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Removal of cadmium and hexavalent chromium from electroplating waste water using thiocarbamoyl chitosan

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ABSTRACT

Thiocarbamoyl chitosan (TC-Chitosan) was prepared, characterized and evaluated for the removal of Cr(VI) and Cd(II) from electroplating waste effluents. TC-Chitosan was characterized by various spectral techniques like SEM, EDAX, BET and FTIR. It was observed that Cd(II) adsorption was maximum at alkaline pH (7.5) in contrast to acidic pH (2.0) for Cr(VI). Langmuir isotherm model fitted better compared to the Freundlich model indicating monolayer adsorption. Equilibrium studies revealed a maximum adsorption capacity of 666.7 mg/g for Cd(II) and 434.8 mg/g for Cr(VI). The sorption process was found to follow pseudo second order kinetics with a rate constant of 0.0498 and 0.028 g/mg/h for Cr(VI) and Cd(II) respectively. Thermodynamic parameters such as ΔS, ΔH and ΔG indicated the suitability of TC-Chitosan towards the removal of Cr(VI) and cadmium. Simultaneous removal of both Cr(VI) and Cd(II) were achieved and applied to the removal of these heavy metals from electroplating wastewater.

1. Introduction

Chitosan is a cationic aminopolysaccharide copolymer of *N*-acetylglucosamine and glucosamine. It is obtained by the alkaline, partial deacetylation of chitin, which originates from shells of crustaceans such as crabs and prawns (Muzzarelli, 1973). The chelating ability of chitin and chitosan has been progressively improved by the specific functionalization of these carbohydrate polymers, and later on by the studies of biosorption (Muzzarelli, 1973, 2011; Muzzarelli et al., 2012). Use of functionalized chitosan on the removal of various pollutants have been adequately reviewed (Gerente, Lee, Le Cloirec, & McKay, 2007, Wan Ngah et al., 2011; Verma, Dash, & Bhunia, 2012) It is also reported that the presence of sulfur containing groups like xanthate (Sankararamakrishnan, Dixit, Iyengar, & Sanghi, 2005; Sankararamakrishnan and Sanghi, 2006), dithiocarbamate (Muzzarelli, Tanfani, Mariotti, & Emanuelli, 1982; Muzzarelli & Tanfani, 1982; Khan et al., 2011), mercapto acetyl groups (Cardenas, Parra, & Taboada, 2001), thiol (Merrifield, Davids, MacRae, & Amirbahman, 2004), thiourea (Wang, Wang, & Ma, 2010a; Wang et al., 2010b) etc., have been found to enhance the capacity of the biosorbent. Thus, in this paper in an effort to improve the efficiency of Chitosan, thiocarbamoyl chitosan (TC-Chitosan) has been synthesized and evaluated for the removal of both Cd(II) and Cr(VI). In the literature few reports are available on the removal of both Cr(VI) and Cd(II) by the sorbent (Panda, Das, Rao, & Mishra, 2011; Shaw, 1980). Thus, systematic evaluations of TC-Chitosan on the adsorption of Cr(VI) and Cd(II) have been carried out and Langmuir, Freundlich models, thermodynamic and kinetic parameters have been evaluated. Finally the applicability of the adsorbent has been demonstrated with real electroplating effluents.

2. Materials and methods

2.1. Materials

Chitosan (flakes) was purchased from Sigma Chemicals and used in the present study without any further purification. The degree of deacetylation was reported to be 85% by the manufacturer. Glutaraldehyde and thiourea were purchased from Sigma–Aldrich and used without further purification. Stock solution of Cd(II) and Cr(VI) were prepared using $Cd(NO_3)_2 \cdot 4H_2O$ (BDH chemicals) and $K_2Cr_2O_7$ (BDH Chemicals) respectively. All the inorganic chemicals used were analar grade and all reagents were prepared in Millipore milli-Q deionised water.

2.2. Chemical modification of the chitosan flakes (TC-Chitosan)

TC-Chitosan was prepared with 1 g of thiourea and 0.5 ml glutaraldehyde introduced in 20 ml of demineralized water and reacted for 16 h (over night). After the reaction between thiourea and glutaraldehyde, 1 g of chitosan was added to the solution, then placed under agitation for 72 h. Finally, the functionalized chitosan flakes (TC-Chitosan) was separated by filtration and rinsed several times with water and dried at room temperature overnight. The

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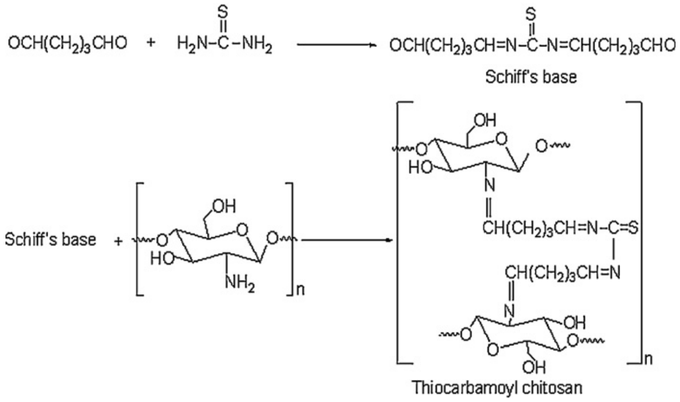


Scheme 1. Formation of Thiocarbamoyl chitosan.

yield was found to >80%. EDAX plots give the elemental compostion which is discussed in Section 3.1.1. The reaction scheme for the formation of TC-Chitosan is presented in Scheme 1.

2.3. Metal concentration analysis

Dissolved Cadmium was determined by Aanalyst 400 Perkin Elmer Atomic Absorption Spectrophotometer using an air-acetylene burner. The measurements were done at wavelength 228.8 nm using a slit width of 0.7 nm. Hexavalent Chromium was determined by spectrophotometry using diphenylcarbazide method (APHA, 1995) after suitable dilutions. 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. All assays were carried out in triplicate and only mean values are presented.

2.4. Wastewater samples

The samples were acquired from a local electroplating industry located in Kanpur City, U.P. India. The wastewater samples were analyzed promptly after collection using standard analytical methods (APHA, 1995). The characteristics of chromium containing waste water are: color: brownish yellow, pH < 1, Cr(VI) 3015 mg/l and that of cadmium are: color: straw yellow, pH 12.13, Cd(II) 1504 mg/l, cyanide 3322 mg/l.

2.5. Adsorption batch experiments

Batch experiments were carried out with synthetic solutions of Cd(II)/Cr(VI) in 100 mL flasks with stopper at 100 rpm of orbital stirring in an incubator shaker, at room temperature and 4 h of contact time with the adsorbent. Samples were then filtered with Whatman No. 42 filter paper, diluted and analyzed for Cd(II) and Cr(VI). Unless otherwise stated the parameters with synthetic water were: sample volume 20 ml, sorbent dose 1 g/l, initial metal ion concentration 100 mg/l, equilibration time 4 h. Initial solution pH was maintained at 2 and 7.5 for Cr(VI) and Cd(II) respectively. For pH studies the pH was varied from 1 to 10 keeping the other conditions the same. For kinetic studies the sample volume was maintained at 50 ml and at every one hour sample was withdrawn for analysis. For equilibrium studies the initial metal ion concentration from 100 to 1000 mg/l. The adsorbents used were all sieved through a sieve of 0.4–0.6 mm particle size range.

2.6. Studies with real electroplating wastewater

The effect of sorbent dose was carried out with real electroplating wastewater whereby the sorbent dose was varied from 1 to 15 g/l keeping the other conditions same as with synthetic wastewater. Since the electroplating wastewater had very high concentrations of Cd(II)/Cr(VI), it was diluted before use to the working range.

3. Results and discussion

3.1. Characterization of the chemically modified biosorbent

3.1.1. Scanning electron microscope (SEM)

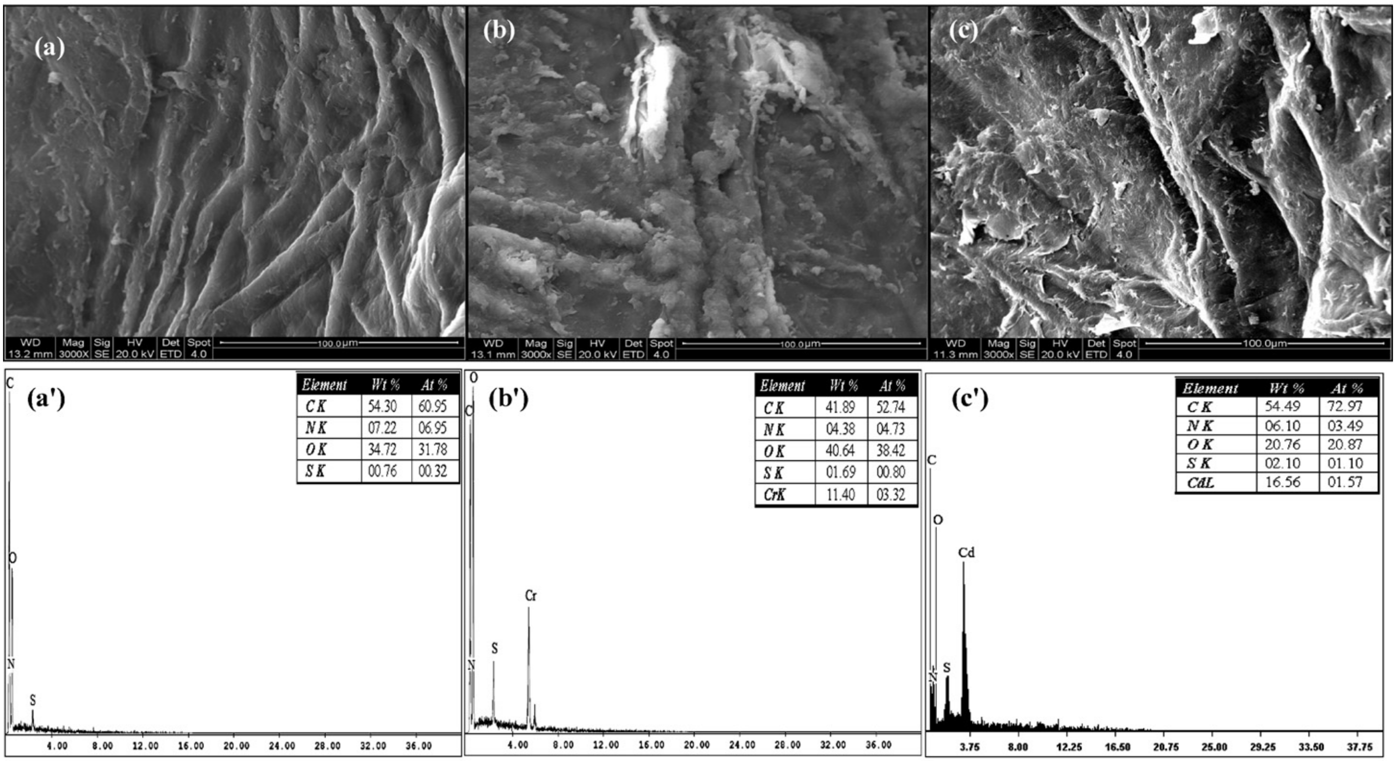
The field emission scanning electron microscopy (FE-SEM, Supra 40 VP, Zeiss, Germany) was used to observe the surface morphology of TC-Chitosan and TC-Chitosan before and after loading with Cr(VI) and Cd(II). The samples were gold coated to improve its conductivity to obtain good images. We present here the representative images of the samples (Fig. 1). It could be observed that there is a distinct change in surface morphology after adsorption of Cr(VI) and Cd(II) (Fig. 1(a), (c) and (e)). EDX plot (Fig. 1(b)) further confirmed the presence of sulfur on the chitosan backbone and weight percentage of sulfur was found to be 0.76%. Adsorption of Cr(VI) and Cd(II) can be seen from the EDX plots Fig. 1(d) and (f) respectively.

3.1.2. FTIR spectra of TC-Chitosan

The FTIR spectra of unloaded and loaded TC-Chitosan with Cr(VI) and Cd(II) were acquired with a Tensor 27 (Bruker, Germany) in the attenuated total reflectance (ATR) mode using a Ge crystal (Fig. 2). The infrared spectrum of thiocarbamoyl chitosan (a) shows a band at 3450 cm^{-1} due to the elongation of the N–H and O–H bonds, therefore, it can be assigned to several functional groups present in the sample as RNH_2 primary amines, R_2HN secondary amines, and alcohols. The band at 2852 cm^{-1} could be attributed to the C–H (CH_3, CH_2) bond elongation, this band is characteristic of materials with saturated carbons or sp^3. The band at 1630 cm^{-1} stretching frequency is characteristic of the C=O bond of an amide is present in all the spectra. The band at 1425 cm^{-1} is due to the C–O–H bond flexion; this band generally appears very close to the CH_2 bands. The peak at 1630 cm^{-1} is due to the cross-linking of chitosan, which corresponds to stretching vibrations of C=N bond present on chitosan. The broad band at 1021 cm^{-1} is due to the asymmetric stretching vibrations of S–C–S group which has been shifted after loading to 1071 cm^{-1} and 1064 cm^{-1} for Cr(VI) and Cd(II) respectively. New band at 934 cm^{-1} could be attributed to Cr=O bond formation after Cr(VI) loading. Hexavalent chromium being a powerful oxidizing agent oxidizes TC-Chitosan and in turn gets reduced to Cr(III). The green color of the adsorbent after loading confirms the presence of Cr(III). A similar mechanism has been suggested by Maxcy, Paul Willhite, Green, & Bowman-James (1998) on the adsorption of Cr(VI) by thiourea. From the above observations it could be concluded that sulfur, oxygen and nitrogen atoms play a major role in the adsorption of Cr(VI) and Cd(II) ions. Based on the above discussions, a suitable mechanism has been proposed for the adsorption of Cr(VI) (Fig. 3) and Cd(II) (Fig. 4).

3.2. Effect of initial pH

A pH effect test is performed to determine the pH of adsorption at which maximum uptake of metal occurs. The pH from 2 to 10 was adjusted initially with either hydrochloric acid or sodium hydroxide (0.1 M). No efforts were made to maintain the pH throughout the adsorption procedure. For Cd(II), the removal increased from 52.4% to 96.2% with increase of pH from 6.0 to 8.0 and thereafter remained



(a')

Element	Wt %	At %
C K	54.30	60.95
N K	07.22	06.95
O K	34.72	31.78
S K	00.76	00.32

(b')

Element	Wt %	At %
C K	41.89	52.74
N K	04.38	04.73
O K	40.64	38.42
S K	01.69	00.80
CrK	11.40	03.32

(c')

Element	Wt %	At %
C K	54.49	72.97
N K	06.10	03.49
O K	20.76	20.87
S K	02.10	01.10
CdL	16.56	01.57

Fig. 1. SEM images of plain TC-Chitosan (a); Cr(VI) loaded TC-Chitosan (b); Cd(II) loaded TC-Chitosan (c) and their corresponding EDX plots of plain(a′); Cr(VI) loaded TC-Chitosan (b′) and Cd(II) loaded TC-Chitosan (c′).

constant with increase in pH (Fig. 3). Further experiments were carried out at pH 7.5 and higher pH values were not resorted to due to the precipitation of cadmium ions as hydroxides at high pH values. The low uptake capacity of cadmium ions at lower pH values could be attributed to the protonation of amino groups and unavailability of the amine groups for complexation with cadmium. Another aspect could be attributed to the competition of H^+ ions compete with cadmium ions to same binding sites on the adsorbent.

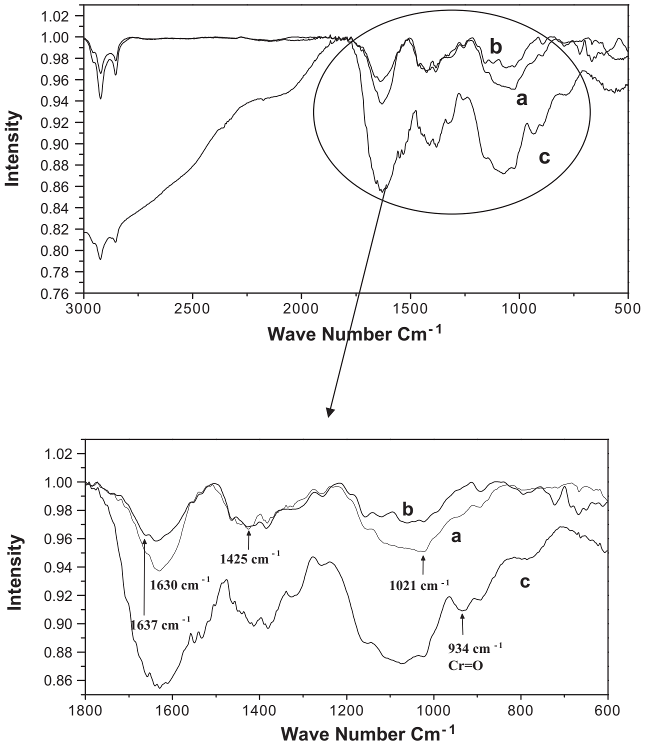


Fig. 2. FTIR Spectra of (a) unloaded TC-Chitosan, (b) Cd(II) loaded TC-Chitosan and (c) Cr(VI) loaded TC-Chitosan.

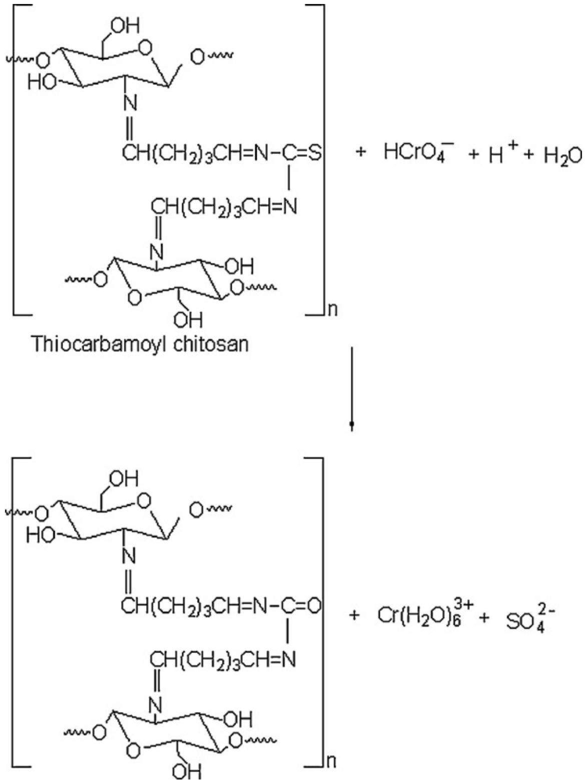


Fig. 3. Reaction mechanism for the adsorption of Cr(VI) by TC-Chitosan.

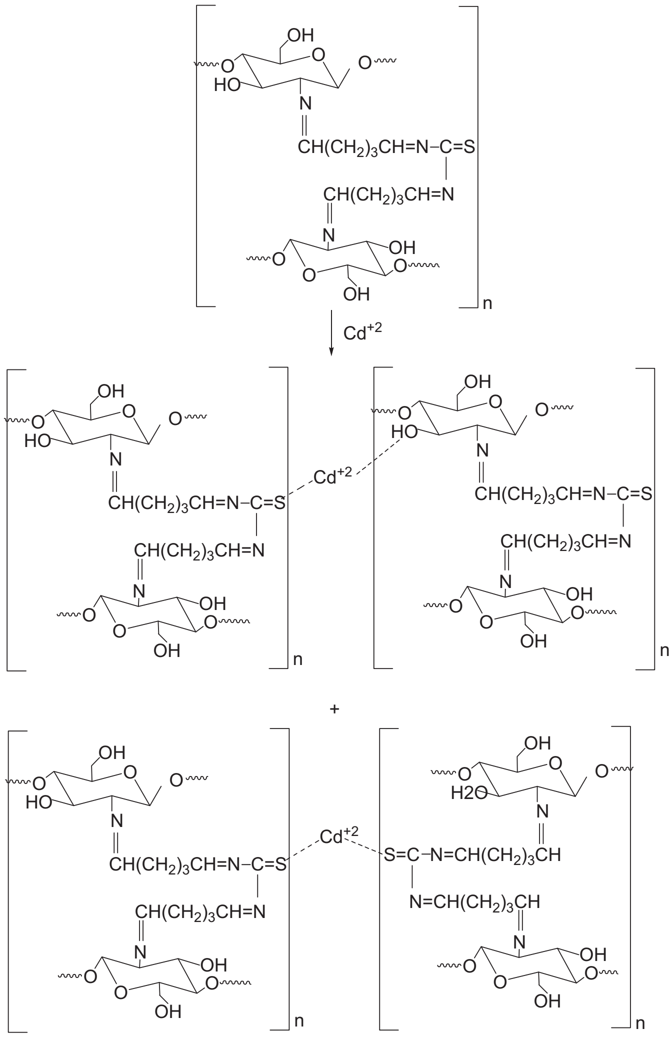


Fig. 4. Reaction mechanism for the adsorption of Cd(II) by TC-Chitosan.

In the case of Cr(VI) (Fig. 5), the amount adsorbed increased from 72.5% to 89.2% when the pH was increased from 1 to 2 and then further increase in pH resulted in decreased uptake capacity. The pHzpc of the chitosan is reported to be 6.2 (Muzzarelli, 1977). Below pHzpc of chitosan, sorbent is positively charged with the protonated amino group whereas the sorbate is negatively charged (Cr(VI) exists as $HCrO_4^-$). Hence there exists an electrostatic interaction between the sorbent and sorbate followed by the reduction of Cr(VI) to Cr(III) by the thiocarbamoyl groups.

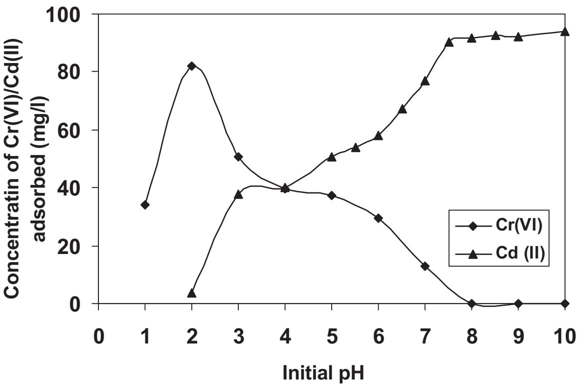


Fig. 5. Effect of initial pH.

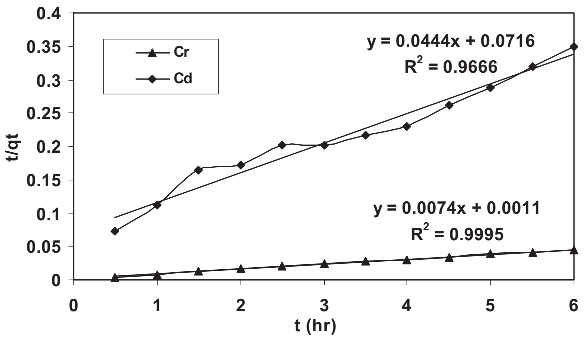


Fig. 6. Pseudo Second order Plot for Cr(VI) and Cd(II).

3.3. Sorption kinetics

The kinetics of Cd(II)/Cr(VI) removal by TC-Chitosan indicated rapid binding of the sorbate by the sorbent during the first few minutes followed by a slow increase until a state of equilibrium is reached. The necessary time to reach this equilibrium was 4 h for both the metal ions studied and further increase in equilibration time up to 24 h showed no change in the uptake capacity. Hence, the equilibrium time was maintained at 4 h in subsequent analysis.

Kinetics of heavy metals adsorption was modeled by the pseudo second order equation (Ho et al., 1997).

$$\frac{t}{q_t} = \frac{1}{(k' q_e^2)} + \frac{t}{q_e} \tag{1}$$

where k' the pseudo second-order rate constant of adsorption (g/mg/min); q_e and q_t are the amounts of metal ion sorbed (mg/g) at equilibrium and at time t, respectively. Linear plots of t/q_t vs t for Cd(II) and Cr(VI) are shown in Fig. 6. It is evident from the figure that the prepared adsorbent followed pseudo second order kinetics for the concentration range studied. The rate constants for Cd(II) and Cr(VI) were found to be 0.028 and 0.0498 g/mg/h respectively.

3.4. Sorption equilibrium

The isotherm studies were conducted at pH 2 for Cr(VI) and pH 7.5 for Cd(II) The resulting data were analyzed with the Langmuir and Freundlich isotherms. The results best fitted the Langmuir isotherm, where the adsorbate assumes a monomolecular layer onto the surface of the adsorbent. The linearized form of the Langmuir isotherm equation is:

$$\frac{1}{q_e} = \frac{1}{Q_b C_e} + \frac{1}{Q} \tag{2}$$

where q_e is the amount of solute adsorbed (mg/g) at equilibrium and C_e is the equilibrium concentration (mg/l), the values of the empirical constants Q and b, denote the monolayer capacity and energy of adsorption and were calculated from the slope and intercept of plot between $1/C_e$ and $1/q_e$.

The linearized form of Freundlich isotherm is represented below,

$$\ln\left(\frac{X}{M}\right) = \ln(K_f) + \frac{1}{n}\ln C_e \tag{3}$$

where X is the mass of the adsorbate (mg), M is the mass of the adsorbent (mg), C_e is the equilibrium concentration (mg/l) and K_f and n are constants for a given adsorbent, adsorbate system.

Linearized Langmuir adsorption plots are shown in Fig. 7. The monolayer adsorption capacity from the Langmuir model for TC-Chitosan was found to be higher for Cd(II) (666.7 ± 4.5 mg/g) compared to Cr(VI) (434.8 ± 2.6 mg/g). The Freundlich model constant K_f and n for Cr(VI) was found to be 1.32 mg/g and 1.24

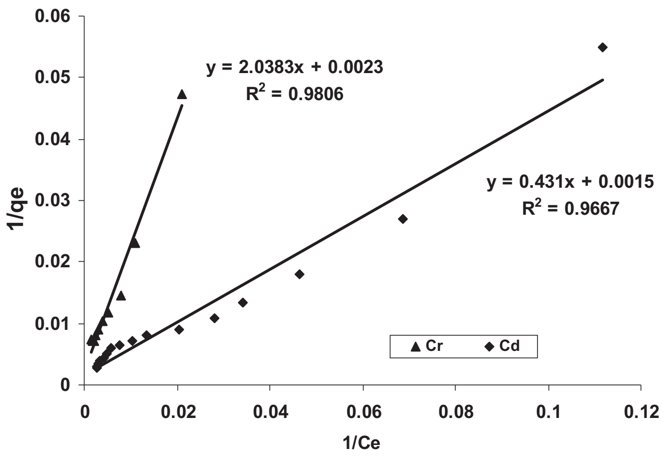


Fig. 7. Linearized Langmuir Plot for Cr(VI) and Cd(II).

respectively. Similarly K_f and n for Cd(II) was found to be 6.46 mg/g 1.49 respectively The main advantage of the sorbent used in the present study is the ability to remove both Cd(II) and Cr(VI) species. Functionalization of thiocarbomyl groups enhances the adsorption capacity and the values obtained were found to be considerably higher than plain chitosan. The maximum adsorption capacity reported for Cr(VI) and Cd(II) with plain chitosan was found to be 34.4 mg/g (Sankararamakrishnan and Sanghi, 2006) and 5.93 mg/g (Jha et al., 1988) respectively. Comparisons of some widely used adsorbents with their sorption capacities obtained are listed in Table 1. It should be noted that the adsorption capacities in the current study is higher than those reported in literature.

3.5. Thermodynamic parameters

Mechanism of adsorption was determined by valuating the thermodynamic parameters such as ΔS°, ΔH° and ΔG°. Using Van't Hoff Eq. (4) the value of ΔS and ΔH was determined.

$$\log K_c = \frac{\Delta S^\circ}{2.303} - \frac{\Delta H^\circ}{2.303\ RT} \tag{4}$$

The value of ΔG° was evaluated using the Eq. (5) given below,

$$\Delta G^\circ = -RT \ln K_c \tag{5}$$

where R is the gas constant, T is the temperature in Kelvin and K_c is the equilibrium constant, determined by Eq. (6) where C_A (mg/l) is the amount of solute adsorbed by the adsorbent at equilibrium and C_e is the equilibrium concentration (g/l).

$$K_c = \frac{C_A}{C_e} \tag{6}$$

For Cd(II) and Cr(VI) systems, log K_c was plotted against $1/T$ and the plots were found to be linear. Using these plots, ΔS° and ΔH° were determined from intercept and slope respectively. The data obtained are presented in Table 2. Chemisorption process is indicated by the positive values of ΔS° and ΔH° for both the systems. Positive value of the entropy also indicates the irreversibility and stability of the adsorption process (Panda et al., 2011). Negative of value of ΔG° indicates the feasibility and spontaneity of the process.

3.6. Simultaneous removal of Cr(VI) and Cd(II) from synthetic samples

Experiments were conducted to test the ability of TC-Chitosan towards the removal of Cr(VI) and Cd(II) simultaneously. Varying concentrations of Cr(VI) and Cd(II) were prepared as shown

Table 1
Comparison of adsorption capacities various biosorbents towards Cd(II) and Cr(VI).

Biosorbent	Metal ion uptake capacity (mg/g)		Reference
	Cd(II)	Cr(VI)	
Coconut coir pith	–	76.3	Namasivayam and Sureshkumar, 2008
Mangrove leaves	–	8.87	Elangovan, Philip, & Chandraraj (2008)
Water lily	–	8.44	Elangovan et al. (2008)
Mucorhiemalis	–	53.5	Tewari, Vasudevan, & Guha (2005)
Red rose waste	–	48.75	Shafqat, Bhatt, Hanif, & Zubair (2008)
Pectin-rich fruit	0.9	–	Schiewer and Patil, 2008
Bamboo charcoal	12.08	–	Wang et al. (2010a,b)
Saw dust	0.29	–	Sharma, Kaur, Kaur (2009)
Hazelnut shell	5.42	–	Bulut and Tez (2007)
Almond shell	3.18	–	Bulut and Tez (2007)
Prepared activated carbon	104.17	–	Fouladi Tajar, Kaghazchi, Soleimani (2009)
Penicilliumsimplicissimum	52.50	–	Fan et al. (2008)
Dolochar	1.9	2.1	Panda et al. (2011)
Exhausted Coffee	1.4	1.4	Shaw (1980)
Plain Chitosan Flakes	5.93		Jha et al. (1988)
Plain Chitosan Flakes		34.4	Udaybhaskar, Iyengar, Leela, Rao, Prabhakara (1990)
Xanthated Chitosan	–	625.0	Sankararamakrishnan and Sanghi, 2006
Xanthated Chitosan	357.1	–	Sankararamakrishnan et al. (2007)
TC-Chitosan	666.1	434.8	Present study

Table 2
Thermodynamic parameters on the adsorption of Cr(VI) and Cd(II) on TC-Chitosan.

Ion	t (°C)	T (K)	$1/T$	C_A (g/l)	C_e (g/l)	K_c	ln K_c	Log K_c	ΔG (kJ/mol)	ΔS (J/mol)	ΔH (kJ/(mol/K))
Cd(II)	35	308	0.00325	2.5	0.0923	27.12	3.30	1.43	−8.45	3.66	9.15
	50	323	0.00309	2.5	0.0902	27.72	3.32	1.44	−8.92		
	65	338	0.00296	2.5	0.0893	27.99	3.33	1.45	−9.36		
Cr(VI)	35	308	0.00325	5.0	0.0917	54.50	3.99	1.74	−10.24	4.73	1.86
	50	323	0.00309	5.0	0.0875	57.14	4.04	1.76	−10.86		
	65	338	0.00296	5.0	0.0860	58.10	4.06	1.76	−11.41		

Table 3
Simultaneous removal of Cd(II) and Cr(VI) from synthetic solutions using TC-Chitosan.

Initial concentration (mg/l)		Percentage removed (%)	
Cd(II)	Cr(VI)	Cd(II)	Cr(VI)
50	100	96.0	98.2
50	50	97.2	97.5
100	50	96.2	98.9
100	100	96.5	98.9

in Table 3 with a dose rate of 5 g/l. Initially the pH of the solution was adjusted to 7.5 and equilibrated for 4 h. A known amount of the solution was taken and analyzed for Cd(II). Then the solution pH was decreased to 2 and again equilibrated for another 4 h and the solution was filtered and concentration of Cr(VI) was determined by the standard method. The results obtained are shown in Table 3. Evidently, the adsorbent could be used for the simultaneous removal of Cr(VI) and Cd(II) from waste water streams.

3.7. Removal of Cr(VI) and Cd(II) from electroplating wastewater

Both Cd(II) and Cr(VI) containing waste water was diluted 20 times to obtain the working range. For Cd(II) wastewater cyanide was present in appreciably concentration (3322 mg/l). Hence even with 20 times dilution a dose rate of 15 g/l was found necessary to bring the Cd(II) concentration from 75 mg/l to <0.2 mg/l. Whereas for Cr(VI) a dose rate of 10 g/l was sufficient to lower the concentration of Cr(VI) to 0.5 mg/l.

4. Conclusions

Chemical modification of the chitosan flakes with thiourea group increased the adsorption. Adsorption studies were modeled by both followed Langmuir and Fruendlich isotherms. A very high adsorption capacity of 666.1 and 434.8 mg/g was observed for Cd(II) and Cr(VI) respectively. Adsorbent–Adsorbate kinetics exhibited pseudo second order. Thermodynamic studies revealed the chemisorption process between adsorbent and adsorbate system. The adsorption process was found to be spontaneous and irreversible.

Applicability of the adsorbent in real electroplating effluent was successfully demonstrated for the both the ions. Due to the presence of cyanide ions in Cd(II) containing effluent, increased adsorbent dose of TC-Chitosan was found necessary. Thus, TC-Chitosan is found to be an efficient adsorbent for the removal of both Cr(VI) and Cd(II) from industrial effluents.

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