Thermodynamics, Kinetics, and Regeneration Studies for Adsorption of Cr(VI) from Aqueous Solutions using Modified Cellulose as Adsorbent

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Cellulose adsorbent was prepared by ATRP grafting of glycidyl methacrylate onto a cellulose backbone with subsequent functionalization with ethanediamine, and then used for the removal of Cr(VI) from aqueous solution. Batch experiments were carried out to investigate the effects of initial pH and initial Cr(VI) concentration on the adsorption performance. The optimum pH for adsorption of Cr(VI) ranged from 2 to 3, and the maximum uptake of Cr(VI) from solution was 500 mg/g at pH 3.0 and 50 °C. Langmuir and Freundlich isotherms were applied to the adsorption process, and the thermodynamic parameters were calculated. The results showed that the sorption process to be feasible, spontaneous, and endothermic. Kinetics studies revealed that the pseudo-second-order kinetic model fitted well with the experimental data and the intra-particle diffusion was not the only rate-determining step for Cr(VI)sorption onto adsorbent. The cellulose adsorbent before and after Cr(VI) adsorption were characterized using scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX), Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). Regeneration of cellulose adsorbent loaded with Cr(VI) can be achieved by treating with 2.0M NaOH.

Keywords: Cellulose adsorbent; Cr(VI); Adsorption; Kinetics; Thermodynamics

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INTRODUCTION

Chromium (VI) compounds have found widespread use in electroplating, metal finishing, chromate preparation, leather tanning, cooling towers of heavy industry, atomic power plants, mining, metallurgy operations, *etc*. However, they can be a major threat to public safety because of an increase in discharge into the ecosystem from waste streams, their toxic effects, and other adverse effects on receiving waters (Saha and Orvig 2010; Saha *et al*. 2011; Kaya *et al*. 2014; Liang *et al*. 2014; Zhang *et al*. 2014). According to the World Health Organization (WHO), the health effects of long term exposure to chromium (VI) levels over 0.1 ppm can cause respiratory problems, kidney problems, and liver damage (Bhaumik *et al*. 2014). Therefore, it is necessary that industries treat their effluents to reduce the Cr(VI) concentration in water and wastewater to acceptable levels before its transport and cycling into the natural environment.

A long list of methods have been applied to reduce and recover the toxic heavy metals from final effluent (Peng *et al*. 2004; Golder *et al*. 2007; Bhuvaneshwari and Elango 2009; Liu *et al.* 2009; Saha and Orvig 2010; Saha *et al*. 2011; Xing and Beauchemin 2011; Xie *et al.* 2011; Wang *et al.* 2013; Wu *et al.* 2013; Song *et al*. 2014). The methods described by these authors include chemical precipitation, oxidation, coagulation, ion exchange, reverse osmosis, solvent extraction, flocculation, membrane separation, filtration, evaporation, electrolysis, and adsorption. Among all the treatment processes mentioned, adsorption using the chelating properties of adsorbents is one of the effective and widely considered techniques for the removal of toxic heavy metals from wastewaters. Various adsorbents have been developed for removing heavy metal ions from aqueous solutions, such as clay (Zhao *et al.* 2013), ion exchange resins (Kusku *et al.* 2014), activated carbon (Bayrak *et al.* 2013), carbon nano-tubes (Kumar *et al.* 2013), and metal oxides (Xu *et al.* 2014). In particular, cellulose, the main constituent of plants, is the most abundant biomass in the world. It is renewable, cheap, biodegradable, and can be chemically modified for enhancing its effectiveness by introduction of new functional groups (O'Connell *et al.* 2006; Liu and Sun 2008). There is intensive research nowadays for the application of cellulosic material for hazardous contaminant adsorption from aqueous wastes.

In this work, an adsorbent was prepared by ATRP grafting of glycidyl methacrylate (GMA) onto a cellulose backbone with subsequent functionalization with ethanediamine. The use of the ATRP technique instead of conventional redox grafting methods can provide good control of the graft length and composition, and the subsequent functionalization with ethanediamine can produce amine functional groups, NRH. The latter can be protonated to form NRH_2^+ in aqueous solution, thus having the ability to adsorb the anionic pollutants through electrostatic interaction. The obtained adsorbent was then used to remove Cr(VI) from aqueous solution. Batch adsorption experiments were conducted to evaluate the Cr(VI) adsorption behavior including kinetics, equilibrium, and regeneration studies. The effects of adsorbent amount, pH, contact time, and initial Cr(VI) concentration on the adsorption capacity were investigated. The rate kinetics and equilibrium parameters were determined. Adsorption isotherm models and thermodynamic parameters were also investigated to know the adsorption behavior.

EXPERIMENTAL

Materials

Cotton linter was used as the cellulose material. The ionic liquid (1-buty1-3-methylimidazolium chloride, BMIMCl, mp.73 ^{o}C) was obtained from Henan Lihua Pharmaceutical Co., Ltd. Copper-(I) bromide (CuBr) was treated according to Matyjaszewski *et al*. (1999). CuBr was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol three times. The compound was dried under vacuum at 60 °C overnight. Chloroacetyl chloride was purchased from Enterprise Group Chemical reagent Co., Ltd. Glycidyl methacrylate (GMA), 2,2'-dipyridyl,ethanol absolute and other reagents were all analytical grade and used as received. Potassium dichromate ($K_2Cr_2O_7$) was used as a source of Cr(VI). All aqueous solutions and standards were prepared using deionized water.

Preparation of Cellulose Adsorbent

Graft copolymerization

Cellulose was first dissolved in BMIMCl completely, and then 3 folds amount of chloroacetyl chloride was added with a pipet into the cellulose solution. The mixture was stirred in water bath at 40 ^{o}C under N_2 atmosphere for 2 h. After the end of the reaction, the temperature was reduced, and the catalyst Bpy and Cu(I)Br was introduced. Then nitrogen-degassed GMA was added with a separatory funnel. The molar ratio of the reactant was as follows: [Cellulose ester]:[CuBr]:[Bpy]:[GMA]=1:1:1:100. The polymerization was allowed to react for a 4 h period at 20 ^oC or 30 ^oC, and then it was stopped by exposing the mixture to air. Finally, the obtained product was precipitated into de-ionized water, washed by ethanol absolute, repeatedly Soxhlet-extracted to remove homopolymer using acetone solution, and then freeze-dried. The monomer conversion was calculated from the weight balance.

Ring-opening reaction

The obtained grafted cellulose (5g) was dispersed in 200 mL ethanediamine (EDA) solution containing small amount of sodium carbonate. The mixture was reacted at 50 to 90 ^oC for 2 h. The amine-functionalized adsorbent was filtered, washed with distilled water and acetone, and then dried in vacuum at 60 ^oC.

Batch Experiments

The point of zero charge of the adsorbent was determined by the following procedure (Lataye *et al.* 2006): A series of 50 mL conical flasks were prepared with a cork stopper, each containing 20 mL of 0.01 M KNO_3 solution. The initial pH (pH_0) in each flask was adjusted between 3 and 11 by adding either 0.1 M KOH or 0.1 N HNO_3. The adsorbent (0.2 g) was added to each flask, and the flasks were securely capped immediately. The suspensions were then shaken and allowed to equilibrate for 24 h. The difference between the initial and final pH (pH_f) values ($\Delta pH = pH_0 - pH_f$) was plotted against the pH_0. The point of intersection of the resulting curve with abscissa, at which a Δ pH value of zero gave the pH_{pzc}.

Batch adsorption studies were performed at room temperature by shaking 100 mg of cellulose adsorbent with 100 mL of Cr(VI) solutions in 250 mL. Then, the mixtures were stirred by a water bath shaker at 200 rpm for a predetermined period. Afterwards, the resultant solution was filtered out, and the filtrate was analyzed for its Cr(VI) concentration by a spectrophotometric method using a UV VIS spectrophotometer (T6, China PERSEE Co. Ltd.). The parameters affecting the adsorption process, *i.e.*, pH, agitation time, initial Cr(VI) concentration, and adsorption temperature were studied. The pH of the aqueous solution was adjusted using 0.01N HCl and 0.01N NaOH solutions. All experiments were replicated thrice for all the adsorbents and results were averaged. The amount of Cr(VI) adsorbed by the cellulose adsorbent(q) and the removal percentage (R%) of Cr(VI) were calculated for each run by following expressions,

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$R\% = \frac{C_i - C_0}{C_i} \times 100 \tag{2}$$

where q is the adsorption capacity (mg/g), C_i, C_0, and C_e are the initial, outlet, and equilibrium concentrations of Cr(VI) (mg/L), V is the volume of Cr(VI) solution (mL), and W is the total amount of cellulose adsorbent (g).

Adsorption isotherm studies were carried out with five different initial concentrations of Cr(VI) from 100 mg/L to 600 mg/L at pH 3, contact time 3 h, and adsorbent dosage level of 1.0 g/L.

Kinetic studies of adsorption were also carried out at concentration of 100 mg/L at different temperature wherein the extent of adsorption was analyzed at regular time intervals.

Regeneration

Regeneration of adsorbent as well as recovery of adsorbate material is quite important, and the desorption and regeneration experiments were conducted with different types of desorbing agents through a batch technique. The adsorbent loaded with Cr(VI) was placed in the desorption medium and was stirred at 200 rpm at room temperature for 3 h. The elution ratio was calculated from the amount of Cr(VI) adsorbed on the adsorbent and the amount of Cr(VI) desorbed. The adsorption-desorption cycle was repeated several times to determine the reusability of the adsorbent.

Characterization

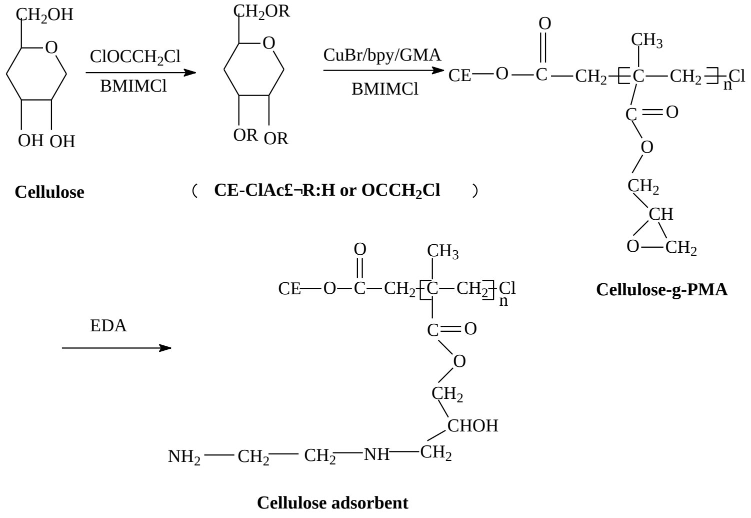
The Fourier transform infrared (FTIR) spectra of cellulose adsorbent before and after sorption were recorded with a AVAT-AR360 FT-IR spectrometer (Nicolet, USA) in the range of 4000 to 400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) analyses of the sorbents before and after sorption were conducted on a ESCALAB 250 spectrometer (Thermo Scientific, USA). Scanning electron microscopy (SEM) images of the sorbents before and after adsorption were obtained with a XL30 ESEM-TMP environmental scanning electron microscope (Philips-FEI, Holland). The X-ray diffraction (XRD) pattern of adsorbent before and after adsorption were performed on an X/Pert Pro MPD X-ray diffractometer (Philips, Holland). The energy-dispersive X-ray spectroscopy (EDX) analysis of cellulose adsorbent before and after adsorption were analyzed with a Nova NanoSEM 230 field-emission microscope (FEI, Hillsboro, US).

RESULTS AND DISCUSSION

Preparation and Characterization of the Adsorbent

Scheme 1 represents the functional reaction involved in the adsorbent preparation. There was remarkable weight gain of cellulose after graft copolymerization of GMA, and the monomer conversion was found to be 49.8%. The epoxy group content in the graft copolymer was determined to be 2.739 mmol/g by the pyridine-HCl titration method (Anirudhan and Senan 2011). After ring-open reacting with EDA, the epoxy group on the grafted cellulose was 100% converted to an amino group, which was confirmed by a nearly zero value of epoxy group content of cellulose adsorbent.

Results of FT-IR analysis of the cellulose, grafted cellulose, and cellulose adsorbent are shown in Fig. 1. Compared to the cellulose spectrum (Fig. 1a), the appearance at 1728 cm^{-1}, 906 cm^{-1}, and 848 cm^{-1} of grafted cellulose (Fig. 1b) were related to the GMA structure, indicating the successful ATRP grafting of GMA onto cellulose. After the ring-opening reaction, the characteristic peaks of epoxy group disappeared (Fig. 1c), while a broad band ranging from about 3100 to 3500 cm^{-1} corresponds to the combination of the stretching vibration of both OH and NH groups. In addition, a new signal appearing at 1571 cm^{-1} could be assigned to the deformation vibration of the NH group (Lin *et al*. 2013).



Scheme 1. Synthesis route of cellulose adsorbent

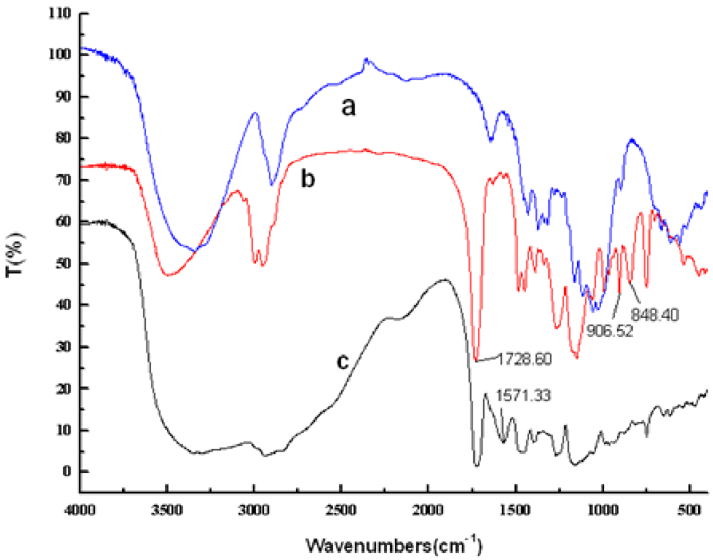


Fig. 1. FTIR spectra of cellulose (a), cellulose-g-GMA (b), and cellulose adsorbent (c)

Effect of pH

The variation of (pH_0 - pH_f) with initial pH_0 is shown in Fig. 2. The value of pH_{pzc} was found to be 7.92.

Solution pH plays an important role during the adsorption process, for the variation of pH can affect the surface charge of the cellulose adsorbent, the degree of ionization, and speciation of adsorbate (Elliott and Huang 1981; Bajpai *et al*. 2004). In this study, the adsorption of Cr(VI) as a function of pH was conducted in the initial pH range of 1.0 to 8.0, and results are shown in Fig. 3. It can be seen that the adsorption performance of the cellulose adsorbent was highly pH dependent. Cr(VI) removal efficiency was found to decrease with an increase in the initial pH. The optimum pH range for Cr(VI) removal was found to be between 2 and 3, and a maximum 99.6% of removal efficiency was obtained. The results were consistent with the findings reported previously by Saha *et al*. (2013a,b) and Saha and Saha (2014), where the maximum adsorption of Cr(VI) by chattim tree saw dust, mosambi peel, and mango leaves was found in each case at pH=2. At a lower pH (pH≤3) value, the dominant form of Cr(VI) is $HCrO_4^-$, while the surface of adsorbent is charged positively (pH_{pzc}=7.92). The stable forms of chromium such as H_2CrO_4 and CrO_3 exist as polynuclear species at high Cr(VI) concentration (Bayat 2002), and hence the low pH value results in a higher percentage removal of Cr(VI). The decrease in adsorption of Cr(VI) by increasing the value of pH may be due to the dual competition between both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates.

Previous work reported that when Cr(VI) comes in contact with organic substances or reducing agents, Cr(VI) is easily or spontaneously reduced to Cr(III) in an acidic medium due to its high redox potential value (Park *et al.* 2004a,b; 2005a,b,c). In this work, the mechanism of Cr(VI) removal by cellulose adsorbent is an electrostatic attraction process in which Cr(VI) are present in the form of anions, such as $HCrO_4^-$ and $Cr_2O_7^-$, while the surface of cellulose adsorbent has positive charges. The adsorption characteristics of Cr(VI) on the cellulose adsorbent were determined to be different from those observed on biomass or biomass-based activated carbons. The different adsorption behaviors were caused by the different surface properties of the materials. In our paper, the reaction sites for Cr(VI) are -NRH groups at the chain end, which should not be treated as biomaterials or organic substances to follow a biosorption process. This idea is also supported by studies from other laboratories on similar types of materials (Baes *et al.* 1997; Garg *et al.* 2004; Wartelle and Marshall 2005).

Basically, the authors have studied the oxidation states in the adsorption studies and found that the reduction of Cr(VI) to Cr(III) is very low. Therefore, in the present work the dominant mechanism is modeled as adsorption of Cr(VI) species. Since the main goal was the removal of total chromium from solution, much emphasis was focused on total removal, particularly on hexavalent chromium. In fact, Cr(VI) adsorption on adsorbent is not completely "adsorption" but "adsorption + reduction". Therefore, further work will be carried out to check the reduction of Cr(VI).

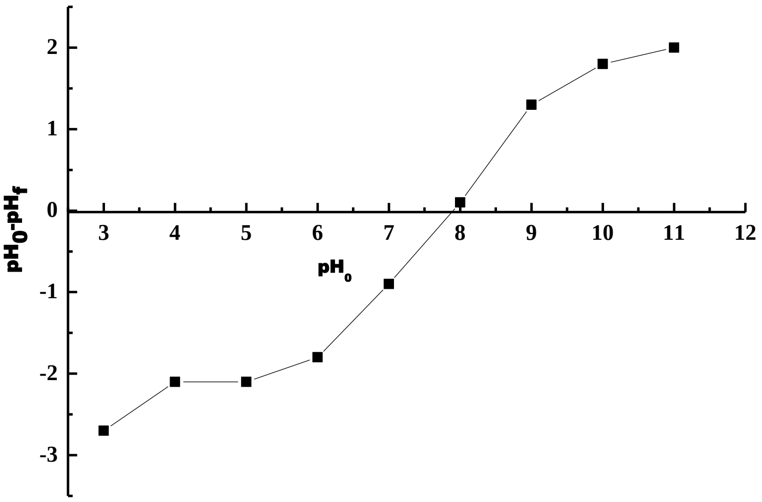


Fig. 2. Variation of (pH_0 - pH_f) with initial pH_0

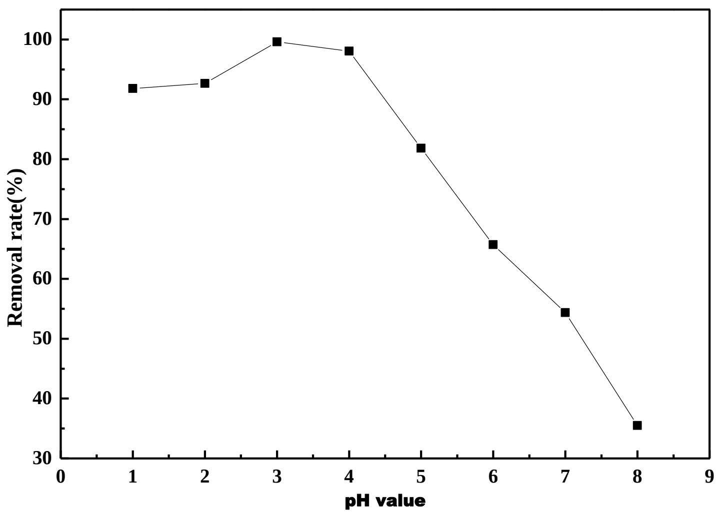


Fig. 3. Effect of pH on the Cr(VI) removal

Effect of Cr(VI) Initial Concentration

The influence of initial concentration of Cr(VI) on adsorption was studied by varying it from 30 to 500 mg·L^{-1} at an initial pH value of 3 while maintaining an adsorbent amount of 1.0 g·L^{-1} and a contact time of 3 h duration. The obtained result is presented in Fig. 4. It is shown that with an increase in the initial concentration from 30 to 500 mg·L^{-1}, the removal rate decreased from 99.6% to 62.4% and the adsorption capacity increased from 30.0 to 311.8 mg·g^{-1}. The decrease in the removal ratio of Cr(VI) with increasing initial concentration may be due to the fact that the adsorbent has a limited number of active sites, which would have become saturated above a certain concentration. On the other hand, the increase in adsorption capacity with an increase in initial Cr(VI) concentration may attributed to increased rate of mass transfer due to increased concentration of driving force (Juang *et al.* 1997; Dönmeza and Aksu 2002; Garg *et al.* 2008).

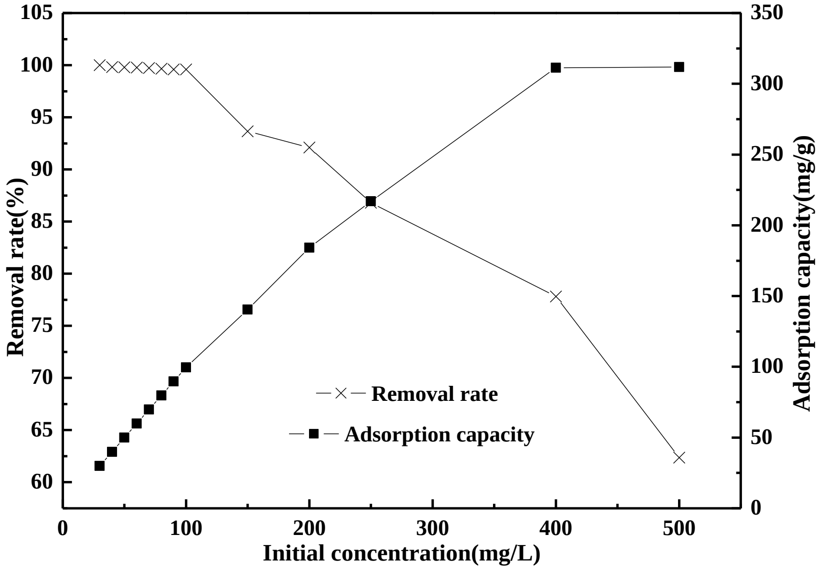


Fig. 4. Effect of Cr(VI) initial concentration on the adsorption capacity and Cr(Ⅵ) removal rate

Adsorption Isotherms

The adsorption equilibrium data for the Cr(VI) removal were obtained using Cr(VI) initial concentration between 100 mg/L and 500 mg/L at an adsorbent dosage level of 1.0 g/L. Two of the most commonly used isotherm models, Langmuir and Freundlich models, were adopted to analyze the isotherm data. The mathematical expressions are given by Eqs. 3 and 4, respectively, as follows,

$$\frac{C_e}{q_e} = \frac{1}{b \cdot Q_0} + \frac{C_e}{Q_0} \tag{3}$$

$$\log q_e = \log K + \frac{1}{n} \log C_e \tag{4}$$

where q_e is the amount of chromium (VI) adsorbed at equilibrium (mg·g^{-1}), Q_0 is the Langmuir maximum adsorption capacity (mg·g^{-1}), C_e is the equilibrium concentration of the Cr(VI) (mg·L^{-1}), and b (L ·mg^{-1}) is the Langmuir constant. K and n are Freundlich's constants related to adsorption capacity and the heterogeneity factor, respectively.

The Langmuir model (Eq. 3) is an ideal model for homogeneous monolayer adsorption. The model assumes uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. Meanwhile, the Freundlich model (Eq. 4) is an empirical equation in nature, assuming that the sorption process takes place on heterogeneous surfaces and sorption capacity is associated with the concentration of adsorbate in the liquid phase at equilibrium.

The Langmuir and Freundlich isotherm for adsorption of Cr(VI) on cellulose adsorbent at different temperatures are illustrated in Figs. 5 and 6. The calculated parameters for isotherm models are presented in Table 1. It can be seen that the maximum adsorption capacity of Cr(VI) calculated from Langmuir model was 500 mg/g at 50℃, higher than that of cellulose-g-acrylonitrile graft copolymers (371.96 mg/g) (Hajeeth *et al*. 2014), mosambi peel (250 mg/g) (Saha *et al*. 2013a), chattim tree saw dust (333.33 mg/g) (Saha *et al*, 2013b), mango leaves (250.23 mg/g) (Saha and Saha 2014), cellulose-g-styrene copolymer (123.4 mg/g) (Zhang *et al*. 2012), and other biosorbent, such as gelatin (200 mg/g) (Mahmoud and Mohamed, 2014a), Gelatin-Grafted-Yeast (240 mg/g) (Mahmoud and Mohame, 2014b), and novel silica gel (100 mg/g) (Abdel-Fattah and Mahmoud 2011).

Table 1. Calculated Parameters and the Regression Equations for the Langmuir Model

Temperature (^{o}C)	Langmuir parameters			Freundlich parameters		
	q_0（mg/g）	b（L/mg）	R^2	K	1/n	R^2
20	324.67	0.1259	0.9916	116.55	0.1951	0.9708
30	374.53	0.1245	0.9902	126.12	0.2117	0.9760
40	384.62	0.1566	0.9933	137.72	0.1987	0.9766
50	500.00	0.1667	0.9959	167.03	0.1580	0.9675
60	370.37	0.2700	0.9971	182.98	0.1409	0.9603

The Langmuir model was found to describe the adsorption more successfully than the Freundlich model for all the temperatures studied, according to the coefficients of determination, R^2. The value of the Langmuir parameter b, which is related to the binding energy, was found to increase with increase in temperature, indicating the contribution of stronger binding sites at higher temperature conditions (Deniz *et al*. 2006).

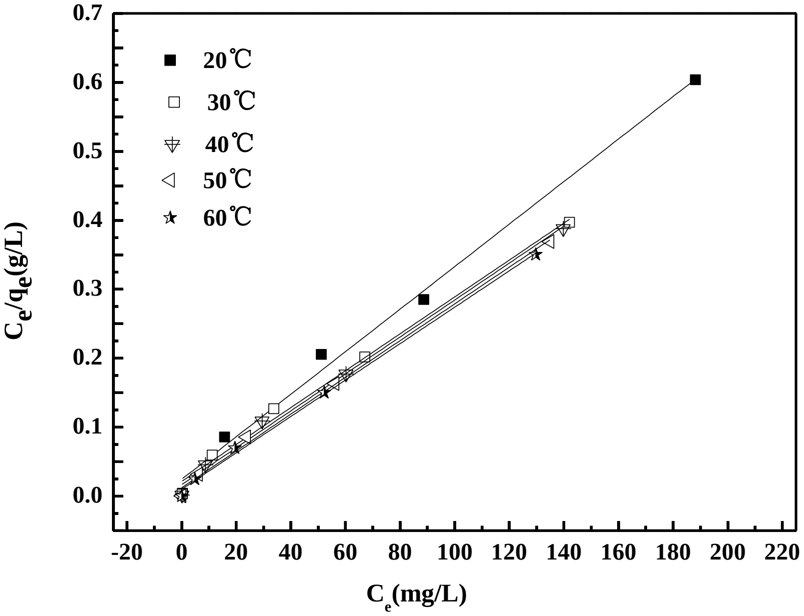


Fig. 5. Langmuir isotherms for Cr (VI) adsorption on cellulose adsorbent

The magnitude of the Freundlich parameter *n* gives an indication of feasibility of the adsorption (Ncibi *et al*. 2006). The 1/*n* value was in the range 0.1 to 0.5, which indicates that the adsorption process is feasible. For both the isotherm models, the adsorption capacity also increased as temperature was increased. This suggest the endothermic nature of the adsorption process.

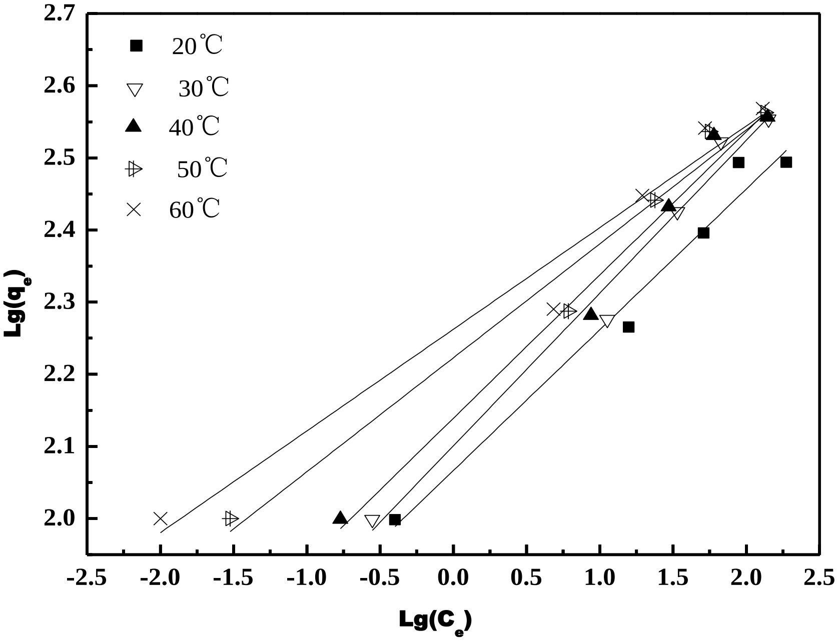


Fig. 6. Freundlich isotherms for Cr (VI) adsorption on cellulose adsorbent

To confirm the favorability of Cr(VI) adsorption onto cellulose adsorbent, the separation factor (R_L) was calculated by the following equation,

$$R_L = \frac{1}{1+bC_0} \tag{5}$$

where R_L is a dimensionless separation factor indicating the shape of the isotherm, b is the Langmuir constant, and C_0 is the initial Cr(VI) concentration. If $R_L = 0$, $R_L > 1$, and $0 < R_L < 1$, it represents that the isotherm is irreversible, unfavorable, and favorable, respectively (Mohan *et al.* 2005). The values of R_L at different temperature were determined and listed in Table 2. It can be seen that all R_L values were in the range 0 to 1, indicating good uptake of Cr(VI) toward the adsorbent.

Table 2. Values of RL at Different Temperature

Temperature (°C)	20	30	40	50	60
RL	0.0736	0.0743	0.0600	0.0566	0.0357

Thermodynamics for Adsorption

Thermodynamic parameters such as free energy (Δ*G*), enthalpy (Δ*H*), and entropy (Δ*S*) are crucial for determining the spontaneity of an adsorption process. These parameters, which are estimated to evaluate the feasibility and endothermic nature of the adsorption process, can be calculated from the following equations,

$$\Delta G = -RT \ln b \tag{6}$$

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

where R is the ideal gas constant 8.314 (J mol^{-1} K^{-1}) and T is temperature (K).

The values of Δ*G* can be calculated according to the values of *b* (presented in Table 3), while Δ*H* and Δ*S* are obtained from the slope and intercept by plotting ln *b* versus $1/T$. The obtained values of thermodynamic parameters are listed in Table 3. The increasingly negative values of Δ*G* with temperatures indicates the spontaneity and feasibility of the sorption of Cr(VI) on the cellulose adsorbent.

Table 3. Results of Calculated Thermodynamic Parameters

Temperature (°C)	△*G* (kJ/mo)	△*S* (kJ/(mol•K))	△*H* (kJ/(mol))
20	-4.580	44.26	8.394
30	-4.708	43.22	
40	-5.460	44.24	
50	-5.802	43.93	

The positive value of Δ*H* indicated the endothermic nature of adsorption process, and the positive values of Δ*S* at different temperatures indicate the increase in the randomness in the (solid + liquid) interface. The parameters are all supporting each other and confirming the positive influence of temperature for Cr(VI) adsorption on the adsorbent .

Kinetics Study

The effect of adsorption time on Cr(VI) removal was investigated to determine an optimum contact time for the adsorption of Cr(VI) on cellulose adsorbent (Fig. 7). As can be seen from the figure, there was a rapid uptake kinetics within 30 min, with adsorption equilibrium attained within 3 h. The pseudo-first-order kinetic model (Eq. 8) and pseudo-second-order kinetic model (Eq. 9) were applied to studied the sorption kinetics of Cr(VI) onto cellulose adsorbent.

$$\log(q_e - q_t) = \log q_e - k_1 t \qquad (8)$$

$$\frac{\mathrm{t}}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (9)$$

In Eqs. 8 and 9, q_e and q_t are the amounts of Cr(VI) adsorbed (mol/g) at equilibrium and at time *t* (min), respectively, and k_1 (min^{-1}) and k_2 (g·mg^{-1}·min^{-1}) are the rate constants of the pseudo-first-order kinetic model and the pseudo-second-order kinetic model, respectively.

The results are presented in Table 4 and in Figs. 7 and Fig. 8.

Table 4. Pseudo-First-Order Dynamic Equations and Parameters

Temperature	Pseudo-first-order dynamic parameters		Pseudo-second-order dynamic parameters		
(°C)	k_1	R^2	k_2	q_e	R2
20	0.0204	0.9513	0.0016	103.1	0.9975
30	0.0177	0.9767	0.0025	102.0	0.9990
40	0.0190	0.9738	0.0036	102.0	0.9949
50	0.0242	0.8939	0.0043	101.0	0.9996
60	0.0194	0.9739	0.0050	101.0	0.9997

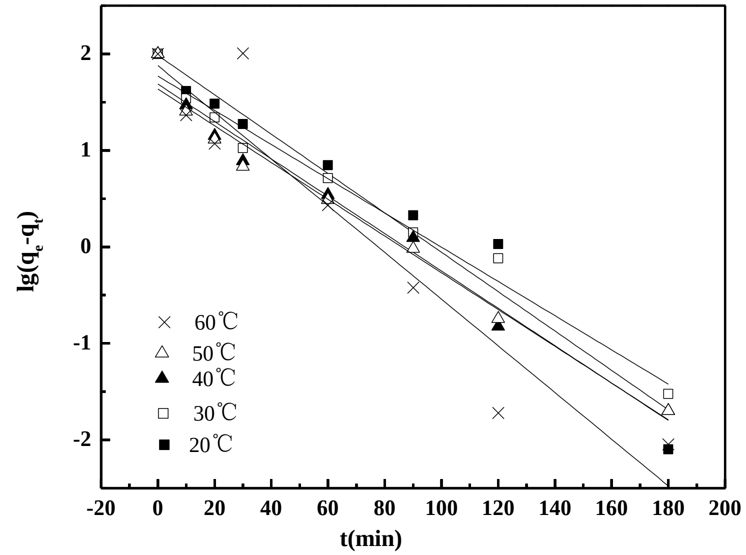


Fig. 7. Pseudo-first-order curve of Cr(VI)

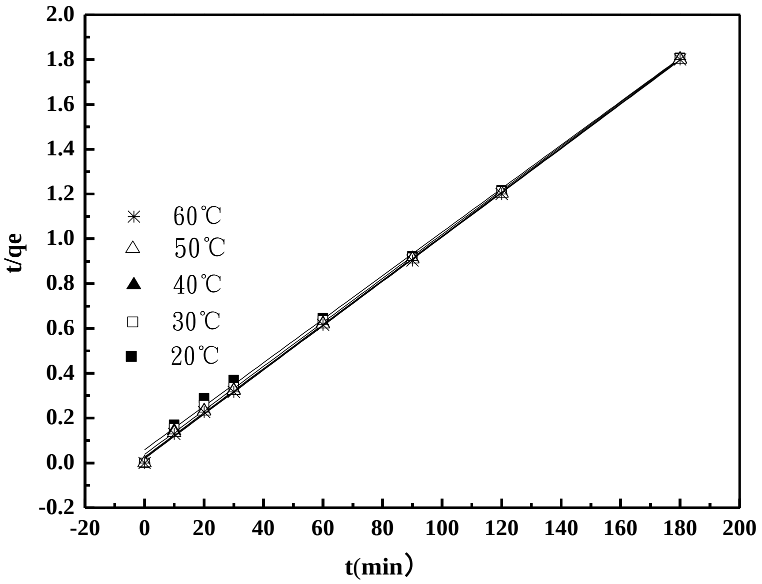


Fig. 8. Pseudo-second-order curve of Cr(Ⅵ)

From the results, it could be found that the pseudo-second-order model provided a better relationship for kinetics of adsorption process, because the values of correlation coefficients for the pseudo-second-order model of all examined data were found to be very high ($R^2 \geqslant 0.99$), indicating a better fit with the experimental data compared to the pseudo-first-order kinetic model.

Intra-particle diffusion model was also applied (Eq. 10) to study the effect of intra-particle diffusion resistance on sorption. Figure 9 illustrates the plots of q_t *vs.* $t^{1/2}$. It shows that there is a two-stage linear region over the entire time range; one was attributed to the membrane diffusion, while the other was attributed to the intra-particle diffusion.

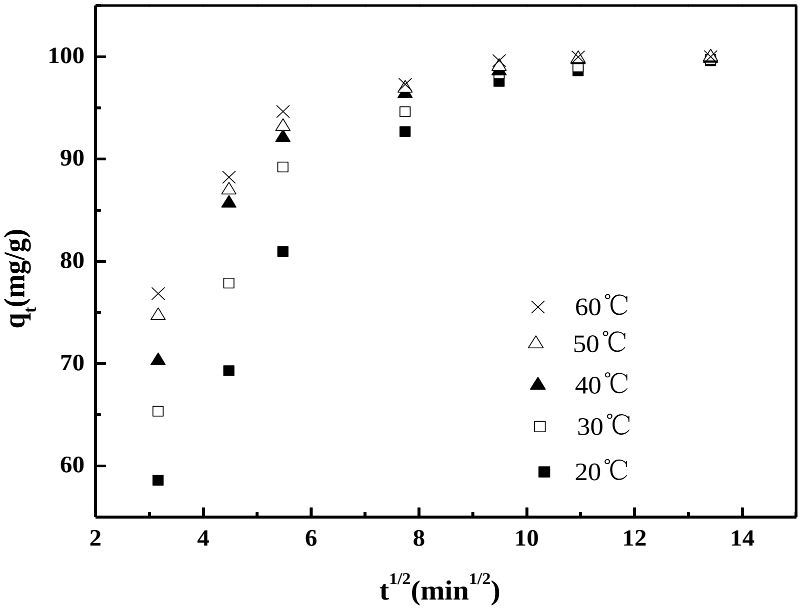


Fig. 9. Diffusion curve

The linear portions of the curves do not pass through the origin. This implies that the intra-particle diffusion was not the only phenomenon to govern the adsorption process. Both the membrane diffusion as well as intra-particle diffusion contribute to the rate-determining step. The slope of the initial linear portion of the curve was calculated to derive the intra-particle rate constant K_T, and the results are presented in Table 5.

$$q_t = K_T t^{1/2} + C \tag{10}$$

In Eq. 10, K_T is the intra-particle diffusion coefficient (mmol·g^{-1}·min$^{-1/2}$).

Table 5. Intra-particle Diffusion for Adsorption of Cr(VI) by Cellulose Adsorbents at Different Temperatures

Temperature (°C)	Intra particle diffusion parameters		R^2
	KT	*C*	
20	4.009	54.00	0.8069
30	3.080	65.08	0.7208
40	2.439	72.42	0.6454
50	2.129	76.28	0.6630
60	1.935	78.67	0.6355

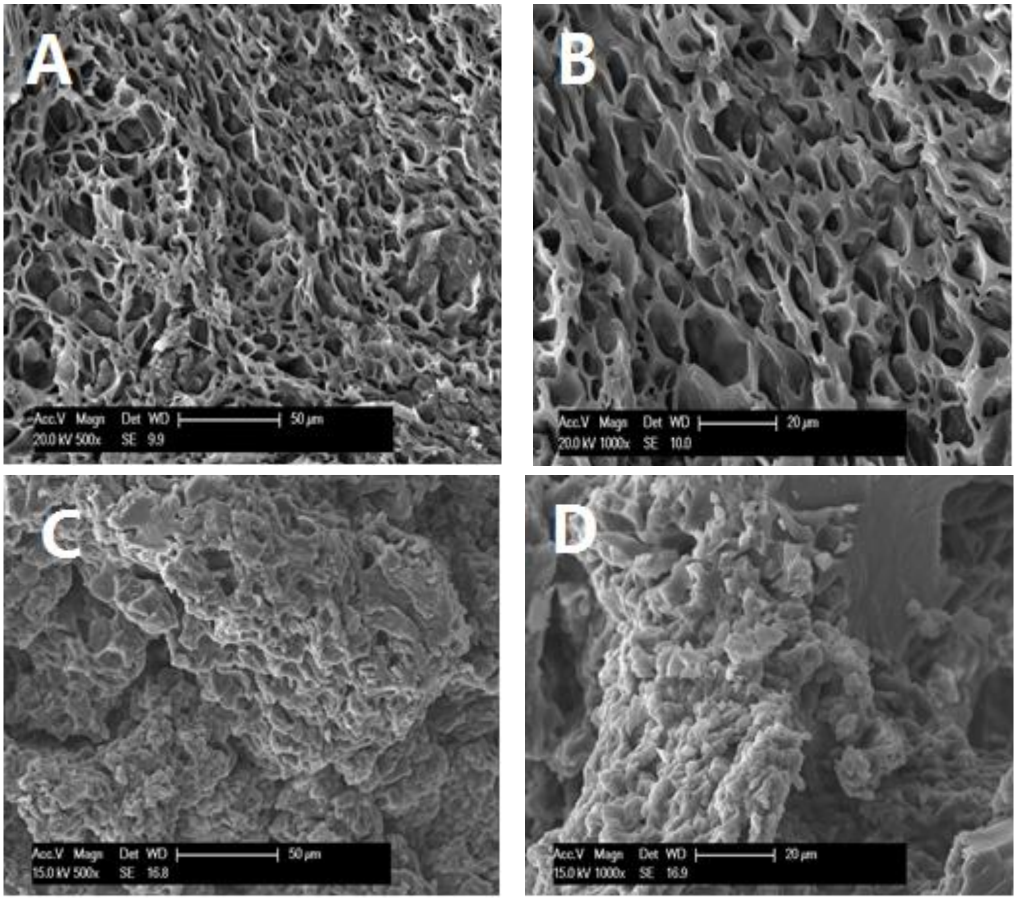


Fig. 10. ESEM micrograph of cellulose adsorbent before (A and B) and after (C and D) adsorption

Characterization of Adsorbent

ESEM images of cellulose adsorbent before and after adsorption are shown in Fig. 10. It can be observed that the surface of the adsorbent after adsorption changed, and the visible pores of the adsorbent had disappeared or had been filled up.

EDX analysis was then carried out on the cellulose adsorbent pre-adsorption and the Cr(VI) loaded adsorbent samples post adsorption. The EDX spectra obtained are shown in Fig. 11. These spectra indicate the presence of the adsorbed Cr(VI) on the cellulose adsorbent material as evidenced by the Cr peak at 5 to 6 keV. Coupled with the results from the adsorption studies, the EDX plots provide clear evidence for the physical presence of the adsorbed metal on the cellulose adsorbent.

To identify the possible functional groups on cellulose adsorbent involved in the binding of Cr(VI), FTIR spectra were obtained before and after metal adsorption. If a ligand coordinates to a metal, the energy of the ligand material will most likely be perturbed leading ultimately to subtle shifts in the absorption peaks in the FTIR spectra. These FTIR absorption bands are usually shifted to lower or higher frequencies. Figure 12 shows the FTIR spectra of cellulose adsorbent before and after Cr(VI) adsorption. There was a small shift of the ring vibration peak at 1573 cm^{-1} in cellulose adsorbent to 1657 cm^{-1} for Cr(VI)-loaded adsorbent.

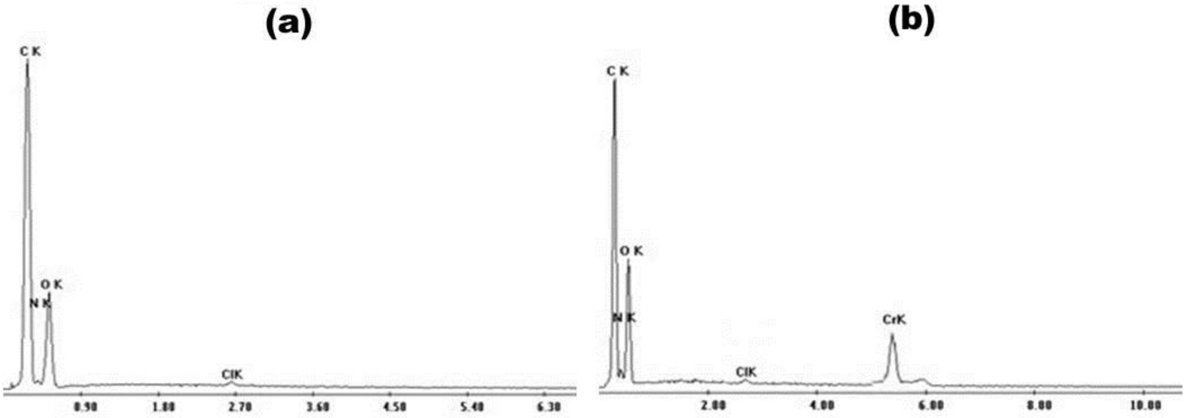


Fig. 11. EDX spectra of cellulose adsorbent pre- adsorption (a) and post adsorption (b)

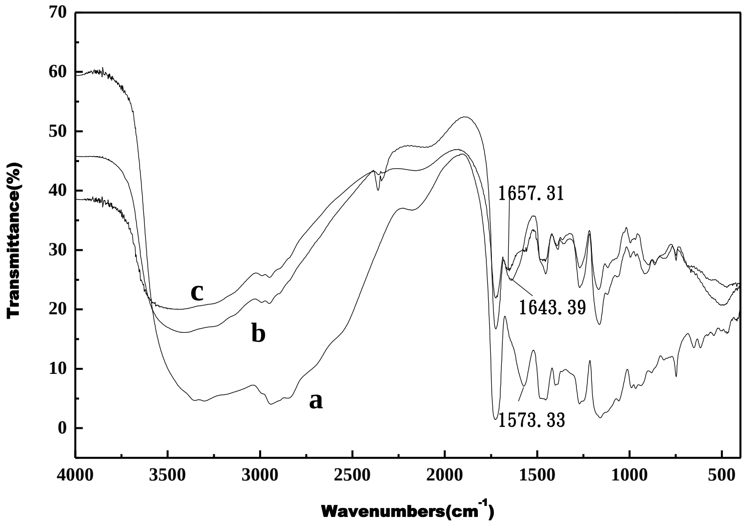


Fig. 12. The FT-IR spectrum of cellulose adsorbent (a) and Cr(VI) loaded adsorbent (b and c)

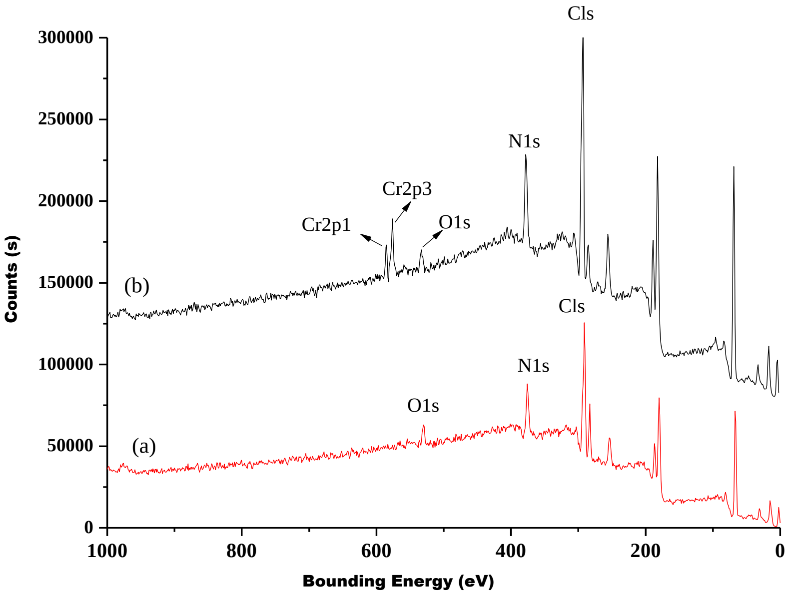


Fig. 13. XPS spectra for (a) cellulose adsorbent and (b) Cr(VI) loaded cellulose adsorbent

XPS spectra are also widely used to distinguish different forms of the same element and to identify the existence of a particular element in a material (Dambies *et al*. 2001). The surface structure of cellulose adsorbent before and after Cr(VI) adsorption was investigated by XPS spectra (Fig. 13). The results showed that the Cr peak is observed at 570 to 590eV after Cr(VI) adsorption, indicating the existence of Cr atoms on the surface of adsorbent.

Regeneration of Cellulose Adsorbent

From an economical point of view, the regeneration of cellulose adsorbent was investigated by conducting regeneration study with different types of desorbing agents (Table 6) using batch experiments. It could be seen that the NaOH solutions was found to be the most effective desorbing agent.

Table 6. Effect of Different Desorbing Agents on the Desorption Percentage

Desorbing agents	Concentration	desorption percentage（%）
HCl	0.5mol/L	13.5
HNO_3	0.5mol/L	12.8
H_2O	—	20.7
NaOH	1mol/L	92.4
NH_3OH	1mol/L	50.6
HCl/ thiourea	Mixture of 8% thiourea and1mol/L HCl	33.6
HNO_3/ thiourea	Mixture of 8% thiourea and 1mol/L HNO_3	29.8
*Desorption conditions: Volume of desorbing agents ,20 mL; temperature, 30℃; contact time,2 h.		

The relationship between the desorption percentage and the concentration of NaOH was studied and results are shown in Fig. 14. The percentage of desorption increased with the increase in NaOH concentration and was 98.0% when 2.0 M of NaOH was used as a desorption agent.

Figure 15 shows the ESEM images of the cellulose adsorbent after regeneration. The results show that the micro-pores on the surface of the adsorbent appeared again after regeneration with NaOH solutions.

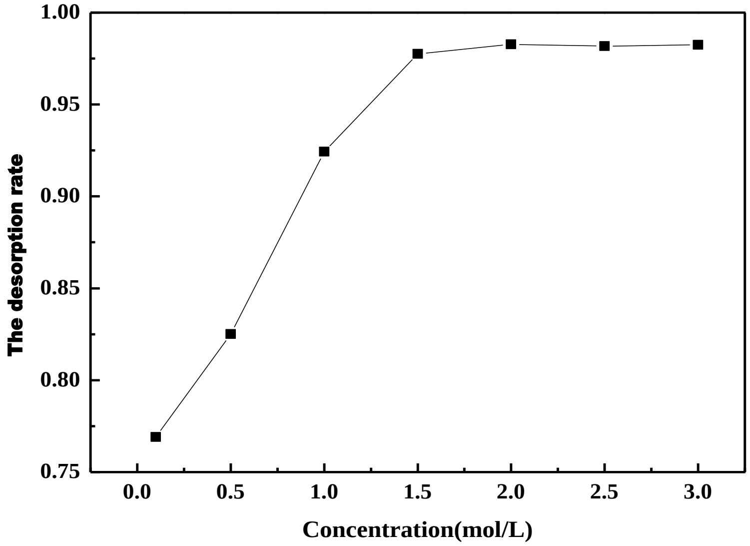


Fig. 14. Effect of sodium hydroxide aqua concentration on the desorption

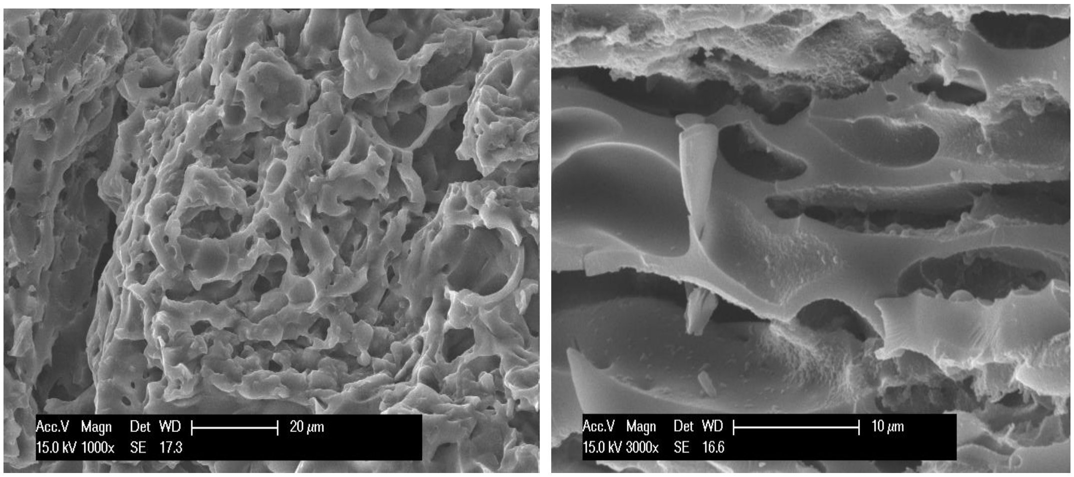


Fig. 15. ESEM images of cellulose adsorbent after regeneration

The reusability of adsorbent was studied by repeating the adsorption-desorption cycles, and the results are shown in Table 7.

Table 7. Relationship between Adsorption Capacity & Desorption Percentage and Adsorption-Desorption Cycles

Adsorption-desorption Cycles	1	2	3	4	5
Adsorption capacity (mg/g)	97.46	92.61	88.58	85.27	82.73
Desorption percentage (%)	98.0	96.3	95.6	93.2	91.5
* Desorbing agents:2.0M NaOH; Cr(VI) initial concentration:100 mg/L.					

The data presented in the table show that the adsorbent could be reused five times at least without noticeable change in adsorption capacity during the repeated adsorption-desorption operations. The above results indicated that the cellulose adsorbent had excellent ability of reuse in Cr(VI) adsorption by using 2.0M NaOH desorbing agent.

CONCLUSIONS

A modified cellulose adsorbent was synthesized and then used for the removal of Cr(VI) from aqueous solutions. Batch experiments were performed to study the effects of adsorption conditions on adsorptive performance. Equilibrium data could be well modeled by the Langmuir isotherm, and a kinetic study showed that the adsorption process followed the pseudo-second-order kinetics model. Thermodynamic parameters were calculated, and the results showed that the adsorption process is spontaneous and endothermic in nature. Characterization with ESEM, EDX, FTIR, and XPS confirmed the binding of Cr (VI) onto the cellulose adsorbent. The Cr(VI)-loaded cellulose adsorbent can be regenerated by treating with a 2.0 M NaOH solution and reused at least five times without noticeable change in adsorption capacity.

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REFERENCES CITED

Abdel-Fattah, T. M., and Mahmoud, M. E. (2011). “Selective extraction of toxic heavy metal oxyanions and cations by a novel silica gel phase functionalized by vitamin B4,” *Chemical Engineering Journal* 172(1), 177-183.

Anirudhan, T. S., and Senan, P. (2011). “Adsorptive potential of sulfonated poly(glycidylmethacrylate)-grafted cellulose for separation of lysozyme from aqueous phase: Mass transfer analysis, kinetic and equilibrium profiles,” *Colloid Surface A*, 377(1-3), 156-166.

Baes, A. U., Okuda, T., Nishijima, W., Shoto, E., and Okada, M. (1997). “Adsorption and ion-exchange of some groundwater anion contaminants in an amine modified coconut coir,” *Water Sci. Technol*. 35(7), 89-95.

Bajpai, J., Shrivastava, R., and Bajpai, A. K. (2004). “Dynamic and equilibrium studies on adsorption of Cr(VI) ions onto binary bio-polymeric beads of cross linked alginate and gelatin,” *Colloid Surface A* 236(1-3), 81-90.

Bayat, B. (2002). “Comparative study of adsorption properties of Turkish fly ashes. II. The case of chromium (VI) and cadmium (II),” *J. Hazard. Mater.* 95(3), 275-290.

Bayrak, Y., Topallar, H., Karagoz, B., and Kilic, I. (2013). “Kinetics and thermodynamics of Cr(VI), Cu(II), and Ni(II) adsorption on activated carbon prepared from rice hulls,” *Journal of Dispersion Science and Technology* 34(9), 1248-1256.

Bhaumik, M., Choi, H. J., McCrindle, R. I., and Maity, A. (2014). "Composite nanofibers prepared from metallic iron nanoparticles and polyaniline: High performance for water treatment applications," *Journal of Colloid and Interface Science* 425, 75-82.

Bhuvaneshwari, D. S., and Elango, K. P. (2009). "Solvent hydrogen bonding and structural influences on the Cr-VI oxidation of anilines in aqueous acetic acid medium," *Journal of the Indian Chemical Society* 86(3), 242-249.

Dambies, L., Guimon, C., Yiacoumi, S., and Guibal, E. (2001). "Characterization of metal ion interactions with chitosan by X-ray photoelectron spectroscopy," *Colloids and Surfaces A – Physicochemical and Engineering Aspects* 117(2-3), 203-214.

Deniz, T., Yavuz, H., and Denizli, A. (2006). "Synthesis of tentacle type magnetic beads as immobilized metal chelate affinity support for cytochrome c adsorption," *International Journal of Biological Macromolecules* 38(2), 126-133.

Dönmeza, G., and Aksu, Z. (2002). "Removal of chromium(VI) from saline wastewaters by *Dunaliella* species," *Process Biochemistry* 38(5), 751-762.

Elliott, H. A., and Huang, C. P. (1981). "Adsorption characteristics of some Cu(II) complexes on alumino-silicates," *Water Research* 15(7), 849-855.

Golder, A. K., Chanda, A. K., Samanta, A. N., and Ray, S. (2007). "Removal of Cr(VI) from aqueous solution: Electrocoagulation vs chemical coagulation," *Separation Science and Technology* 42(10), 2177-2193.

Garg, U. K., Kaur, M. P., Garg, V. K., and Sud, D. (2008). "Removal of nickel (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach," *Bioresource Technology* 99(5), 1325-1331.

Garg, V. K., Gupta, R., Kumar, R., and Gupta, R. K. (2004). "Adsorption of chromium from aqueous solution on treated sawdust," *Bioresour. Technol.* 92(1), 79-81.

Hajeeth, T., Sudha, P. N., Vijayalakshmi, K., and Gomathi, T. (2014). "Sorption studies on Cr(VI) removal from aqueous solution using cellulose grafted with acrylonitrile monomer," 66, 295-301.

Juang, R. S., Wu, F. C., and Tseng, R. L. (1997). "The ability of activated clay for the adsorption of dyes from aqueous solutions," *Environmental Technology* 18(5), 525-531.

Kaya, K., Pehlivan, E., Schmidt, C., and Bahadir, M. (2014). "Use of modified wheat bran for the removal of chromium (VI) from aqueous solutions," *Food Chemistry* 158, 112-117.

Kumar, R., Ansari, M. O., and Barakat, M. A. (2013). "DBSA doped polyaniline/multi-walled carbon nanotubes composite for high efficiency removal of Cr(VI) from aqueous solution," *Chemical Engineering Journal* 228, 748-755.

Kusku, O., Rivas, B. L., Urbano, B. F., Arda, M., Kabay, N., and Bryjak, M. (2014). "A comparative study of removal of Cr(VI) by ion exchange resins bearing quaternary ammonium groups," *Journal of Chemical Technology and Biotechnology* 89(6), 851-857.

Lataye, D. H., Mishra, I. M., and Mall, I. D. (2006). "Removal of pyridine from aqueous solution by adsorption on bagasse fly ash," *Industrial & Engineering Chemistry Research* 45(11), 3934-3943.

Liang, S., Guo, X., Lautner, S., and Saake, B. (2014). "Removal of hexavalent chromium by different modified spruce bark adsorbents," *Journal of Wood Chemistry and Technology* 34(4), 273-290.

Lin, C. X., Qiao, S., Liu, D. H, and Liu, M. H. (2013). "Cellulose functionalization via ATRP grafting of glycidyl methacrylate for Cr(VI) adsorption," *Chinese Journal of*

Chemistry 31(12), 1551-1556.

Liu, J. T., Zhang, W. D., Ren, Z. Q., and Ma, J. A. (2009). "The separation and concentration of Cr(VI) from acidic dilute solution using hollow fiber renewal liquid membrane," *Industrial & Engineering Chemistry Research* 48(9), 4500-4506.

Liu, S., and Sun, G. (2008). "Radical graft functional modification of cellulose with allyl monomers: Chemistry and structure characterization," *Carbohydrate Polymers* 71(4), 614-625.

Mahmoud, M. E., and Mohamed, R. H. A. (2014a). "Biosorption and removal of Cr (VI)–Cr (III) from water by eco-friendly gelatin biosorbent," *Journal of Environmental Chemical Engineering* 2(1), 715-722.

Mahmoud, M. E., and Mohamed, R. H. A. (2014b). "Separation of Cr(VI) from water by green reduction reaction and adsorptive removal on gelatin-grafted-yeast biosorbent," *Separation Science and Technology* 49(6), 868-876.

Matyjaszewski, K., Miller, P. J., Shukla, N., Immaraporn,B., Gelman, A., Luokala, B. B., Siclovan, T. M., Kickelbick, G., Vallant, T., Hoffmann, H., and Pakula, T. (1999). "Polymers at interfaces: Using atom transfer radical polymerization in the controlled growth of homopolymers and block copolymers from silicon surfaces in the absence of untethered sacrificial initiator," *Macromolecules* 32(26), 8716-8724.

Mohan, D., Singh, K. P., and Singh, V. K. (2005). "Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth," *Industrial & Engineering Chemistry Research* 44(4),1027-1042.

Ncibi, M. C., Mahjoub, B., and Seffen, M. (2006). "Biosorption of phenol onto *Posidonia oceanica* (L.) seagrass in batch system: Equilibrium and kinetic modeling," *Canadian Journal of Chemical Engineering* 84(4), 495-500.

O'Connell, D. W., Birkinshaw, C., and O'Dwyer, T. F. (2006). "A chelating cellulose adsorbent for the removal of Cu(II) from aqueous solutions," *Journal of Applied Polymer Science* 99(6), 2888-2897.

Park, D., Yun, Y.-S., and Park, J. M. (2004a). "Reduction of hexavalent chromium with the brown seaweed *Ecklonia* biomass," *Environ. Sci. Technol.* 38(18), 4860-4864.

Park, D., Yun, Y.-S., Cho, H. Y., and Park, J. M. (2004b). "Chromium biosorption by thermally treated biomass of the brown seaweed, *Ecklonia* sp.," *Ind. Eng. Chem. Res.* 43(26), 8226-8232.

Park, D., Yun, Y.-S., Jo, J. H., and Park, J. M. (2005a). "Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*," *WaterRes.* 39(4), 533-540.

Park, D., Yun, Y.-S., and Park, J. M. (2005b). "Use of dead fungal biomass for the detoxification of hexavalent chromium: Screening and kinetics," *Process Biochem.* 40(7), 2559-2565.

Park, D., Yun, Y.-S., and Park, J. M. (2005c). "Studies on hexavalent chromium biosorption by chemically treated biomass of *Ecklonia* sp.," *Chemosphere* 60, 1356-1364.

Peng, C. S., Meng, H., Song, S. X., Peng, C. S., Meng, H., Song, S. X., Lu, S., and Lopez-Valdivieso, A. (2004)."Elimination of Cr(VI) from electroplating wastewater by electrodialysis following chemical precipitation," *Separation Science and Technology* 39(7),1501-1517.

Saha, B., and Orvig, C. (2010). "Biosorbents for hexavalent chromium elimination from industrial and municipal effluents," *Coordination Chemistry Reviews* 254(23-24),

2959-2972.
Saha, R., Nandi, R., and Saha, B. (2011). "Sources and toxicity of hexavalent chromium," *Journal of Coordination Chemistry* 64(10), 1782-1806.
Saha, R., and Saha, B. (2014). "Removal of hexavalent chromium from contaminated water by adsorption using mango leaves (*Mangifera indica*)," *Desalination and Water Treatment* 52(10-12), 1928-1936.
Saha, R., Mukherjee, K., Saha, I., Ghosh, A., Ghosh, S. K., and Saha, B. (2013a). "Removal of hexavalent chromium from water by adsorption on mosambi (*Citrus limetta*) peel," *Research on Chemical Intermediates* 39(5), 2245-2257.
Saha, R., Saha, I., Nandi, R., Ghosh, A., Basu, A., Ghosh, S. K., and Saha, B. (2013b). "Application of chattim tree (devil tree, *Alstonia scholaris*) saw dust as a biosorbent for removal of hexavalent chromium from contaminated water," *The Canadian Journal of Chemical Engineering* 91(5), 814-821.
Song, H., Shang, J., Ye J. H., and Li, Q. (2014). "Investigations on photoelectrocatalytic reduction of Cr(VI) over titanium dioxide anode and metal cathode," *Thin Solid Films* 551, 158-162.
Wang, G., Chang, Q., Han, X. T., and Zhang, M. Y. (2013). "Removal of Cr(VI) from aqueous solution by flocculant with the capacity of reduction and chelation," *Journal of Hazardous Materials* 248, 115-121.
Wartelle, L. H., and Marshall, W. E. (2005). "Chromate ion adsorption by agricultural byproducts modified with imethyloldihydroxyethylene urea and choline chloride," *Water Res*. 39(13), 2869-2876.
Wu, L.M., Liao, L. B., Lv, G. C., Qin, F. X., He, Y. J., and Wang, X. Y. (2013). "Micro-electrolysis of Cr(VI) in the nanoscale zero-valent iron loaded activated carbon," *Journal of Hazardous Materials* 254, 277-283.
Xu, L. H., Zeng, H. Y., Liao, M. C., Xu, S., Zhang, Z. Q., and Li, Q. (2014). "Effect of temperature on microstructure and Cr(VI) adsorption capacity of MgAl metal oxides," *Journal of Inorganic Materials* 29(5), 529-533.
Xie, K., Huang, K., Yang, L. R., Yu, P. H., and Liu, H. Z. (2011). "Three-liquid-phase extraction: A new approach for simultaneous enrichment and separation of Cr(III) and Cr(VI)," *Industrial & Engineering Chemistry Research* 50(22), 12767-12773.
Xing, L., and Beauchemin, D. (2011). "Kinetic study of the reduction of Cr(VI) in natural water using ion exchange chromatography coupled to inductively coupled plasma mass spectrometry," *Journal of Analytical Atomic Spectrometry* 26(10), 2006-2011.
Zhao, Y. X., Yang, S. J., Ding, D. H., Chen, J., Yang, Y. N., Lei, Z. F., Feng, C. P., and Zhang, Z. Y. (2013). "Effective adsorption of Cr(VI) from aqueous solution using natural Akadama clay," *Journal of Colloid and Interface Science* 395, 198-204.
Zhang, X. H., Chen, Y. Z., Liu, H., Wei, Y., and Wei, W. (2014). "Hierarchical alpha-Fe_2O_3 hollow spheres: Facile synthesis, formation mechanism and their application in Cr(VI) removal," *Journal of Nanoscience and Nanotechnology* 14(9), 7167-7173.
Zhang, Y., Xu, L., Zhao, L., Peng, J., Li, C., Li, J., and Zhai, M. (2012). "Radiation synthesis and Cr(VI) removal of cellulose microsphere adsorbent," *Carbohydrate Polymers* 88(3), 931-938

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