibility of the

Table 1: Physicochemical property of the raw and acid-treated sample	ples
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Fig. 1: SEM micrograph of antibiotic residue before (left) and after (right) Cr (VI) adsorption



Fig. 2: FTIR spectra of raw antibiotic residue before and after Cr (VI) adsorption

chromium ions being adsorbed onto the pores and remaining trapped. The results are consistent with previous studies reporting changes in the nature of the adsorbent after adsorption process (Ihsan *et al.*, 2013; Sukumar *et al.*, 2014).

The FTIR Spectra of raw and acid-treated antibiotic residue are showed in Fig. 2. According to many studies, carboxyl groups (-COO⁻), hydroxyl groups (-OH) and amino groups (-NH₂) are the main functional groups responsible for metal sorption (Shaik et al., 2008; Sukumar et al., 2014). Their importance for metal uptake depends on factors such as the quantity of sites, its accessibility, chemical state or affinity between site and metal (Gupta and Rastogi, 2009). The broad peak (3500-3200/cm) was assigned to the stretching of the O-H group because of inter- and intramolecular hydrogen bonding of polymeric compounds (Shin et al., 2012). The stretching bands at 2870-2940 cm⁻¹ were attributed to asymmetric and symmetric C-H stretching in the organic carbon chain (Sukumar et al., 2014). Symmetric stretching vibrations of ionic carboxylic groups (-COO⁻) appeared at 1455 cm⁻¹ (Ningchuan et al., 2011). Some shifts in the wave numbers were observed. The peak 3336 cm⁻¹ was shifted to 3347/cm. This shows that the O-H groups were involved in Cr (VI) binding (Dotto et al., 2012).

Effect of pH: It is has been showed that pH is an important parameter affecting the biosorption process. The adsorption characteristics of Cr (VI) with various pH in the range of 1.0-9.0 are studied at initial concentration of 50 mg/L, using two biomasses as shown in Fig. 3. The maximum binding of Cr (VI) was

observed at pH 1 and it could be due to electrostatic attraction between negatively charged chromium species (chromate/dichromate) and positively charged functional groups onto the surface of biosorbents. Under acidic conditions, the predominant species of Cr (VI) are $(Cr_2O_7)^{2-}$, $(HCrO_4)^{-}$ (Chanil *et al.*, 2013). At pH 1.0, the surface of the sorbent becomes protonated and attracts anionic species of Cr (VI) (Ozer and Ozer, 2003; Selvaraj et al., 2003). As pH increased, overall surface charge on adsorbent became negative and biosorption rate was decreased. In alkali conditions, carboxylate group exists in deprotonated form and had net negative charge (Davis et al., 2003; Shin et al., 2012; Sukumar et al., 2014). As a result, the surface charge of the biosorbents become negative and biosorption of Cr (VI) was decreased. At a higher pH, that is, in the alkaline range, the surface of the adsorbent will have hydroxyl groups which will not attract the chromate ions that compete with the hydroxyl ions (Vankar et al., 2012).

Effect of the adsorbent dose: Adsorbent dose have a great influence on adsorption process. Figure 4 revealed that the removal of Cr (VI) ions increased with the increase in adsorbent dosages. The removal remained unchanged above 20 g/L of dosage. This was due to the increase in adsorption sites with the increase in the adsorbent dosage. The biomass dosage strongly affected the amount of metals removed from aqueous solutions. Initially increase in the adsorption sites. Similar results have also been reported previously for chromium metal biosorption from aqueous medium

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Fig. 3: Effect of initial pH on the removal (%) of Cr (VI) by raw and acid-treated antibiotic residue



Fig. 4: Effect of biomass dosage on removal of Cr (VI) with raw and acid-treated antibiotic residue

using Rosa bourbonia waste phyto-biomass (Iqbal *et al.*, 2013), immobilized *C. elegans* (Abdel-Razek, 2011), chlorella species biomass (Kanchana *et al.*, 2011), sugarcane bagasse waste biomass (Ihsan *et al.*, 2013) and *T. clypeatus* biomass (Khowala, 2012).

Effect of initial metal concentration: The effect of initial metal ions concentration on adsorption was checked from 10 to 500 mg/L for both chromium ions and the other operating conditions such as shaking (200 rpm), contact time (3 h), biosorbent dose (0.5 g) and pH (1) were constant. The plot of metal removal (%) versus initial metal concentration is shown in Fig. 5. It is evident from the results that percentage of Cr (VI)

removal was gradually decreased according to increasing initial Cr (VI) concentration and acid-treated biosorbent showed a higher biosorption capacity compared to the raw biosorbent under similar conditions. The enhanced removal at low concentration was due to high availability of reactive sites. However, in higher concentration, the reduced availability of reactive sites may slow down the adsorption process (Ihsan *et al.*, 2013), Similar trend of chromium adsorption has also been reported previously as a function of initial metal concentration; e.g., Catla catlascales (Kondapalli and Kaustubha, 2009), solid biomass waste from the biodiesel production (Shanmugaprakash *et al.*, 2013).

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Fig. 5: Effect of initial concentration of Cr (VI) on removal capacity using raw and acid-treated antibiotic residue



Fig. 6: Effect of contact time on the uptake of Cr (VI) onto raw and acid-treated antibiotic residue

Effect of contact time: The experimental results of contact time for the biosorption of Cr (VI) ions onto the raw and acid-treated antibiotic residue are shown in Fig. 6. The results reveal that the amount of heavy metal ion sorption increased rapidly with the contact time initially; then, the rate of biosorption became slower and no further considerable biosorption rate was noted after the equilibrium was reached. The biosorption capacity of Cr (VI) ions increased considerably with increasing contact time up to 180 min, there-after, it was nearly constant. Therefore, for further experiments, the optimum contact time for Cr (VI) was selected as 180. A similar study regarding the effect of contact time has been reported for the removal

of Cr (VI) on pomace (Emine *et al.*, 2006) and on sugarcane bagasse (Shanmugaprakash *et al.*, 2014). Both the authors revealed that the biosorption rate was higher in the initial stage, due to a larger surface area of the biosorbent being available for the biosorption of the metal ions.

Thermodynamics: The Gibbs free energy change (ΔG°) was plotted as a function of temperature, which can be used to confirm the feasibility and the spontaneous nature of the adsorption process. In Fig. 7 the decrease in ΔG° values with increased temperature suggested that Cr (VI) adsorption on the antibiotic residue was a chemical process by nature. The

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Fig. 7: The plot of ΔG° versus T

Table 2: The adsorption thermodynamic parameters of the Cr (VI) on raw and acid-treated antibiotic residue

	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	$\Delta S^{\circ} (kJ/mol/K)$
Raw	298	-20.05	1.37	0.0719
	303	-20.37		
	313	-21.05		
	323	-21.85		
Acid-treated	298	-21.30	-2.05	0.0646
	303	-21.60		
	313	-22.26		
	323	-22.91		

adsorption thermodynamics parameters (ΔG° , ΔH° and ΔS°) of Cr (VI) on the raw and acid-treated antibiotic residue were given in Table 2. The ΔG° values were calculated to be -20.53 and -21.30 kJ/mol at 298 K for raw and acid-treated, respectively. The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the biosorption. The value of ΔH° was positive, indicating that the sorption reaction is endothermic. The negative values of ΔH° indicated that the adsorption process was exothermic.

The ΔS° values estimated were positive, indicating that the adsorption process is driven by enthalpy change. Similar results were reported by other types of adsorbents, including dead fungal biomass of marine *Aspergillus niger* (Yasmin *et al.*, 2009) and raw and acid-treated green alga *Oedogonium hatei* from aqueous solutions (Gupta and Rastogi, 2009).

Adsorption isotherm:

Biosorption kinetics: The adsorption rate constant (k_1) for chromium sorption was calculated from the slope of the linear plot of log (q_e-q_t) versus time. In the latter case, kine-tic data were plotted between t/q against t. A relatively high R² value indicates that the model successfully describes the kinetics of chromium (VI) adsorption. The kinetic rate constants obtained from

first-order and second-order pseudo kinetic model are given in Table 3. It can be seen that regression coefficients of pseudo-second order are slightly deviated from unity. Moreover, the $q_{e,cal}$ values for the first-order model are more close to $q_{e,exp}$ values in comparison to second-order values, suggesting that pseudo-second order is not an appropriate model. Hence, the pseudo-first order kinetic model with higher value of regression coefficient (\mathbb{R}^2 , 0.988 and 0.992 for raw and acid-treated, respectively) fitted well to the data. So the adsorption mechanism can be described well by the pseudo-first-order kinetics.

Modeling of adsorption isotherms: The Langmuir and Freundlich isotherms models are employed to fit the experimental data. The model constants along with correlation coefficients (R^2) obtained from the two isotherm models are listed in Table 4. The high values of the correlation coefficients R^2 suggested that the experimental data fitted well with the shape of the Langmuir isotherms (Iqbal *et al.*, 2013). The Langmuir isotherm model indicates the formation of monolayer coverage of heavy metal ions on the outer surface of biosorbent. Each binding site accepts one Cr (VI) molecule, that sorbed molecules are organized as a monolayer and all sites are energetically equivalent

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	First-order model				Second-order	Second-order model		
Biomass	$q_{e, exp} (mg/g)$	$k_1 \times 10^{-3} (min^{-1})$	q _{e, cal} (mg/g)	R ²	k ₂ ×10 ⁻³ (g/mg)	/min) q _{e, cal} (mg/g)	R ²	
Raw	2.21	23.237	2.85	0.988	3.11	3.18	0.927	
Acid-treated	2.38	26.853	2.95	0.992	4.28	3.16	0.952	

Table 3: Summary of sorption data evaluated by different kinetic models for the raw and acid-treated antibiotic residue (pH 1.0)

Table 4: Langmuir and freundlich isotherm constants for the adsorption of Cr (VI) onto raw and acid-treated antibiotic residue at different temperatures

Biomass	Temperature (K)	Langmuir constant			Freundlich c	Freundlich constant		
		K _c (L/mol)	$q_e(mg/g)$	R ²		K _f (L/mg)	R ²	
Raw	298	3273.72	7.42	0.999	0.424	0.798	0.857	
	303	3253.25	7.77	0.999	0.426	0.819	0.860	
	313	3257.86	7.94	0.999	0.427	0.830	0.862	
	323	3416.69	8.13	0.998	0.425	0.864	0.863	
Acid-treated	298	5415.21	9.53	0.995	0.365	1.280	0.800	
	303	5291.88	10.04	0.996	0.377	1.300	0.811	
	313	5183.08	10.63	0.996	0.373	1.350	0.797	
	323	5079.09	11.09	0.995	0.377	1.370	0.798	

and there is no interaction between sorbed molecules (Emine *et al.*, 2006). The biosorption capacity of heavy metal ions were found in accordance with previous studies for the adsorption of chromium using rose waste biomass (Iqbal *et al.*, 2013), sugarcane bagasse waste biomass (Ihsan *et al.*, 2013) and *B. subtilis* biomass (Sukumar *et al.*, 2014).

CONCLUSION

The Cr (VI)-antibiotic residue showed considerable potential for the removal of Cr (VI) (95.07% for acidtreated and 88.61% for raw) within 180 min from 50 mg/L of aqueous solution. The bioadsorption isotherm obeys Langmuir isotherm and pseudo first-order kinetic models. From the results, it is clear that isolate antibiotic residue could be a good biosorbent and can be used for removal of Cr (VI) from industrial wastes and further study for application of this technology in field is required.

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