



Modeling and evaluation on removal of hexavalent chromium from aqueous systems using fixed bed column

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ABSTRACT

Removal of hexavalent chromium by xanthated chitosan was investigated in a packed bed up-flow column. The experiments were conducted to study the effect of important design parameters such as bed height and flow rate. At a bed height of 20 cm and flow rate of 5 mL min^{-1} , the metal-uptake capacity of xanthated chitosan and plain chitosan flakes for hexavalent chromium was found to be 202.5 and 130.12 mg g^{-1} respectively. The bed depth service time (BDST) model was used to analyze the experimental data. The computed sorption capacity per unit bed volume (N_0) was 4.6 ± 0.3 and $78.3 \pm 2.9 \text{ g L}^{-1}$ for plain and xanthated flakes respectively at 10% breakthrough concentration. The rate constant (K_a) was recorded as 0.0507 and $0.0194 \text{ L mg}^{-1} \text{ h}^{-1}$ for plain and xanthated chitosan respectively. In flow rate experiments, the results confirmed that the metal uptake capacity and the metal removal efficiency of plain and xanthated chitosan decreased with increasing flow rate. The Thomas model was used to fit the column sorption data at different flow rates and model constants were evaluated. The column was successfully applied for the removal of hexavalent chromium from electroplating wastewater. Five hundred bed volumes of electroplating wastewater were treated in column experiments using this adsorbent, reducing the concentrations of hexavalent chromium from 10 mg L^{-1} to 0.1 mg L^{-1} .

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1. Introduction

Chromium compounds find their way to the environment mainly through tanning and electroplating industries. Chromium, essentially exists in two forms namely Cr(VI) and Cr(III). Cr(III) is proved to be biologically essential to mammals as it maintains an effective glucose, lipid and protein metabolism. In contrast, Cr(VI) is highly toxic as it can diffuse as CrO_4^{2-} or HCrO_4^- through cell membranes. Major toxic effects of Cr(VI) are chronic ulcers, dermatitis, corrosive reaction in nasal septum and local effects in lungs. WHO (World Health Organization) and BIS (Bureau of Indian Standards) recommended guideline value for chromium (as total chromium) in drinking water as 0.05 mg L^{-1} (desirable) with no relaxation on permissible limit [1,2]. The tolerance limit for Cr(VI) for discharge into inland surface water is 0.1 mg L^{-1} [3,4] have recently reviewed the methods available of the removal of hexavalent chromium from water and wastewater. Conventional heavy metal removal processes such as precipitation, ion exchange, reverse osmosis have many limitations such as safe disposal of sludge and cost. Sorption appears as a simple and low-cost method, with a great potential of becoming an actual alternative to conventional ones, overcoming

the problems of insufficient efficiency and difficult waste handling derived from the precipitation method. Among the various adsorbents, adsorption onto activated carbon (granular or powdered) is widely used; there is still a need to develop low cost and easily available adsorbents for the removal of heavy metal ions from the aqueous environment. Hence in recent years, research has been focused on the use of various biomasses including raw rice bran [5], ethylenediamine-modified rice hull [6], hazelnut shell [7], saw dust, sugar beet pulp, maize cob, sugarcane baggase [8], pine needles, olive cake, wool, almond, soya [9], maple saw dust [10], saw dust activated carbon [11] and sugarcane bagasse [12], etc. The main disadvantages of these adsorbents are that they are not fully characterized and the adsorption capacity was found to be very low. Chitosan is a biodegradable, biocompatible, non-toxic biopolymer, reported to be an efficient heavy metal scavenger due to the presence of amino group and is widely used in wastewater treatment applications [13]. Earlier, we have investigated xanthate functionalized chitosan for the removal of Cr(VI) in batch mode [14]. Using xanthated chitosan, a very high adsorption capacity of 625 mg g^{-1} was observed for Cr(VI) at reaction pH of 3 and adsorption equilibrium was achieved within 16 h for initial Cr(VI) of $50\text{--}1000 \text{ mg L}^{-1}$. The sorption capacity parameter obtained from a batch experiment is useful in providing information about effectiveness of metal-biosorbent system. However, the data obtained under batch conditions are generally not applicable to most treat-

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Nomenclature

C_0	inlet Cr(VI) concentration (mg L^{-1})
C_b	outlet total chromium concentration (mg L^{-1})
V_{eff}	volume of the effluent (mL)
F	volumetric flow rate (L h^{-1})
ν	linear flow rate (cm h^{-1})
t_{total}	total flow time (h)
t_b	time at which Cr(VI) concentration in the effluent reached 0.1 mg L^{-1} (h)
t_e	time at which Cr(VI) concentration in the effluent reached 9.9 mg L^{-1} (h)
Δt	mass transfer zone (h)
m_{ad}	amount of chromium adsorbed in the column (mg g^{-1})
m_{total}	total amount of chromium sent to column (g)
N_0	sorption capacity of bed (g L^{-1})
K_a	bed depth service model rate constant ($\text{L mg}^{-1} \text{ h}^{-1}$)
Z	bed height (cm)
t	service time (h)
k_{Th}	Thomas model constant ($\text{L mg}^{-1} \text{ h}^{-1}$)
Q_0	maximum solid-phase concentration of solute (mg g^{-1})
Q	uptake capacity (mg g^{-1})
M	sorbent mass (g)
V	throughput volume (L)

ment systems where contact time is not sufficiently long for the attainment of equilibrium. The practical application of heavy metal sorption is most effectively carried out in a packed bed column, as it efficiently utilize the sorbent capacity and results in an improved quality of the effluent. Studies have been reported for the removal of Cr(VI) in a packed bed column [15–18]. However, the applicability of the adsorbent towards real industrial wastewater has not been explored.

Hence, in the present investigation, the ability of xanthated chitosan to remove Cr(VI) in a packed up-flow column was evaluated. Effects of design parameters, such as bed height and flow rate, on chromium sorption have been examined. In addition, the removal capacity of Cr(VI) in electroplating effluent has also been investigated.

2. Materials and methods

2.1. Materials

Chitosan flakes were acquired from India Sea foods, Cochin, India and used without any further purification. The degree of deacetylation was reported to be 88% by the manufacturer. Glutaraldehyde and carbondisulfide were purchased from Sigma–Aldrich and used without further purification. All the inorganic chemicals used were analar grade and all reagents were prepared in Millipore milli-Q deionized water.

2.2. Chemical modification of the chitosan flakes

Chitosan flakes were cross-linked with glutaraldehyde and chemically and characterized as described earlier [14]. Chitosan flakes (ca. 0.5 g) were suspended in methanol (100 mL), and a 25% aqueous glutaraldehyde solution (0.046 mL, 0.12 mmol) was added. After stirring at room temperature for 6 h, the product was filtered. Cross-linked chitosan flakes (0.5 g) were treated with 25 mL of 14% NaOH and 1 mL of CS_2 . The mixture was stirred at room tempera-

Table 1

Physical and chemical characteristics of xanthated chitosan.

Properties	Quantitative value
Geometric mean size (mm)	0.30
Bulk density (g cm^{-3})	0.26
Surface area ($\text{m}^2 \text{ g}^{-1}$)	0.49
Pore diameter (Å)	70.05
S (%)	0.47
N (%)	4.07
Na (%)	0.18
Cl (%)	0.28

ture for 24 h. The obtained orange product, cross-linked xanthated chitosan were washed thoroughly with water, air dried and used for further experiments. The physical characteristics of the prepared adsorbent are given in Table 1. Energy dispersive X-ray analysis is a useful tool to identify within short analysis time the kinds of element contained in solid specimen. The elemental composition was obtained from Energy Dispersive Analysis by X-ray (EDAX) by SEM-FEI Quanta 200 instrument.

2.3. Sorption–desorption in fixed bed column reactor

Sorption in a continuous flow system was done in a fixed bed column reactor (2.0 cm i.d., 50 cm column length). Each bed of sorbent of desired height was underlain by 4 cm^3 of glass wool and 6 cm^3 of 3 mm glass beads. The addition of glass wool and glass beads was made to improve the flow distribution. The schematic diagram of the reactor is shown in Fig. 1. Metal ion solution having an initial concentration of 10 mg L^{-1} was adjusted to pH 3 and pumped through column at a desired flow rate by a peristaltic pump (Miclins) in an up-flow mode. Samples were collected from the exit of the column at different time intervals and analyzed. Operation of the column was stopped when the effluent metal concentration exceeded a value of 9.9 mg L^{-1} . The column bed was then rinsed by passing 100 mL deionized water in upward direction at the same speed as used for biosorption from the total chromium metal solution. All experiments were carried out in duplicates and the deviations were within 5%. For all graphical representations, the

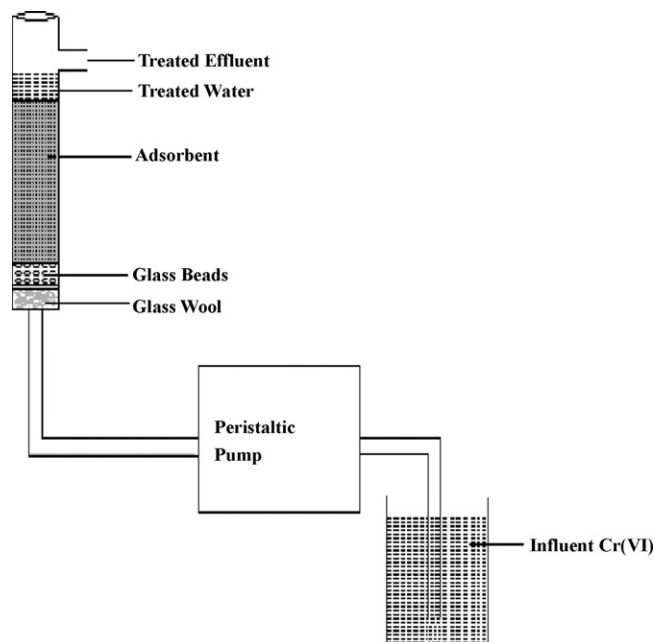


Fig. 1. Schematic representation of laboratory based small column for fixed bed studies.

mean values were used. All statistical analyses were made using ORIGIN PRO 6.1 software.

2.4. Analysis of total chromium and hexavalent chromium

Dissolved hexavalent chromium was determined by the spectrophotometric method at 540 nm using diphenyl carbazide method [19] after suitable dilutions. The lower limit of detection was found to be $1.7 \mu\text{g L}^{-1}$. Each sample was analyzed twice. The co-efficient of variation in the duplicate samples was 2.5%. The average Cr(VI) concentration in 10 aqueous calibration check samples spiked with 0.3 mg L^{-1} Cr(VI) was $0.3 \pm 0.003 \text{ mg L}^{-1}$. Calibration was carried out daily with freshly prepared Cr(VI) standards, before the sample analysis.

Total chromium concentrations (includes dissolved Cr(VI) and Cr(III)) in solution were assessed by Analyst 400 Perkin Elmer Atomic Absorption Spectrophotometer. The measurements were done at wavelength 357.9 nm using a slit width of 0.7 nm and air acetylene flame. The co-efficient of variation was found to be 3.7% with a standard deviation of 0.12 mg L^{-1} for a concentration of 3.00 mg L^{-1} . Experimental samples were filtered using Whatman 0.45 mm filter paper and the filtrates after suitable dilutions, were analyzed. Control experiments showed that no sorption occurred on either glassware or filtration systems.

2.5. Wastewater samples

The sample was acquired from a local electroplating industry located in Kanpur City, U.P., India during June 2009. The wastewater sample was analyzed promptly after collection using standard analytical methods [19]. The characteristics of electroplating wastewater were: color: yellow, pH: <1, chromium(VI): 3015 mg L^{-1} .

2.6. Modeling and analysis of column data

The performance of packed bed is described through the concept of the breakthrough curve. Both, the time until the sorbed species are detected in the column effluent (breakthrough point) at a given concentration, and the shape of the concentration–time profile or breakthrough curve, are very important characteristics for operation, dynamic response and process design of a sorption column because they directly affect the feasibility and economics of the

sorption phenomena. Experimental determination of these parameters is very dependent on column operating conditions such as feed pollutant concentration and flow rate. A breakthrough curve is usually expressed in terms of effluent pollutant concentration (C) or normalized concentration defined as the ratio of effluent pollutant concentration to inlet pollutant concentration (C/C_0) as a function of flow time (t) or volume of effluent (V_{eff}) for a given bed height. Effluent volume (V_{eff}) calculated from Eq. (1):

$$V_{\text{eff}} = F \cdot t_{\text{total}} \quad (1)$$

where t_{total} and F are the total flow time and volumetric flow rate.

The quantity of metal retained in the column represented by the area above the breakthrough curve (C versus t), is obtained through numerical integration [20]. Dividing the metal mass adsorbed (m_{ad}) by the sorbent mass (M) leads to the uptake capacity (Q) of the biomass.

The breakthrough time (t_b , the time at which metal concentration in the effluent reached 0.1 mg L^{-1}) and bed exhaustion time (t_e , the time at which metal concentration in the effluent exceeded 9.9 mg L^{-1}) were used to evaluate the mass transfer zone (Δt) given by Eq. (2):

$$\Delta t = t_e - t_b \quad (2)$$

Total amount of metal sent to column (m_{total}) can be calculated from Eq. (3):

$$m_{\text{total}} = C_0 \cdot F \cdot t_e \quad (3)$$

Total metal removal percent with respect to flow volume can be calculated from Eq. (4):

$$\text{Total metal removal (\%)} = \frac{m_{\text{ad}}}{m_{\text{total}}} \times 100 \quad (4)$$

A number of mathematical models have been developed for the use in design of column parameters. Among various models, model proposed by [21] is widely used [17,22]. The simplified equation of Bohart and Adams model is as follows:

$$t = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (5)$$

where C_0 is the initial metal ion concentration (mg L^{-1}); C_b is the breakthrough metal ion concentration (mg L^{-1}); N_0 is the sorption capacity of bed (mg L^{-1}); v is the linear velocity (cm h^{-1}) and K_a is the rate constant ($\text{L mg}^{-1} \text{ h}^{-1}$).

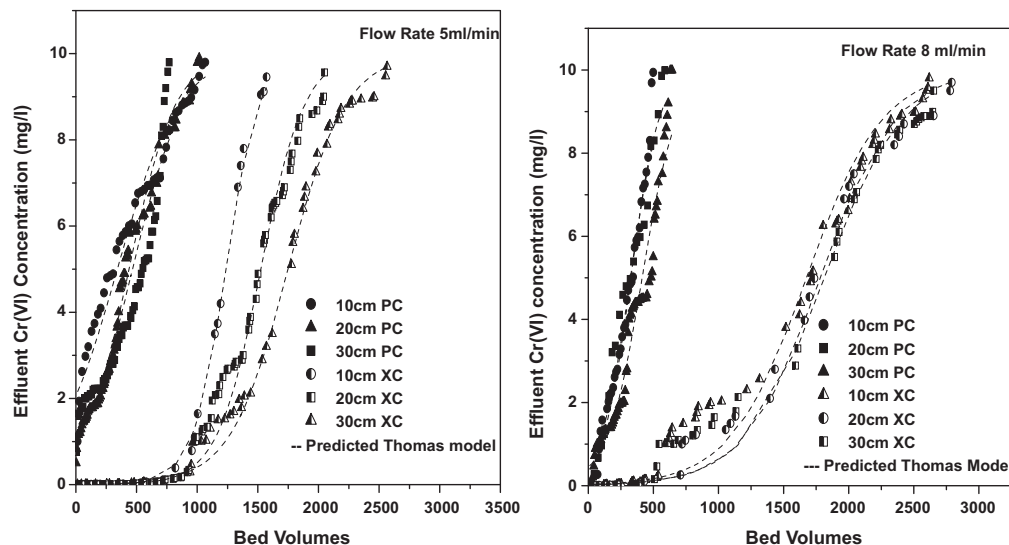


Fig. 2. Breakthrough curves at different flow rates obtained for plain (PC) and xanthated chitosan (XC). Conditions: initial Cr(VI) concentration 10 mg L^{-1} ; pH 3.

Table 2
Column data and parameters obtained for plain and xanthated chitosan.

Adsorbent ^a	Flow rate (L h ⁻¹)	Bed depth (cm)	t _b (h)	t _e (h)	Δt (h)	Uptake (mg g ⁻¹)	% Removal
PC	0.30	10	2	124	122	107.10	35.02
		20	3	188	185	130.12	59.02
		30	5	359	354	130.60	44.37
XC	0.30	10	124	193	69	139.34	76.40
		20	262	647	385	202.25	66.00
		30	372	776	404	173.56	72.20
PC	0.48	10	10	44	34	57.70	53.83
		20	15	77	62	56.13	61.95
		30	16	146	130	69.07	61.00
XC	0.48	10	57	220	163	140.12	61.01
		20	86	420	334	135.16	63.23
		30	140	610	470	133.30	61.20

^a Conditions: influent pH 3; initial Cr(VI) concentration 10 mg L⁻¹.

Eq. (5) can be used to determine the service time (t), of a column of bed height Z , given the values of N_0 , C_0 and K_a which must be determined for laboratory columns operated over a range of velocity values, v .

Successful design of a column sorption process required prediction of the concentration–time profile or breakthrough curve for the effluent. Various mathematical models can be used to describe fixed bed adsorption. Among these, the Thomas model [23] is simple and widely used. The linearized form of Thomas model can be expressed as follows:

$$\ln\left(\frac{C_0}{C_b} - 1\right) = \frac{k_{Th}Q_0M}{F} - k_{Th}C_0V \quad (6)$$

where k_{Th} is the Thomas model constant (L mg⁻¹ h⁻¹), Q_0 is the maximum solid-phase concentration of solute (mg g⁻¹), V is the throughput volume (L), F is the volumetric flow rate (L h⁻¹) and M is the sorbent mass (g).

3. Results and discussion

3.1. Effect of flow rate

In the first stage of removal studies in the continuous-flow fixed column with plain and xanthated chitosan, the flow rate was changed from 5 to 8 mL min⁻¹ while the inlet Cr(VI) concentration in the feed was held constant at 10 mg L⁻¹ at pH 3.0. The plots of comparative normalized Cr(VI) concentration versus effluent volume at different flow rates are given in Fig. 2. As indicated in Fig. 2, at the lowest flow rate of 5 mL min⁻¹, relatively higher uptake values

were observed for Cr(VI) biosorption to both plain and xanthated chitosan. In general, for both the adsorbent, sharper breakthrough curves were obtained at higher flow rates. The breakpoint time and total adsorbed chromium quantity also decreased with increasing flow rate. This behavior can be explained by the fact that Cr(VI) biosorption is affected by insufficient residence time of the solute in the column. This insufficient time decreases the bonding capacity of the chromium ions on to xanthate and amino group present in the biosorbent [24]. Even though more shortened mass transfer zone (usually preferable) was observed at the highest flow rate, the total metal removal percentage (a reflective of system performance) and the metal uptake were actually observed maximum at lowest flow rates. The sorption data were evaluated and the total sorbed quantities, maximum Cr(VI) uptakes and removal percents with respect to flow rate are presented in Table 2. It is also observed that at column bed height of 10 cm, maximum Cr(VI) uptake and removal percentage were obtained as 139.3 mg g⁻¹ and 76.4% respectively, at 5 mL min⁻¹ for xanthated chitosan and 107.1 mg g⁻¹ and 35.0% respectively for plain flakes.

3.2. Application of Thomas model

To determine the maximum solid-phase concentration (Q_0) at different bed depth in column, the data were fitted to the Thomas equation model by using linear regression analysis. Table 3 illustrates the model constant (k_{Th}), maximum solid-phase concentration (Q_0) and correlation coefficient for plain and xanthated chitosan. It is clear from the table and Fig. 2, that the model gave a good fit for the experimental data obtained for both plain and xan-

Table 3
Parameters predicted from Thomas model for plain and xanthated chitosan.

Adsorbent	Flow rate (L h ⁻¹)	Bed height (cm)	k _{Th} (L mg ⁻¹ h ⁻¹)	q _{Th} (mg g ⁻¹)	R ²
PC	0.30	30	0.0013	39.41 ± 0.21	0.9858
		20	0.0013	47.62 ± 0.31	0.9649
		10	0.0026	28.00 ± 0.20	0.9824
XC	0.30	30	0.0016	55.69 ± 0.32	0.9047
		20	0.0006	50.54 ± 0.28	0.9010
		10	0.0061	44.00 ± 0.33	0.9384
PC	0.48	30	0.0031	36.24 ± 0.15	0.9406
		20	0.0055	28.37 ± 0.10	0.9881
		10	0.0118	28.66 ± 0.13	0.9347
XC	0.48	30	0.0003	43.59 ± 0.23	0.9275
		20	0.0004	46.40 ± 0.32	0.9260
		10	0.0018	57.99 ± 0.39	0.9180

Conditions: initial Cr(VI) concentration 10 mg L⁻¹; influent pH 3.

Table 4
Adsorption capacities of few adsorbents obtained from column study.

Material used for Cr(VI) removal	Adsorption Capacity (mg g ⁻¹)	pH	Reference
Coconut coir pith	201.47	1.83	[25]
Jute fiber (PANI-jute)	4.66	3	[17]
Acid modified waste activated carbons	288.19	3	[26]
Carbon slurry	28.0	2.08	[27]
Cetyl tri methyl ammonium bromide	0.366	1.15–1.39	[28]
Olive oil industry waste	3.33	1–2	[29]
Chitosan-Fe ⁰ Nanoparticles	32	6	[30]
Synthesized chitosan Resin	100.9	3.5	[31]
Chitosan-bound FeC nanoparticles	10.5	7.5	[32]
Xanthated chitosan	202.25	3	This work

thated chitosan. Higher values of Q_0 were obtained for xanthated chitosan compared to plain chitosan indicating that uptake capacity of xanthated chitosan is higher than the plain chitosan. This was in agreement with our earlier studies involving batch reactors [14].

Adsorption capacities of few adsorbents obtained from column study are shown in Table 4. It is evident from Table 4 that xanthated chitosan exhibits high adsorption capacity compared to other adsorbents.

3.3. Effect of bed height

Using Bohart–Adams approach at least nine individual column tests must be conducted to collect the required laboratory data which is a time consuming task. A technique has been described by Hutchins [33] which requires only three column tests to collect the necessary data. In this technique, called the bed depth service time (BDST) approach the Bohart–Adams equation is expressed as

$$t_b = aZ + b \quad (7)$$

where

$$a = \text{slope} = \frac{N_0}{C_0 v} \quad (8)$$

$$b = \text{intercept} = \frac{1}{k_a C_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (9)$$

t_b is the time at which metal concentration in the effluent reached 0.1 mg L⁻¹ (h) and Z is the bed height (cm). The parameters N_0 and K_a can be calculated from the slope of the linear plot of t_b versus Z . Fig. 3 shows the BDST plot for plain and xanthated chitosan for a volumetric flow rate of 8 mL min⁻¹ (linear flow rate = 152.8 cm h⁻¹). The linear relationship obtained for total chromium sorption on xanthated and plain chitosan flakes from the bed depth plot for a breakthrough concentration of 1 mg L⁻¹ at an initial concentration of 10 mg L⁻¹ is given in Eqs. (10) and (11), respectively:

$$t_b = 41.5Z + 11.33 \quad (10)$$

$$t_b = 3Z + 4.33 \quad (11)$$

The BDST plots obtained for xanthated and plain chitosan for a 90% breakthrough concentration at an initial concentration of

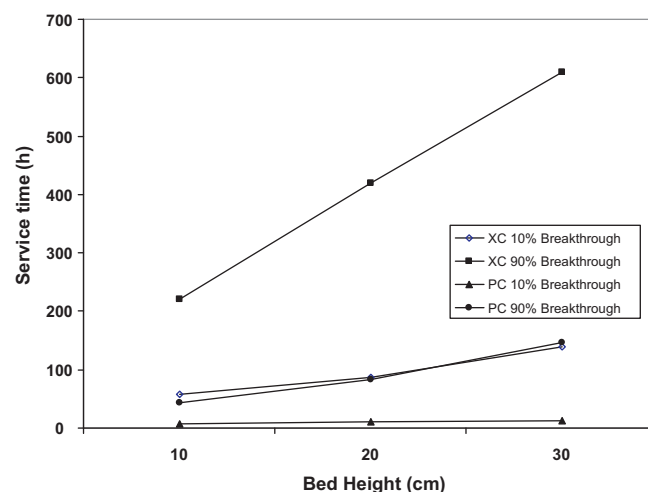


Fig. 3. Bed depth service time plots for plain (PC) and xanthated chitosan (XC). Conditions: initial Cr(VI) concentration 10 mg L⁻¹, linear flow rate 95.5 cm h⁻¹ (volumetric flow rate 5 mL min⁻¹) influent pH 3, breakthrough concentration 1 and 9 mg L⁻¹.

10 mg L⁻¹ are given by Eqs. (12) and (13), respectively:

$$t_b = 195Z + 26.67 \quad (12)$$

$$t_b = 51.25Z - 11.33 \quad (13)$$

The saturation concentrations (N_0) and the rate constant (K_a) obtained from BDST for plain and xanthated chitosan flakes are given in Table 5. The BDST model parameters can be useful to further scale up the process for other flow rates without further experimental run.

3.4. Mechanism of adsorption and regeneration of the adsorbent

The probable mechanisms of adsorption between Cr(VI) and xanthated chitosan have already been discussed in detail earlier [14]. In brief, there exists an electrostatic attraction between protonated xanthated chitosan and negatively charged chromate ions. This is followed by the reduction of Cr(VI) by xanthate to Cr(III) and complexation of Cr(III) with unreacted xanthate. This mechanism is in accordance with other studies reported earlier [34,35,17]. It was observed that after adsorption experiments, biosorbent was green in color (Fig. 4) indicating the presence of Cr(III) in the column (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.). The presence of Cr(III) in the loaded sorbent was further confirmed by the epr spectra with g value of 1.99 [36]. To evaluate the nature of the species in the effluent, speciation studies were done on the effluent water. It is evident from Fig. 5 that after 1200 bed volumes Cr(III) was found in the effluent and it reached a maximum of 2.0 mg L⁻¹ and remained constant thereafter. From this observation it could be concluded that after adsorption and reduction of Cr(VI) to Cr(III), part of it complexes with xanthate group and the repulsion of unreacted protonated Cr(III) to aqueous phase also takes place.

Table 5
Parameters predicted from BDST model for plain and xanthated chitosan.

Adsorbent	10% Breakthrough			90% Breakthrough		
	N_0 (g L ⁻¹)	K_a (L mg ⁻¹ h ⁻¹)	R^2	N_0 (g L ⁻¹)	K_a (L mg ⁻¹ h ⁻¹)	R^2
PC	4.6 ± 0.3	0.0507	0.985	63.4 ± 1.8	0.0194	0.964
XC	78.3 ± 2.9	0.0194	0.971	279.9 ± 6.5	0.0082	0.999

Conditions: initial Cr(VI) concentration 10 mg L⁻¹ bed height: 10, 20, and 30 cm; influent pH 3; linear flow rate 152.8 cm h⁻¹ (volumetric flow rate 8 mL min⁻¹).

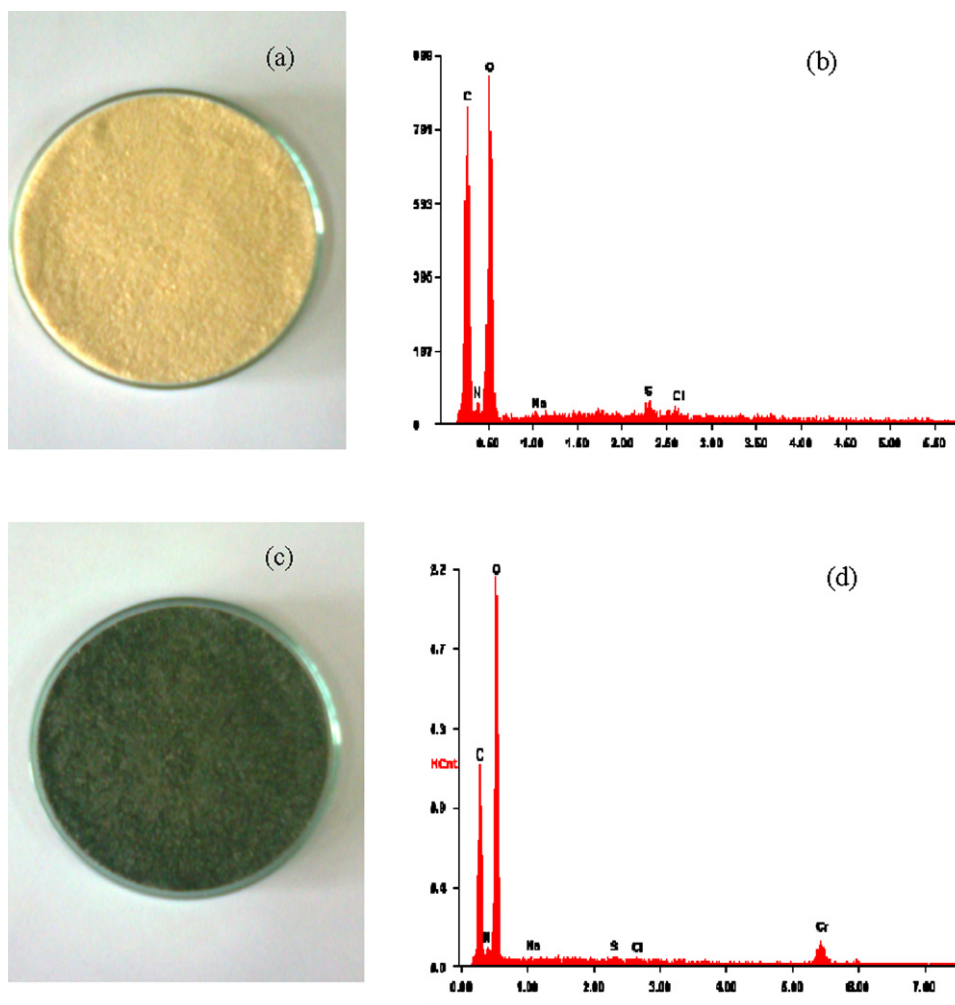


Fig. 4. Photographs and EDAX plots of unloaded (a and b) and loaded xanthated chitosan (c and d).

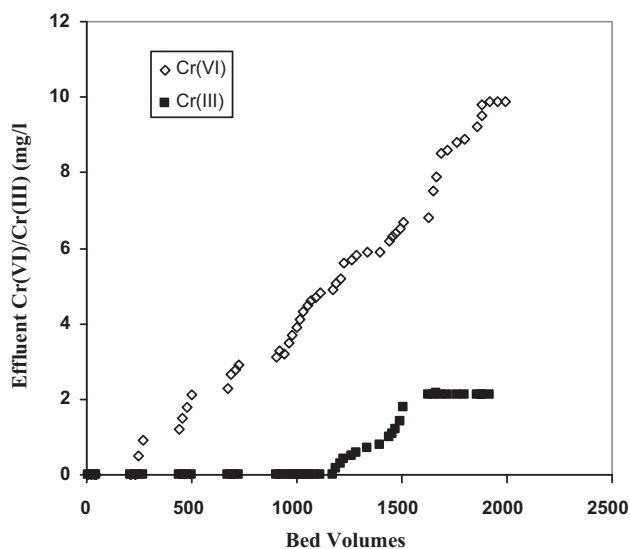


Fig. 5. Speciation studies on the treated effluent. Conditions: Initial Cr(VI) 10 mg L^{-1} , pH 3, flow rate 5 mL min^{-1} , bed depth 10 cm.

In the present study, attempts were not made for regeneration as prolonged use of the column resulted in reduction of Cr(VI) to Cr(III) and immobilization of Cr(III) in the column. The presence of Cr(III) in the loaded adsorbent was evident from the green color

Fig. 4. Hence it could be concluded that toxic Cr(VI) was detoxified to Cr(III) and immobilized in the column and hence the disposal of this sludge is not hazardous to the environment.

3.5. Treatment of electroplating wastewater

Electroplating wastewater obtained from the local industry was diluted to obtain the working range of the present study. Column breakthrough curves for removal of Cr(VI) from the wastewater are shown in Fig. 6. Chromium(VI) uptake and removal efficiency have been depicted in Table 6. It is observed that for electroplating wastewater, at a column height of 20 cm and a flow rate of 5 mL min^{-1} , Cr(VI) uptake was found to be 129.2 mg g^{-1} , whereas for synthetic solution it was 202.25 mg g^{-1} . In the case of percentage Cr(VI) removal, xanthated chitosan exhibited 46.3% and 66.0% for wastewater and synthetic solutions, respectively. These results prove that xanthated chitosan could be effectively used for the treatment of electroplating wastewater.

Table 6

Sorption process parameters for chromium contaminated electroplating wastewater using xanthated chitosan.

Bed depth (cm)	t_b (h)	t_e (h)	Δt (h)	Uptake (mg g^{-1})	% Removal
10	58	166	108	116.6	56.10
20	139	470	331	129.2	46.53
30	179	673	494	125.5	50.43

Conditions: flow rate 0.30 L h^{-1} , influent pH 3, initial Cr(VI) concentration 10 mg L^{-1} .

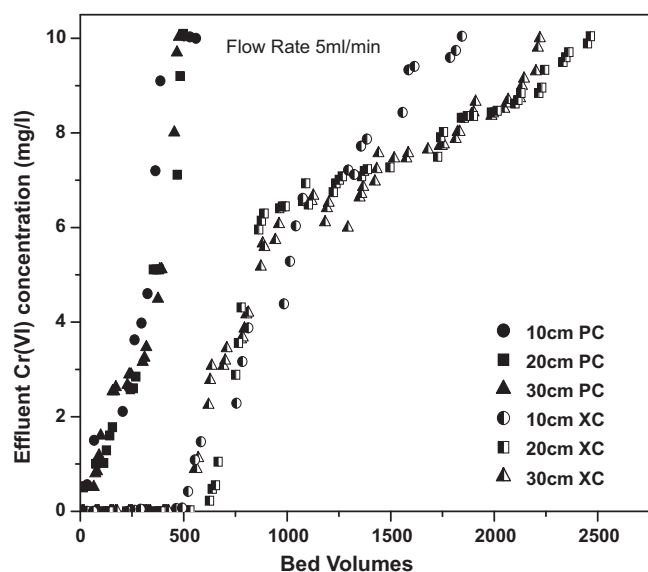


Fig. 6. Breakthrough curves for biosorption of Cr(VI) from electroplating effluent using plain (PC) and xanthated chitosan (XC). Conditions: initial Cr(VI) concentration 10 mg L^{-1} , pH 3.

4. Conclusion

Xanthated chitosan was found to be an effective biosorbent for the removal of hexavalent chromium from aqueous systems. With a flow rate of 5 mL min^{-1} and an increase in bed height from 10 to 20 cm resulted in improved sorption performance from 139.24 mg g^{-1} to 202.25 mg g^{-1} respectively. Functionalization of plain chitosan with xanthate group resulted in increased sorption capacity. The BDST model constants were determined and proposed for the use in column design. The computed sorption capacity per unit bed volume (N_0) was 4.6 ± 0.3 and $78.3 \pm 2.9 \text{ g L}^{-1}$ for plain and xanthated flakes respectively at 10% breakthrough concentration. The Thomas model was successfully used to fit the column data at different flow rates and the constants were evaluated. The sorption capacity exhibited by xanthated chitosan was found to be 129.2 mg g^{-1} and 202.25 mg g^{-1} for electroplating wastewater and synthetic solution respectively. The mechanism of sorption was found to be electrostatic attraction followed by reduction of Cr(VI) to Cr(III) and immobilization of Cr(III) in the column. Finally, high sorption capacity, decontamination and immobilization of Cr(VI) to Cr(III) on the column reactor can be effectively used for continuous biosorption process of electroplating wastewater at larger scale of operation.

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