



Removal of chromium hexavalent ion from aqueous solutions using biopolymer chitosan coated with poly 3-methyl thiophene polymer

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ABSTRACT

Adsorption capacity of Cr(VI) onto chitosan coated with poly 3-methyl thiophene synthesized chemically was investigated in a batch system by considering the effects of various parameters like contact time, initial concentration, pH and temperature. Cr(VI) removal is pH dependent and found to be maximum at pH 2.0. Increases in adsorption capacity with increase in temperature indicate that the adsorption reaction is endothermic. Based on this study, the thermodynamic parameters like standard Gibb's free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were evaluated. Adsorption kinetics of Cr(VI) ions onto chitosan coated with poly 3-methyl thiophene were analyzed by pseudo-first-order and pseudo-second-order models. The Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption equilibrium studies of chitosan coated with poly 3-methyl thiophene at different temperatures. Langmuir isotherm shows better fit than Freundlich and Temkin isotherms in the temperature range studied. The results show that the chitosan coated with poly 3-methyl thiophene can be efficiently used for the treatment of wastewaters containing chromium as a low cost alternative compared to commercial activated carbon and other adsorbents reported. In order to find out the possibility of regeneration and reuse of exhausted adsorbent, desorption studies were also performed.

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1. Introduction

The removal of toxic metal ions from wastewater is an important and widely studied research area. One of the heavy metals that have been a major focus in wastewater treatment is chromium. The toxicity caused by hexavalent chromium is high and therefore priority is given to regulate this pollutant at the discharge level. Industrial effluents from tanning, electroplating, paint, textile industries, etc. contain chromium species above the maximum contaminant level [1]. Even though both trivalent and hexavalent forms of chromium exist in industrial wastewater, the hexavalent form has been considered to be more hazardous due to its carcinogenic properties [2]. The permissible limit for hexavalent chromium in industrial wastewaters is 0.1 mg/l. In order to reduce Cr(VI) in these effluents to the standard level, an efficient and low cost method needs to be developed. The various methods of removal of Cr(VI) from industrial wastewater include filtration, chemical precipitation, adsorption, electrodeposition and membrane systems or even ion exchange processes. Chemical precipitation and reduction process needs another separation techniques for the treatment and disposal of high quantities of waste metal residual sludge pro-

duced. These techniques use a lot of treatment chemicals and the residual Cr(VI) concentration required in the treated wastewater is not achieved because of the structure of the precipitates. The application of membrane systems for the wastewater treatment has major problems like membrane scaling, fouling and blocking. The drawback of the ion exchange process is the high cost of the resin while the electrodeposition method is more energy intensive than other methods. Among these methods adsorption is one of the most economically favorable and a technically easy method [3].

In recent years, investigations have been carried out for the effective removal of large quantities of Cr(VI) from wastewater using low cost, non-conventional adsorbents which are economically viable [4].

It is observed from previous studies, that conducting electroactive polymers can be used effectively for removal of some of toxic metal ions from aqueous solutions [5–7]. Conducting electroactive polymers such as polypyrrole (PPy), polyaniline (PAni) and polythiophene (PTh) have attracted a great deal of attention in recent years due to their interesting electrical and electrochemical behaviors [8–11]. In the current research poly (3-methyl thiophene) is employed for removal of Cr(VI) from aqueous solution and is reported for the first time. In this study polythiophene was prepared by chemical oxidative polymerization technique using iron (III) chloride (FeCl_3) in chloroform and used as coating onto chitosan for removal of Cr(VI). In overall oxidative doping of poly-

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thiophene conducting polymers electrons are delocalized along the conjugated backbone of conducting polymers, usually through overlap of π -orbitals resulting in an extended π -system with a filled valence band. By removing electrons from the π -system (“p-doping”), a charged unit called a bipolaron is formed. The oxidation process is accompanied by the insertion of anions of acid electrolyte (y^-) in order to maintain the charge neutrality of the final polymer. This research paper deals with the investigation of Cr(VI) removal from aqueous solution by adsorption onto chitosan coated with poly 3-methyl thiophene. The adsorption isotherms, kinetics and its mechanism at different temperatures are discussed.

2. Experimental procedure

2.1. Materials

Chitosan (high molecular weight) and all the other reagents used were of analytical grade, supplied by Sigma–Aldrich. The chitosan was ground and sieved through 35–50 μm mesh before use. The aqueous solution of Cr(VI) was prepared by dissolving potassium dichromate in double distilled water. The pH of the solution was varied using either hydrochloric acid or sodium hydroxide.

2.2. Adsorbent preparation

Polymerization of 3-methyl thiophene was carried out in non-aqueous solution. 4 ml freshly distilled 3-methyl thiophene was dissolved in 100 ml chloroform (CHCl_3). In order to prepare poly 3-methyl thiophene (P3MTh/SD), 10.0 g chitosan (35–50 mesh) immersed in 100 ml of 3-methyl thiophene monomer solution (0.4 M) was prepared in chloroform at nitrogen atmosphere for 12 h before polymerization. 100 ml of oxidant solution (0.8 M FeCl_3 in chloroform) was added via a dropping funnel while the reaction mixture was stirred vigorously, and then the reaction was allowed to continue for 4 h at room temperature. Because of the polymerization, the solution yielded a greenish black precipitate. The precipitate was then washed with copious amounts of double distilled deionized water and methanol and the resulting precipitate (polymer coated as a very thin film on the surface of chitosan) was allowed to dry at 60 °C for 2 h and sieved (35–50 mesh size) before use.

2.3. Batch adsorption studies

Batch studies were conducted in a temperature-controlled shaker using 100 ml of potassium dichromate solution and a fixed adsorbent dosage of 0.1 g. The agitation speed of the shaker was fixed at 200 rpm for all batch experiments. Samples at different time intervals (0–300 min) were taken and centrifuged. The concentration of the samples was analyzed in a spectrophotometer (Hitachi UV-2000 model) using 1,5-diphenylcarbazide as the complexing agent at the wavelength of 540 nm [12].

Isotherm studies were conducted in a series of 250 ml Erlenmeyer flasks. Each flask was filled with 100 ml of Cr(VI) solution having different initial concentrations and the solution was adjusted to pH 2.0. After equilibration, the samples were separated and analyzed for their Cr(VI) content. Adsorption studies were carried out at different temperatures (303, 313 and 323 K) to obtain the equilibrium isotherms. The initial concentration of solutions taken for this study was 50, 75, 100, 150 and 200 mg/l. The equilibrium adsorption capacity was calculated using the Eq. (1) below,

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C_e are the initial and equilibrium concentration (mg/l) of Cr(VI) ions in

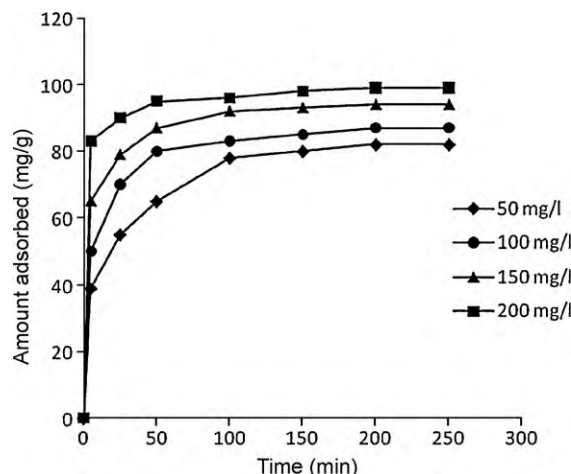


Fig. 1. Effect of initial concentration of Cr(VI) and contact time at $T = 303$ K, pH 2.0.

solution, V (l) is the volume and M (g) is the weight of the adsorbent.

$$\% \text{Desorption} = \frac{m}{m_0} \times 100 \quad (2)$$

Subsequently,

$$M_0 = \frac{(C_0 - C_e)V}{W} \quad (3)$$

where m_0 is mg of the sorbed Cr(VI) onto adsorbent, m is the mg of desorbed Cr(VI) in regenerant solution and V is the volume of regenerant solution (l) and W is the weight of the adsorbent (g).

3. Results and discussion

3.1. Effect of initial concentration of Cr(VI) and contact time

The amount of chromium adsorbed for different initial concentrations onto chitosan coated with poly 3-methyl thiophene is shown in Fig. 1.

The adsorption of Cr(VI) onto chitosan coated with poly 3-methyl thiophene increases with time and then attains equilibrium value at a time of about 200 min. The removal of Cr(VI) was found to be dependent on the initial concentration; the amount adsorbed increasing with increase in initial concentration. Further, the time curve shows that the removal of Cr(VI) is rapid but it gradually slows down until it reaches the equilibrium. At low concentrations the ratio of available surface to the initial Cr(VI) concentration is larger, so the removal becomes independent of initial concentrations. However, in the case of higher concentrations this ratio is low; the percentage removal then depends upon the initial concentration and had only a small influence on the time of contact necessary to reach equilibrium. On changing the initial concentration from 50 to 200 mg/l, the amount adsorbed increased from 82.05 to 99.02 mg/g for a time period of 200 min. The plots are smooth and continuous, suggesting the possible monolayer adsorption of chromium on the surface of chitosan coated with poly 3-methyl thiophene. Consequently, the concentration of Cr(VI) will greatly affect the extent and rate of Cr(VI) uptake onto chitosan coated with poly 3-methyl thiophene.

3.2. Effect of adsorbent dosage

Fig. 2 shows the removal of Cr(VI) by chitosan coated with poly 3-methyl thiophene at different dosages of adsorbent (0.1–0.8 g) at initial concentration of 100 mg/l Cr(VI) solution and 30 °C. From Fig. 2 it was observed that, the percentage of Cr(VI) removal

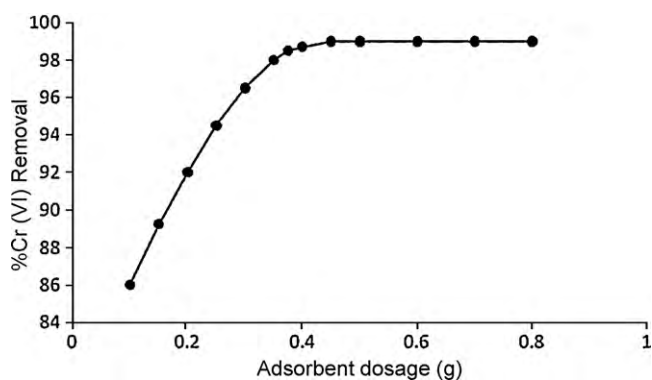
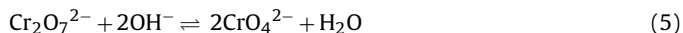
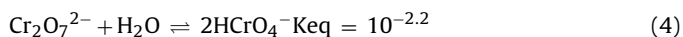


Fig. 2. Effect of adsorbent dosage on Cr(VI) adsorption.

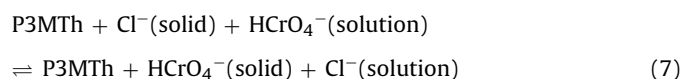
increased from 87.0 to 98.5% with an increase in adsorbent mass from 0.1 to 0.45 g. The percentage removal increased with the chitosan coated with poly 3-methyl thiophene dosage up to a certain limit and then it reached a constant value. The increase in adsorption of Cr(VI) with adsorbent dosage can be attributed to increased surface area and the availability of more adsorption sites.

3.3. Effect of pH

At pH values below 1, the predominant species is H_2CrO_4 . Cr(VI) normally exists in the anionic form, as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- or CrO_4^{2-} forms depending on pH and concentration (Eqs. (4)–(6)). In acidic media (pH 2–4) Cr(VI) exists mostly in the form of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions. At pH between 2 and 6, $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- ions exist in equilibrium, and under alkaline conditions (pH > 8) it exists predominantly as chromate anion.



Removal percentage of Cr(VI) using modified chitosan by polythiophene is strongly affected by pH of the solution. They are effective only at acidic conditions. Sorption of Cr(VI) ion decreases as pH of treated solution increases. Based on this result, removal mechanism might be due to ion exchange process performed at interface of polymer and solution as shown by the following Eq. (7).



Adsorption of Cr(VI) on the chitosan coated with poly 3-methyl thiophene was not significant at pH values greater than 6.0 due to two main reasons (a) dual competition of both anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates, (b) at or above pH value 6.0 the polymer becomes undoped, so there is less or no anion to be exchanged, consequently the uptake of Cr(VI) anions decreased dramatically. However, because of oxidative nature of Cr(VI) under acidic conditions and the electroactive nature of polythiophene, some other possible mechanisms such as redox reactions in removal of Cr(VI) by the used adsorbents cannot be ignored. Cr(III) ions which might be formed during redox reaction between polymer and Cr(VI) ion are believed to be removed by polymer via chelating or complex reactions.

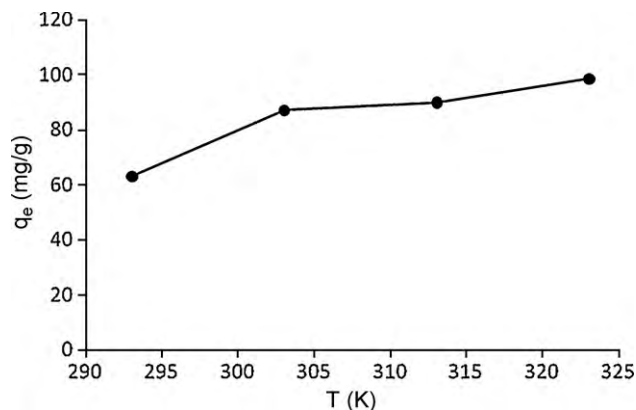


Fig. 3. Effect of temperature for the concentration of 200 mg/l at pH 2.0.

3.4. Effect of temperature

The adsorption of Cr(VI) onto chitosan coated with poly 3-methyl thiophene at different temperatures shows an increase in the adsorption capacity when the temperature is increased. With increase in temperature from 293 to 323 K, the adsorption capacity increased from 63.21 to 98.56 mg/g for the initial concentration of 200 mg/l at pH 2.0, as shown in Fig. 3. This indicates that the adsorption reaction is endothermic in nature because of the chemical interaction between adsorbates and adsorbent as shown in Eq. (7), and the increased rate of intraparticle diffusion of Cr(VI) ions into the pores of the adsorbent at higher temperatures [13].

3.5. Thermodynamic study of adsorption

In order to evaluate the thermodynamic parameters for the adsorption of Cr(VI) onto chitosan coated with poly 3-methyl thiophene, the adsorption studies were carried out at different temperatures 303, 313, 323 and 333 K. The standard free energy change (ΔG°) is the fundamental criterion of spontaneity of a process and can be determined using equilibrium constant as shown below Eq. (8):

$$\Delta G^\circ = -RT \ln K_c \quad (8)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature and K_c is the equilibrium constant. The thermodynamic parameters, such as change in standard enthalpy (ΔH°) and standard entropy (ΔS°) from 303 to 323 K were determined using following Eq. (9).

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

ΔH° and ΔS° were obtained from the slope and intercept of the plot of $\ln K_c$ versus $1/T$ as shown in Fig. 4. Positive value of ΔH° indicates that the adsorption process is endothermic.

The negative values of ΔG° reflect the feasibility of the process and spontaneous nature of the adsorption; moreover the values of ΔG° become more negative with increase in temperature. Table 1 summarizes the results.

Table 1
Thermodynamic data for Cr(VI) adsorption onto chitosan coated with poly 3-methyl thiophene.

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	R^2
303	-6.046			
313	-11.450			
323	-17.187	116.54	0.378	0.9987
333	-21.594			

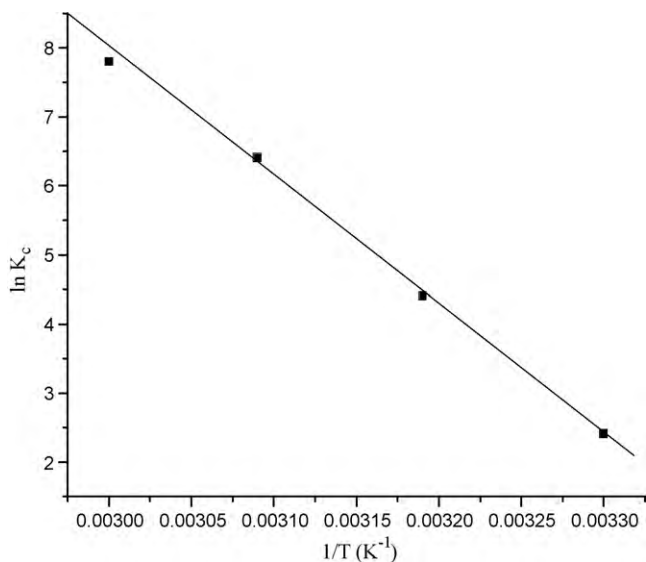


Fig. 4. Plot of $\ln K_c$ vs $1/T$ for Cr(VI) adsorption onto chitosan coated with poly 3-methyl thiophene.

3.6. Adsorption kinetics

The kinetics of adsorption describes the rate of uptake of chromium ions onto the chitosan coated with poly 3-methyl thiophene and this rate controls the equilibrium time. This study reveals that 85–90% of the adsorption takes place within the first hour of contact. The amount of metal ions removed in the first hour of contact increases as the concentration of the metal ion increases. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbents. In order to determine the adsorption kinetics of Cr(VI), the pseudo-first-order, pseudo-second-order and Weber–Morris diffusion models were checked. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (R^2) as shown in Table 2.

3.6.1. Pseudo-first-order model

The pseudo-first-order rate model of Lagergren [14] is based on solid capacity and as described by Eq. (10): where, q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q is the amount of solute adsorbed at any time (mg/g) and k_1 is the adsorption constant. Eq. (10) is integrated for the boundary conditions $t = 0$ to $t > 0$ ($q = 0$ to $q > 0$) and then rearranged to obtain the following linear time dependent function:

$$\log(q_e - q) = \log(q_e) - \left(\frac{k_1}{2.303} \right) t \quad (10)$$

This is the most popular form of pseudo-first-order kinetic model. Constant k_1 and correlation coefficients (R^2) have been cal-

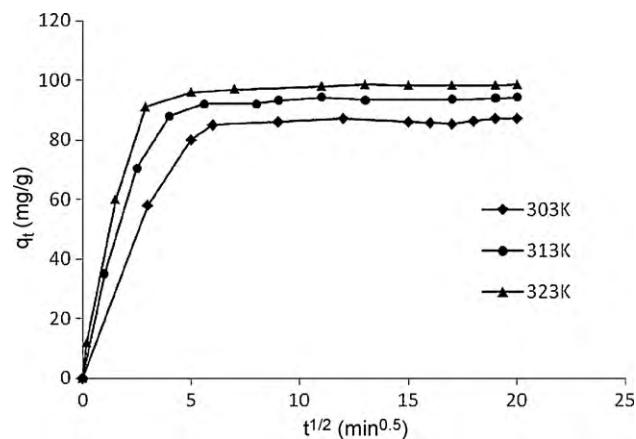


Fig. 5. Intraparticle diffusion plot at different temperatures for the initial concentration of 200 mg/l, pH 2.0.

culated and summarized in Table 2. The R^2 values show that the adsorption of Cr(VI) onto chitosan coated with poly 3-methyl thiophene does not follow first-order kinetics.

3.6.2. Pseudo-second-order model

The pseudo-second-order model [15] can be represented as Eq. (11)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

where k_2 (g/mg min) is the second order rate constant and q_t is the amount adsorbed at time t . The calculated q_e values agree very well with experimental values and regression coefficient of above 0.99 confirms that the adsorption phenomena followed second order kinetics. Similar results have been observed in the adsorption of Cr(VI) by used tyres and sawdust [16].

3.6.3. Intraparticle diffusion model

Intraparticle diffusion model is of major concern because it is the rate-determining step in the liquid adsorption systems. The intraparticle diffusion varies with square root of time [17], as given by Eq. (12) q_t is the amount adsorbed (mg/g),

$$q_t = k_{id} t^{1/2} \quad (12)$$

t is the time (min), k_{id} (mg/g min^{1/2}) is the rate constant of intraparticle diffusion. The intraparticle diffusion rate constant was determined from the slope of the linear gradients of the plot q_t versus $t^{1/2}$ as shown in Fig. 5.

The intraparticle diffusion process is controlled by the diffusion of ions within the adsorbent. The initial curved portion relates to the film diffusion and the latter linear portion represents the diffusion within the adsorbent. The rate constants of intraparticle diffusion

Table 2

Pseudo-first-order and pseudo-second-order models for the adsorption of Cr(VI) onto chitosan coated with poly 3-methyl thiophene.

Kinetic models and its parameters	Initial concentration (mg/l)			
	50	100	150	200
Pseudo-first-order kinetic				
q_e (mg/g)	39.31	60.85	75.06	91.18
$k_1 \times 10^{-3}$ (min ⁻¹)	19.23	12.90	11.72	9.16
R^2	0.9121	0.9234	0.8900	0.8020
Pseudo-second-order kinetic				
q_e (mg/g)	40.51	64.65	81.12	99.02
$k_2 \times 10^{-3}$ (g mg ⁻¹ min ⁻¹)	4.113	5.242	5.812	6.457
R^2	0.9993	0.9996	0.9995	0.9989

Table 3
Rate constant of intraparticle diffusion at different temperatures.

T (K)	k_{id} (mg/g min ^{1/2})
303	2.50
313	2.913
323	3.367

of different initial concentrations onto chitosan coated with poly 3-methyl thiophene are shown in Table 3.

3.7. Adsorption isotherms studies

To quantify the adsorption capacity of chitosan coated with poly 3-methyl thiophene for the removal of Cr(VI) from aqueous solution, the Langmuir, Freundlich and Temkin isotherm models were used at various temperatures.

3.7.1. Langmuir model

This model assumes that the adsorption occurs at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes [18]. The Langmuir type adsorption isotherm indicates surface homogeneity of the adsorbent and hints towards the conclusion that the surface of adsorbent is made up of small adsorption patches which are energetically equivalent to each other in respect of adsorption phenomenon.

The data of the equilibrium studies for adsorption of Cr(VI) onto chitosan coated with poly 3-methyl thiophene follow the following form of Langmuir model Eq. (13):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (13)$$

where C_e is the equilibrium concentration (mg/l) and q_e the amount adsorbed at equilibrium (mg/g). The Langmuir constants Q_0 (mg/g) represent the monolayer adsorption capacity and b (l/mg) relates the heat of adsorption.

The isotherm data Q_0 and b were calculated and reported in Table 4. The high values of correlation coefficient ($R^2 = 0.9991-0.9999$) indicate a good agreement between the parameters and confirms the monolayer adsorption of Cr(VI) onto chitosan coated with poly 3-methyl thiophene surface.

3.7.2. Freundlich model

Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption [19] and is expressed in linear form as shown in Eq. (14).

$$\ln q_e = \ln K_f + b_f \ln C_e \quad (14)$$

where K_f is Freundlich equilibrium constant, C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium (mg/g) and b_f an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range $0.1 < b_f < 1$, adsorption is favorable [20]. This model deals with the multilayer adsorption of the substance on the adsorbent. The related parameters were calculated and reported in Table 4. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent and thus is responsible

Table 4
Adsorption isotherms of chitosan coated with poly 3-methyl thiophene at different temperatures.

T (K)	Langmuir constants			Freundlich constants			Temkin constants		
	Q^0 (mg/g)	b (l/mg)	R^2	K_f (mg/g)	b_f	R^2	B	A (l/mg)	R^2
303	127.62	0.0301	0.9999	22.197	0.4125	0.9280	7.513	54.221	0.9781
313	134.13	0.0324	0.9991	27.112	0.5610	0.8951	7.724	37.527	0.9878
323	145.08	0.0344	0.9993	29.964	0.8614	0.9728	7.901	23.668	0.9383

Table 5
Comparison of adsorption capacities of Cr(VI) with other adsorbents.

Adsorbents	Adsorption capacity (mg/g)	pH	Reference
Leather	459.00	2.0	[22]
Tyres activated carbon	58.50	2.0	[16]
Rubberwood activated carbon	44.05	2.0	[23]
Leaf mould	43.10	2.0	[24]
Coconut shell activated carbon	20.00	2.0	[25]
Hazelnut shell activated carbon	17.70	2.0	[26]
Beech sawdust	16.10	1.0	[27]
Sugarcane bagasse	13.40	2.0	[28]
Coconut shell charcoal	10.88	4.0	[29]
Treated sawdust of Indian Rosewood	10.00	3.0	[30]
Coconut tree sawdust	3.60	3.0	[4]
Chitosan	22.09	3.0	[31]
Non-cross linked chitosan	78.00	5	[32]
Cross linked chitosan	50.00	5	[32]
Chitosan coated with poly 3-methyl thiophene	127.62	2.0	Proposed method

for multilayer adsorption due to the presence of energetically heterogeneous adsorption sites. The greater the values of b_f better is the favorability of adsorption.

3.7.3. Temkin model

Temkin isotherm is based on the heat of adsorption of the ions, which is due to the adsorbate and adsorbent interactions taken in linear form [21], and is given by Eqs. (15) and (16).

$$q_e = \left(\frac{RT}{b}\right) \ln A + \left(\frac{RT}{b}\right) \ln C_e \quad (15)$$

$$\frac{RT}{b} = B \quad (16)$$

where A (l/g) and B are Temkin constants.

From Table 4, the Langmuir adsorption isotherm model yielded the best fit as indicated by the highest R^2 values at all temperatures compared to the other two models. Temkin isotherm constants at different temperatures (Table 4) show that there is a linear fall in the standard enthalpy of adsorption with surface coverage. The Langmuir isotherm model has higher R^2 when compared to the other models, showing the homogeneous nature of the adsorbent. Increases in Langmuir constant b with temperature confirm the endothermic nature of adsorption and Freundlich constant b_f shows the favorability of adsorption at higher temperatures.

3.8. Desorption studies

For performing desorption studies the exhausted 0.1 g of chitosan coated with poly 3-methyl thiophene was treated with 0.01 M NaOH solution for regeneration. It was found that 93% of the sorbed Cr(VI) was recovered. Desorption investigation shows, that the introduced adsorbent can be used frequently without any significant reduction in sorption capacity.

3.9. Comparison of chitosan coated with poly 3-methyl thiophene with other adsorbents

The adsorption capacity of Cr(VI) onto chitosan coated with poly 3-methyl thiophene was compared with other adsorbents reported in literature and is shown in Table 5. It can be observed that a pH of 2.0 was found to be optimum in nearly all cases, whatever the method of activation was. This is consistent with the fact that the Cr(VI) get reduced to Cr(III) to a large extent at pH close to 1.0. Chitosan coated with poly 3-methyl thiophene is found to have a relatively large adsorption capacity of 127.62 mg/g and this indicates that it can be considered a promising material for the removal of Cr(VI) from aqueous solution. Leather is a raw material that exhibits very high adsorption capacity; this could be primarily due to the initial carbon content, activation process as well as the pore development due to the basic morphology of the raw material. It can also be observed that the pure chitosan and cross linked chitosan exhibit quite low adsorption capacity of Cr(VI) than chitosan coated with poly 3-methyl thiophene.

4. Conclusions

It was found that chitosan coated with poly 3-methyl thiophene can be effectively employed for removal of chromium hexavalent ions from aqueous. Chitosan is a very cheap, economical and environmentally friendly substrate for coating of this polymer. Adsorption of Cr(VI) is found to be effective in the lower pH range and at higher temperatures and subsequent desorption is readily achieved upon alkaline treatment of the adsorbent. Increase in adsorption capacity with rise in temperature reveals that the adsorption is chemical in nature and the process is endothermic, which is confirmed by the evaluated thermodynamical parameters. The Langmuir isotherm fits the data better than the Freundlich and Temkin isotherms. Thus, the results show that the chitosan coated with poly 3-methyl thiophene can be effectively applied for the removal of Cr(VI) from wastewater.

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