CHROMIUM (VI) ADSORPTION ONTO ACTIVATED KRAFT LIGNIN PRODUCED FROM ALFA GRASS (*STIPA TENACISSIMA*)

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Activated lignin having a surface area of 1023 $m^2 g^{-1}$ has been prepared from sulfate lignin that was treated by 30% H_2O_2 and carbonized at 300 °C in order to test the chromium (VI) adsorption from aqueous solution. The influence of contact time, pH, initial concentrations of adsorbent and adsorbate, and temperature on the adsorption capacity were investigated. The maximum removal of Cr(VI) was found to be 92.36 % at pH=2 and a contact time of 80 min. Optimal concentration of lignin and Cr(VI) were found to be 3.8 g L^{-1} and 180 mg L^{-1}, respectively. The adsorption kinetics data fitted well with a pseudo-second-order equation, and the rate of removal of chromium was found to speed up with increasing temperature. Activation energy for the adsorption process was found to be 18.19 kJ mol^{-1}. The Langmuir and Freundlich adsorption isotherm models were applied to describe the isotherm and isotherm constants for the adsorption of Cr (VI) on lignin. These constants and correlation coefficients of the isotherm models were calculated and compared. Results indicated that Cr (VI) uptake could be described by the Langmuir adsorption model. The maximum adsorption capacity (q_m) of Cr (VI) on lignin was 75.75 mg g^{-1} at 40°C. The dimensionless equilibrium parameter (R_L) signified a favorable adsorption of Cr (VI) on lignin and was found to be between 0.0601 and 0.818 ($0<R_L<1$). The thermodynamic parameters such as $\Delta G°$, $\Delta S°$, and $\Delta H°$ were calculated, and it was found that the reaction was spontaneous and endothermic in nature. This study indicates that lignin has the potential to become an effective and economical adsorbent for removal Cr (VI) from waste water.

Key words: Lignin; Adsorption; Isotherm Kinetics; Chromium (VI); Removal; Aqueous solution

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INTRODUCTION

Chromium is used in various industrial applications, including the production of stainless steel, electroplating, metal finishing, dyes and pigments, leather tanning , wood preserving, glass, ceramic paints, canning industries, electronics equipments, and catalysis chemical manufacturing (Parcker et al. 2001; Quilntana et al. 2001; Smith et al. 2002; Mohan et al. 2006a). These industrial effluents can contain Cr(VI) from 10 to 100 mg L^{-1} (Nakano et al. 2002), which is much higher than the standard limit of 0.1 mg.L^{-1} in industrial waste water (MATET 1993). Improper treatment of Cr(VI) effluents will pose serious problem to ecosystems and cause great damage. Chromium (VI) effects human physiology by accumulating in the food chain and causes several ailments (Park

and Jung 2001; Garg and Sud 2005; Yong et al. 2006a). The total content of heavy metals is a key attribute of water quality. Cr(VI) remains one of the principal factors of this quality, and its elimination must be as complete as possible.

The increase in water demand and the evolution of legislation affecting industrial waste require the development of new processes for wastewater treatment that are more effective and less expensive. The main techniques that have been used to remove Cr(VI) from waste water conventionally are chemical reduction followed by precipitation (Eckenfelder 1982; Patterson 1985). The drawbacks of using this approach are the consumption of chemical agents and the generation of large amounts of sludge. Other methods, such as membrane filtration, ion exchange, and adsorption in activated carbon are being used to remove Cr(VI) (Rawat and Singh 1992; Montiel et al. 2000a). Among the methods of removing the Cr(VI), the adsorption by activated carbon is the best and most frequently used method (Blajis et al. 1999; Montiel et al. 2000b). This is due to its well-developed porosity and surface functional groups that accounts for its good adsorption (Bailey et al. 1999; Babel and Kurmiawan 2003a; Anbalagan and Juliet 2004). Nevertheless, commercial activated carbon is expensive and requires chelating agents to enhance its performance, thus increasing treatment cost (Oliveira et al. 2005a). For this reason, it is desirable to produce low-cost and efficient sorbents for Chromium (VI). Such low-cost sorbents include industrial or agricultural waste products including waste slurry, lignin, iron hydroxide, straw and nut shells, sawdust, and bark (Babel and Kurmiawan 2003b; Demirbas 2004; Mohan et al. 2006b; Wu et al. 2008a).

Lignin is a natural polymer integrated into the cellular walls of all the vascular plants and accounts for 20 to 40% of wood matter (Wu et al. 2008b). Its world production, by the paper industry, is approximately 50 million tons per year, of which 10% of the material is used. The remainder of the lignin is sometimes discharged in the rivers, causing serious damage to the environment. Lignin comprises various functional groups such as: methoxyl, hydroxyl, phenolic, carboxyl, aromatic, alcohol, aldehyde, etc. (Sakanen and Luding 1971). These properties suggest that lignin has potential to eliminate heavy metals from waste waters.

The aim of the present work was the optimization of the adsorption conditions for the effective removal of Cr(VI) using activated kraft lignin produced from alfa grass. This is a prevalent plant of the western mediterranean, which grows on the semi arid grounds of northern Africa and the southern Spain. Boudy (1950) estimated that alfa grass covered a surface area of approximately at 4.5 millions hectares in Algeria. More recent information has given 3 millions hectares only (Ghebalou 2001). The yields of the exploitation vary with the density of the alfa grass coverage at 400 to 2000 kg ha^{-1} (Ramendo 1975).

For this purpose, we have investigated the influence of pH, temperature, contact time, chromium initial concentration, and dose of adsorbent on Cr(VI) adsorption from water solution. Both kinetic and equilibrium isotherm models were applied to establish the rate of adsorption, adsorption capacity, and mechanism of Cr(VI) adsorption on activated lignin. The thermodynamic parameters were calculated to find the feasibility of the adsorption process.

EXPERIMENTAL

Preparation and Methods of Characterizations of Adsorbent

Lignin was obtained from the black liquor produced from alfa grass (*Stipa tenacissima*) sulfate pulping in a laboratory scale digester of volume 5 liters. The black liquor of concentration 25 - 30% was acidified to pH = 2 - 3 with concentrated sulfuric acid. The suspension was transferred to a settling container, in which lignin and acid liquor were separated at 80 – 90 °C. After that , lignin was washed with distilled water at 55 – 60°C several times to pH = 7 and dried in an oven at 45 - 50 °C for 24 hours. The obtained lignin was mixed with 30% H_2O_2 at a ratio of 1:10 (w/v) in the presence of $NaWO_4$ as catalyst for 30 min. The product was then carbonized at 300 °C in a muffle furnace with a nitrogen flow of 300 ml min^{-1} for 2 hours, follow-up of a cooling by maintaining the same nitrogen flow (Mazourova et al. 2003). Finally, lignin was then ready for use in the following experiments.

The ash was quantified after calcinations of lignin in a muffle furnace. The total C, H, and N were determined by dry combustion in an autoanalyzer CHN-2400 from Perkin Elmer. The measurement of true density of the particles was carried out using a pycnometer with helium (ACCUPYC 1330 TC). Specific surface was determined with an all-gas porosimeter ASAP2010M. The measurement is based on the application of the method of Brunauer, Emmet, and Teller (BET). The total pore volume was determined by liquid nitrogen adsorbed at a relative pressure of $P/P_0 = 0.98$. FT- IR analysis of the activated lignin used in this study was performed using a Fourier transform infrared spectrometer FT/IR-4100-A. The lignin powders were blended with IR-grade KBr, at a ratio of 1:100, in a gate mortar and pressed into tablet form. The spectra of the lignin samples were recorded. The Chromium (VI) concentration was determinated using a spectrophotometer (UV 240 Shimadzu model) with 1,5-diphenyl-carbazide in acid medium at a wavelength of 540 nm.

Batch Adsorption Studies

Batch sorption experiments were carried out in a series of Erlenmeyer flasks of 1000 ml capacity one, covered with a Teflon sheet to prevent contamination and installed on the thermostatic magnetic stirrers .The contents were shaken at speed of 120 rpm. The pH values were measured by a pH-meter Accumet BASIC (mark AB-15). The Chromium (VI) solution was prepared by dissolving 2.5688 g of potassium dichromate ($K_2Cr_2O_7$) 99.99% of purity, in 1000 ml distilled water. Standard solutions of 0.5 N HCl and NaOH were used to adjust the pH of solution. For each sample, the adsorbent was separated from the solution by filtration and the residual Cr(IV) ion concentration was measured.

RESULTS AND DISCUSSION

Characteristics of the Absorbent

The results of the analysis carried out on lignin (Table 1) show that it retained 8 % of moisture and had the following percentage elemental composition: C, 82.6 %; H, 3.1 %; N, 0.04 %; O, 14.1 %, and ash, 1.3 %. The total volume of pores was 1.83 cm^3 g^{-1},

and the specific surface area was 1023 $m^2 g^{-1}$. The total specific surface area was comparable with that obtained by Yong et al. (2006b) on activated carbon produced from K_2CO_3 activation of lignin from reed black liquors. The value of methylene blue sorption 92.3 mg L^{-1} was lower than that of adsorbent produced from wood bark 260 – 300 mg g^{-1} (Becedina et al. 2002). For this reason, it is not recommended for removal of color from waste waters. On the other hand, the iodine adsorption 828 mg g^{-1} shows that the activated lignin was a good adsorbent for cations.

Table 1. Physical and Chemical Properties of Activated Lignin

Parameters	Values	Parameters	values
Total volume of pores($cm^3 g^{-1}$)	1.83	C (%)	82.6
Specific surface area($m^2 g^{-1}$)	1023	H (%)	3.1
Bulk density (kg m^{-3})	350	N (%)	0.04
Moisture (%)	8	O (%)	14.10
Ash (%)	1.3	Iodine number (mg g^{-1})	828
		Methylene blue number (mg g^{-1})	92.3

The FTIR spectrum of activated lignin is shown in Fig. 1. The broad band at 3385.49 cm^{-1} was dominated by the stretching vibrations of aromatic and aliphatic OH groups. The spectra also showed definite bands at 1613.66 - 1700.71 cm^{-1}, which may be assigned to C=C stretching vibrations of skeletal aromatic groups. The 1214.22 cm^{-1} adsorption band was attributed to the C-O-C stretching mode of aryl-alkyl ether. Thus, the band appearing around 1076.96 cm^{-1} indicates the presence of the Si-O group. These results reveal the presence of various functional groups that generally contain oxygen in activated lignin.

Effect of the pH

Many studies on heavy metal adsorption have shown that solution pH is the single most important parameter in the adsorption process (Srivastava et al. 1994). In order to optimize the pH for maximum removal efficiency, sorption experiment were conducted in the initial pH range from 0 to 8 with an initial Cr (VI) concentration of 100 mg L^{-1} and adsorbent dose of 2 g L^{-1}, as shown in Fig. 2. The maximum adsorption of Cr (VI) was around 92.36 % in the pH range 2 - 3. This maximum adsorption of Cr(VI) was explained by higher hydrogen ion (H^+) concentration at low pH values. The negative charges at the surface of internal pores of lignin were neutralized and some new adsorption sites were developed; as a result, the surface provided a positive charge for $HCrO_4^-$ (Sanchez-polo and Rivera-Ultrilla 2002). Depending on the solution pH, Cr(VI) can exist mainly as: chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), hydrogen chromate ($HCrO_4^-$), or chromic acid (H_2CrO_4) according to equations for equilibrium reactions (1) (Cotton et al. 1972; Brito et al. 1997a). $HCrO_4^-$ ions predominantly exist in the solution over $Cr_2O_7^{2-}$ at pH = 2 – 6, and the ionic size of $HCrO_4^-$ is smaller than that of $Cr_2O_7^{2-}$ (Brito et. al. 1997b).
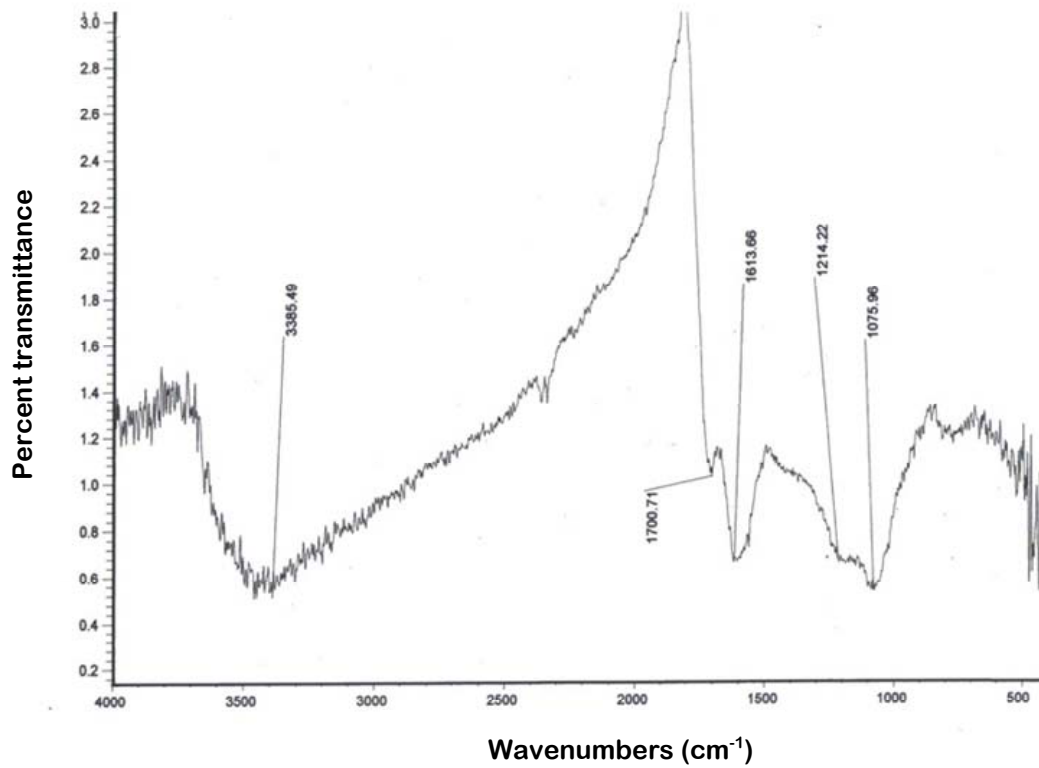
Fig. 1. FTIR spectra of activated lignin

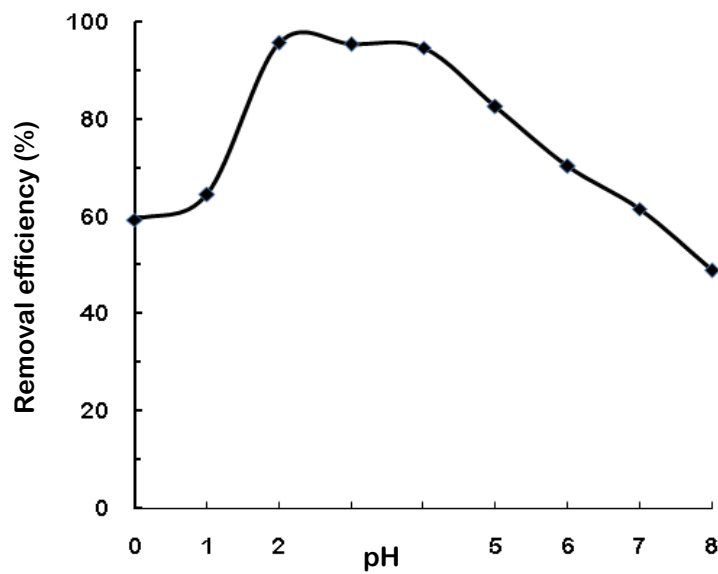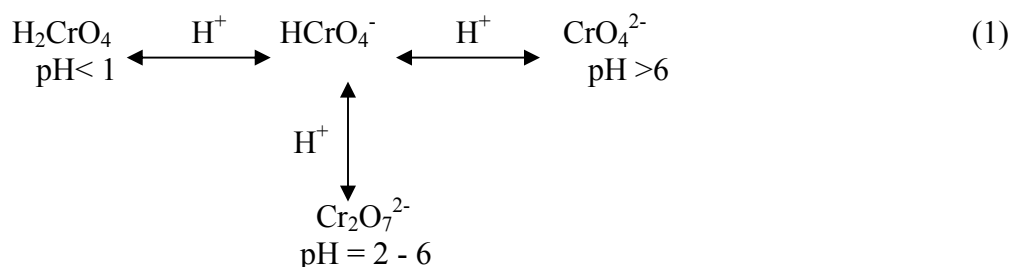**Fig. 2.** Effect of pH on the removal of Cr (VI) concentration by activated lignin

Consequently, the $HCrO_4^-$ ions were able to diffuse and adsorb easily onto the surface of the lignin, compared to $Cr_2O_7^{2-}$ ions. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms (CrO_4^{2-} and $Cr_2O_7^{2-}$). The neutral species H_2CrO_4 formed predominantly at pH< 1 is not rapidly adsorbed on the activated kraft lignin, the surface of which becomes positive in charge. It can be concluded that the active form of Cr(VI) that can be absorbed effectively by the kraft lignin under the conditions of this study is $HCrO_4^-$.

$$H_2CrO_4 \underset{pH<1}{\overset{H^+}{\longleftrightarrow}} HCrO_4^- \overset{H^+}{\longleftrightarrow} CrO_4^{2-} \quad pH>6 \tag{1}$$

$$H^+ \updownarrow$$

$$Cr_2O_7^{2-}$$
$$pH = 2 - 6$$

Effect of the Initial Concentration

According to previous studies (Devaprasath et al. 2007; Baral et al. 2008), the adsorption of chromium is influenced significantly by the initial concentration of Cr(VI) in aqueous solutions. In this study the initial concentration of Cr(VI) was varied from 50 to 280 mg L^{-1} while maintaining the adsorbent dose at 2 g L^{-1}, the temperature at 20 °C, and the pH at 2. The results in Fig. 3 show the effect of variation of the initial concentration on the Cr(VI) removal rate and adsorption capacity of activated lignin. It is noted that the removal rate of Cr(VI) decreased from 98.2 to 12.58 % and the adsorption capacity increased from 23.49 to 95.42 mg g^{-1} when the initial concentration increased from 50 to 280 mg L^{-1}. The reduction in the removal efficiency of chromium is probably due to increase the quantity of the Cr(VI) ions in the solution for the same number of sites and surface of adsorbent. The increase of lignin adsorption capacity is probably due to the complete utilization of adsorption surface and active site available, which is not possible at low concentrations. For the initial concentration value, approximately 180 mg L^{-1}, the optimal values of Cr(VI) removal and adsorption capacity were found to be 72.8% and 68.5 mg g^{-1} respectively.

Effect of Adsorbent Amount

The effect of the amount of adsorbent on the process of adsorption was studied by varying the adsorbent dose from 1 to 10 g L^{-1} with pH = 2 and temperature 20°C. The curves obtained (Fig. 4) show that the removal efficiency of Cr(VI) increased from 25 to 100 % and the adsorption capacity decreased from 17.7 to 5.2 mg g^{-1} when the amount of activated lignin increased from 1 to 10 g L^{-1}. The reduction of the sorption capacity is related to the fact that some of the active centers remain unsaturated during adsorption process. However, with the increase of carbon dose the absolute amount of active centers increases, resulting in an increase of the overall sorption efficiency of the systems. For 3.8 g L^{-1} of activated lignin dose, the optimum values of Cr(VI) removal efficient and adsorption capacity were found to be 48.3 % and 9.5 mg g^{-1}, respectively.
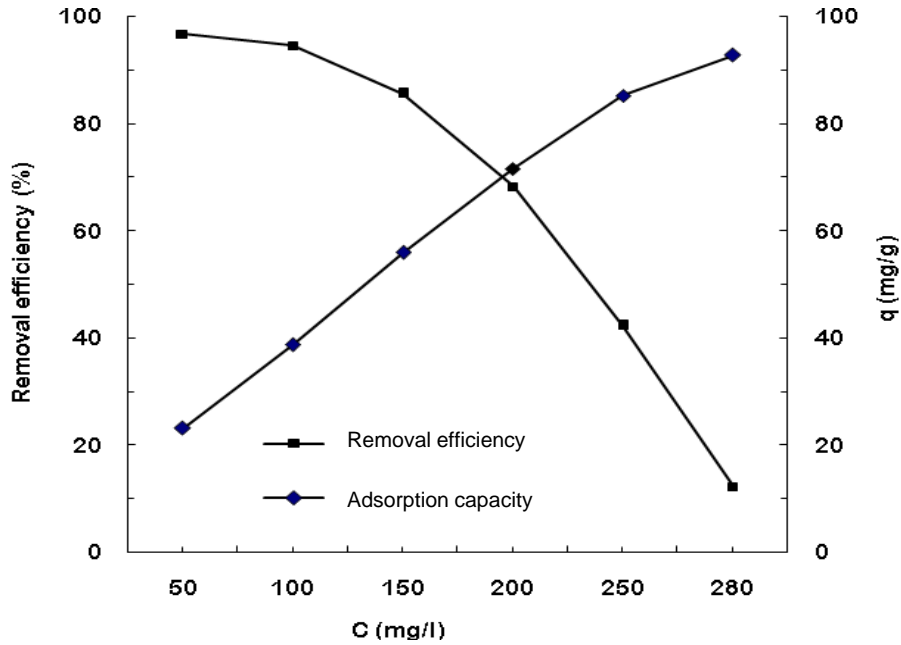
Fig. 3. Effect of initial concentration on Cr (VI) adsorption on activated lignin
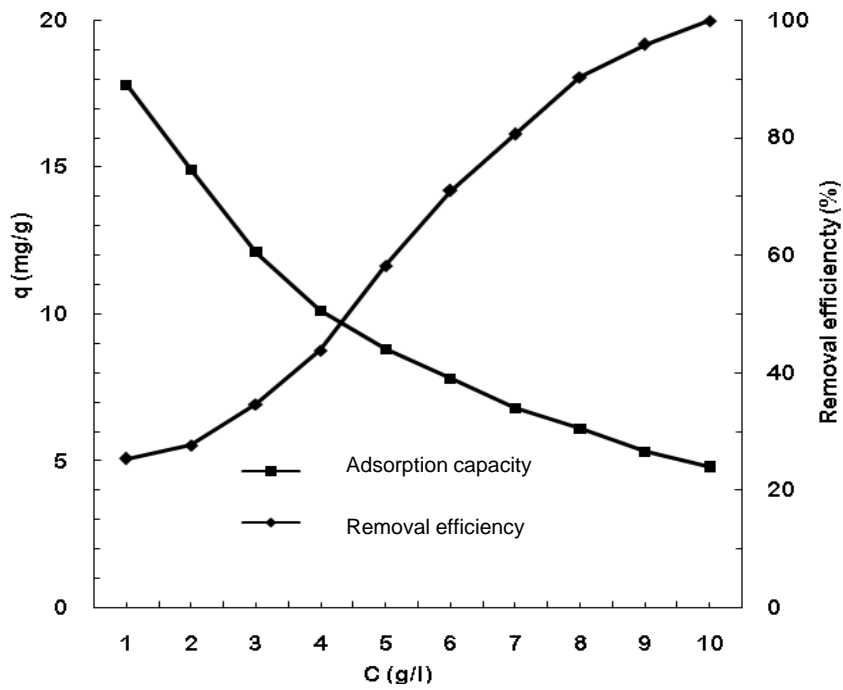

Fig. 4. Effect of activated lignin amount on Cr (VI) adsorption

Effect of the Time of Contact

Experiments were performed in a 1000 ml batch reactor at different temperatures (20, 25, 30, 40 °C), pH= 2, adsorbent dose 1 g L^{-1}, and an initial chromium concentration of 100 mg L^{-1}. After the introduction of the adsorbent and the chromium solution, the samples were magnetically stirred, collected at different time intervals, and filtered through a membrane filter (0.45μm). The Cr(VI) concentrations in the filtrate were determined by spectrophotometer. The curve characteristics of the kinetics of adsorption at various temperatures are presented in Fig. 5, where an initial fast adsorption was followed by a much slower adsorption. This biphasic adsorption pattern was also observed in other studies (Khraisheh et al. 2002; Dogan et al. 2004). The slow adsorption is likely due to external film diffusion on the pore wall surface and pore diffusion into the polymeric matrix, of which surface diffusion may be the primary rate-limiting mechanism. The adsorption capacity increased sharply at the employed temperatures in approximately the first 35- 38 min. The maximal adsorption capacity of activated lignin was reached 98 % of its maximum value which was 52 mg g^{-1} at the temperature of 40 °C. Beyond 38 min, the adsorption capacity increased slowly. The adsorption equilibrium was reached a solid-solution contact time of 80 min, indicating that the equilibrium time was independent of temperature. This time of 80 min was considered sufficient for the significant removal of Cr(VI) and was therefore used for all the further experiments.
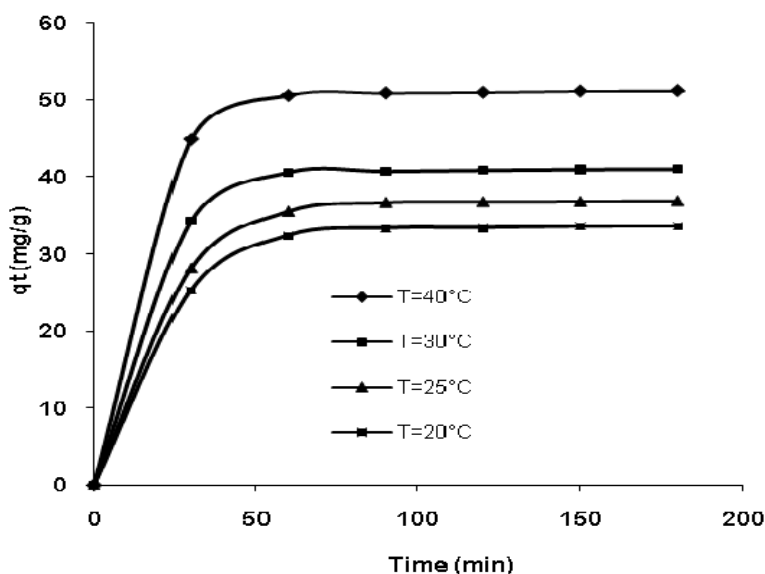

Fig. 5. Effect of contact time on Cr (VI) adsorption on lignin at different temperatures

Adsorption Isotherms

The isotherm of adsorption indicates how the quantities of molecules are distributed between the liquid and solid phase when the adsorption processes reach balance. It is employed to establish the maximum capacity of adsorption of metals on

adsorbents, which is expressed in term of quantity of metal adsorbed per unit of mass of adsorbent used (mg g^{-1} or mmol g^{-1}). In the present investigation the data have been correlated with a suitable isotherm. The Langmuir and Freundlich equations are in common use for describing adsorption equilibrium Cr(VI) removal application. The linear forms of the Langmuir and Freundlich isotherms are represented by the equations as follows.

Langmuir: $C_e/q_e = 1/(K_L q_m) + 1/q_m C_e$ (2)

where K_L - Langmuir equilibrium constant of adsorption (L.mg^{-1}),
       q_m - maximum adsorption capacity (mg.g^{-1}),
       q_e - amount adsorbed at equilibrium (mg.g^{-1}),
       C_e - equilibrium concentration (mg.L^{-1}).

Freundlich: $\log (q_e) = \log K_F + 1/n \log C_e$ (3)

where K_F and n are the isotherm constants of Freundlich.

The Isotherm constants of Freundlich and Langmuir were calculated from the plots C_e/q_e vs. C_e and log (q_e) vs. log C_e respectively, and the results are presented in Table 2.

Table 2. Values of Langmuir and Freundlich Adsorption Constants for Adsorption Cr (VI) on the Lignin at Different Temperatures and pH = 2

Temperature (°C)	Constants of Langmuir				Constants of Freundlich		
	$q_{e\,(exp.)}$ (mg g^{-1})	$q_{e\,(cal.)}$ (mg g^{-1})	R^2 (%)	K_L (L mg^{-1})	K_f (L g^{-1})	n	R^2 (%)
20	40.23	42.73	99.73	0.1403	19.02	6.18	74.11
25	46.71	51.81	99.91	0.1042	21.61	5.91	88.11
30	53.54	59.17	99.98	0.0862	24.06	5.73	87.27
40	64.69	75.75	99.82	0.0786	30.48	6.14	77.84

The value of the coefficient of determination (R^2) ranged from 99.73 % to 99.98 % and was higher for Langmuir isotherm than for the Freundlich isotherm, which ranged from 74.11 % to 88.11 %. As can see in Table 2, the adsorption isotherm of Cr(VI) exhibited Langmuir behavior, which indicates that the uptake occurs on a homogenous surface by monolayer adsorption and can be described in terms of chemisorption as the formation of an ionic or covalent bonds between adsorbent and adsorbate. The Langmuir maximum uptake ($q_{m(cal)}$) increased from 42.73 to 75.75 mg g^{-1}, and the Langmuir constant (K_L) decreased from 0.1403 to 0.0786 L g^{-1} with the temperature increment from 20 to 40 °C. The essential characteristics of the Langmuir isotherm may be expressed in terms of a dimensionless separation factor of equilibrium parameter (R_L) which may be calculated from equation (4).

$R_L = 1/(1 + K_L C_e)$ (4)

The parameter (R_L) is related to the shape of the isotherm according to the following adsorption characteristics: $R_L > 1$ represents unfavorable adsorption; $R_L = 1$ corresponds to a linear relationship; $0 < R_L < 1$ is favorable adsorption, and $R_L = 0$ is irreversible (Babu and Gupta 2008). In the present investigation, R_L remained between 0.061 and 0.818 ($0 < R_L < 1$), which indicates that lignin was a good adsorbent for Cr(VI) ions and that adsorption at various temperatures was more favorable for higher initial concentration than for lower ones.

Thermodynamic Evaluation of the Adsorption Process

In order to understand the mechanism of the process of adsorption of Cr (VI) by lignin, it is essential to determine the thermodynamic parameters, such as the free energy ($\Delta G°$), the enthalpy ($\Delta H°$), and the entropy ($\Delta S°$). These parameters were determined by using equations (5) and (6), and their values are shown in Table 3.

$$\Delta G° = - RT \ln K_L \tag{5}$$

$$(\Delta G°) = (\Delta H°) - T(\Delta S°) \tag{6}$$

where T - temperature in Kelvin degrees,
R - Universal gas constant (8.314 J mol^{-1} K^{-1}),
$\Delta H°$ - standard enthalpy (kJ mol^{-1}),
$\Delta S°$ - standard entropy (kJ mol^{-1} K^{-1}).

Table 3. Thermodynamic Parameters for Adsorption of Cr(VI) on Lignin

$\Delta G°$ (kJ mol^{-1})				$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})
20 C°	25 C°	30 C°	40 C°		
				- 20.68	0.086
-11.21	-11.34	-11.50	-12.03		

The thermodynamic equilibrium constant of adsorption (K_L) can be expressed in term of enthalpy, entropy, and the temperature as described in equation (7). Based on the Langmuir constants K_L, $\Delta G°$ values were -11.21, -11.34, -11.50, and -12.03 kJ mol^{-1} for the system of 20, 25, 30, and 40 °C, respectively. The values of $\Delta H°$ and $\Delta S°$ were determined from the slopes and intercepts of the plot lnK_L versus $1/T$, respectively.

$$\ln K_L = \Delta S°/R - (\Delta H°/RT) \tag{7}$$

The negative values of $\Delta G°$ indicate the spontaneous nature and feasibility of the process. The higher negative value of $\Delta G°$ was found for the system with higher temperature, indicating a more energetically favorable condition for Cr(VI). Free energy was obtained in the interval between -11.35 and - 12.04 kJ mol^{-1}. According to Weng et al. (2008), these results indicate that the mechanism of adsorption is not due to the

exchanges of ions, but the attraction of the anions $HCrO_4^-$ on the electropositive surface of lignin at acid pH. The values of $\Delta H°$ and $\Delta S°$ were found to be - 20.68 kJ mol^{-1} and 0.086 kJ mol^{-1} K^{-1}, respectively. A negative value of $\Delta H°$ indicates the exothermic nature of the process, while a positive value of $\Delta S°$ suggests an increased randomness at the solid/liquid interface during the sorption of Cr(VI) into the lignin.

Kinetics of Adsorption

Several kinetic models were used to explain the mechanism of the process of adsorption. The simple first order equation given by Lagergren (Mohan et al. 2006c) was applied to analyze the data of the kinetic adsorption.

$$dq_t / dt = K_1 \ (q_e - q_t) \tag{8}$$

where q_t (mg g^{-1}) represents the adsorbed Cr(VI) concentration on lignin at fixed time t (min), and K_1 (g L^{-1} mg^{-1}) is a first order reaction coefficient. After integration with an initial condition of $q_t = 0$ at $t = 0$, the equation takes the following form.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{9}$$

The values of K_1 and q_e were calculated from the intercept and slope of the plot of $\ln(q_e - q_t)$ vs. t. The data listed in Table 4 showed values of the correlation coefficient (R^2) ranging from 92.80 % to 97.26 % and $q_{e(cal.)}$ derived from equation (9) decreased with increasing temperature and reached the low value 20.75 mg g^{-1} at a temperature of 40°C. At this temperature, $q_{e\,(exp)}$ reached a maximal value of 51.17 mg g^{-1}.

Table 4. Maximal Adsorption Values of Cr(VI) and Pseudo-First-Order Equation Parameters at Different Temperature

Parameters	Temperature (°C)			
	20	25	30	40
R^2 (%)	97.26	94.82	92.59	92.80
K_1 (min^{-1})	0.0441	0.0441	0.0441	0.0434
$q_{e.(cal.)}$ (mg g^{-1})	25.79	25.36	23.75	20.75
$q_{e(exp.)}$ (mg g^{-1})	33.62	36.96	40.96	51.17

Therefore, the pseudo-first-order equation was not a good fit for Cr(VI) adsorption onto lignin. In such cases, applicability of the pseudo-second-order kinetic is being tested with the rate equation of Lagergren (Eq. 10). From the boundary conditions $t = 0$ and $q_t = 0$, the integrated form of the equation which can be written in the linear form (11).

$$dq_t/dt = K_2(q_e - q_t)^2 \tag{10}$$

$$t/q_e = 1/(K_2.q_e^2) + (1/q_e) \ t \tag{11}$$

The values of K_2 and q_e were calculated from the intercept and slope of plot t/q_t vs. t. Table 5 summarizes the values of the corresponding model fitting parameters, i.e., K_2, correlation coefficients (R^2), $q_{e(exp)}$, and $q_{e(cal.)}$. The values of rate constants were 6.77×10^{-3}, 7.20×10^{-3}, 10×10^{-3}, and 10.9×10^{-3} mn^{-1} for temperatures of 20, 25, 30, and 40 °C, respectively. Dakiki et al. (2002) have reported very similar values for Cr(VI) removal on a variety of adsorbents: wool, 3.96×10^{-3} mn^{-1}; cactus leaves, 6.80×10^{-3} mn^{-1}; sawdust, 9.60×10^{-3} mn^{-1}; almond, 8.80×10^{-3} mn^{-1}; olive cake, 8.99×10^{-3} mn^{-1}, at pH = 2 and 30°C. (R^2) > 99.75 % for all temperatures.

Table 5. Maximal Adsorption Values of Cr (VI) and Pseudo-Second-Order Equation Parameters at Different Temperatures

Parameters	Temperature (°C)			
	20	25	30	40
R^2 (%)	99.75	99.77	99.91	99.96
K_2 (min^{-1})	0.00677	0.0072	0.01	0.0109
$q_{e. (cal.)}$ (mg g^{-1})	34.48	37.59	41.49	51.81
$q_{e (exp.)}$ (mg g^{-1})	33.62	36.96	40.96	51.17

The calculated equilibrium adsorption capacities ($q_{e(cal.)}$) were very close to the experimental amount of adsorption equilibrium ($q_{e(exp)}$); this indicates that the experimental data were well correlated to the pseudo-second-order equation, which is based on the assumption that the rate limiting step is a chemical sorption involving valance force through sharing or exchange of electrons between adsorbent and adsorbate (Mohan et al. 2006d; Kula et al. 2008; Suhas et al. 2007). Successful fitting of this model suggests that chemisorption is the rate controlling step (Ho and McKay 2000). Chromium sorption has also been reported following the pseudo-second-order reaction on raw rice bran (Oliveira et al. 2005b) and sawdust and modified peanut husk (Li et al. 2007).

The rate constant listed in Table 5 was used to determine the activation energy (E_a) of the adsorption process. The Arrhenius equation given as follows was used to calculate E_a.

$$\ln K_2 = \ln A - (E_a/R)\ 1/T \tag{12}$$

where A - pre-exponential factor (min^{-1}),
          R - Universal gas constant (8.314 J mol^{-1} K^{-1}),
          T - absolute temperature (°K),
          E_a - activation energy (kJ mol^{-1}).

From the intercept and slope of plot $-\ln K_2$ vs. $1/T$ (Fig. 6), the activation energy (E_a) and the pre-exponential factor (A) were calculated to be 18.19 kJ mol^{-1} and 12.049 min^{-1}, respectively. The magnitude of the latter value indicates that a chemical adsorption process involved weak interactions between the adsorbent and the adsorbate, and the low value of E_a indicates that the adsorption had low energy barrier and occurred rapidly (Krishnan and Anirudhan 2003).

Comparisons with Other Adsorbents

The maximum adsorption capacity (q_m) of activated lignin determined from the Langmuir model at 40°C was compared with that of various low-cost adsorbents for the adsorption of Cr(VI) (Table 6). All of these adsorbent exhibited a lower adsorption capacity than that of activated lignin, except alligator weed. This could be primarily due to the initial carbon content, the activation process, as well as the pore development due to the basic morphology of lignin. Hence, activated lignin can be considered to be viable low-cost adsorbent for removal of Cr(VI) from aqueous solutions.
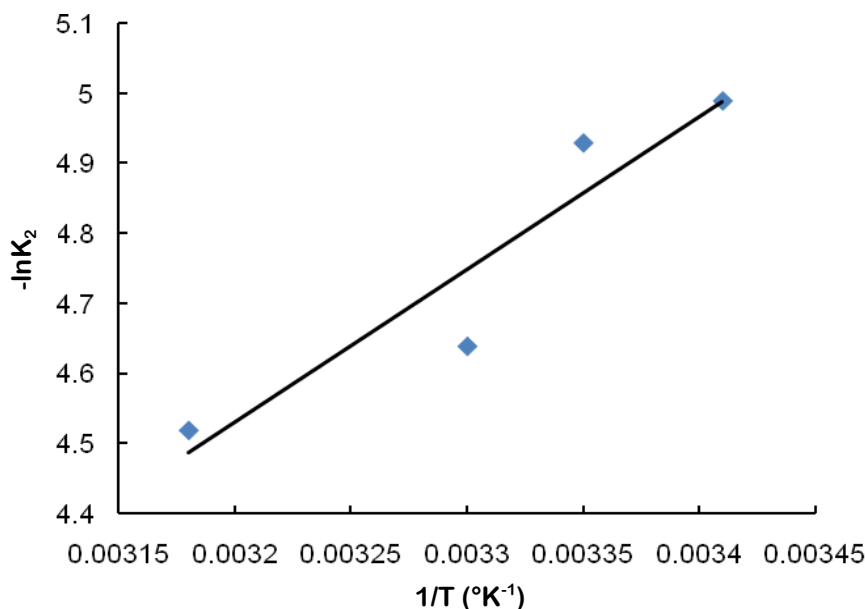
Fig. 6. Arrhenius plot -lnK_2 against 1/T for adsorption of Cr(VI) on lignin

Table 6. Comparison of Adsorption Capacity q_m of Cr(VI) on Various Adsorbents

Adsorbent	$q_{m.}$	pH	References
Neem leaves	62.97	2	Babu and Gupta 2007
Spent activated clay	1.42	2	Chih et al. 2007
Trichoderma Fungal	48.9	6	Liliana and Eliseo 2008
Weed salvina cucullata	13	2	Baral et al. 2008
Black tea leaves	45.5	2	Abul Hossain et al. 2005
Alligator weed	82.57	1	Wang et al. 2008
Reed lignin	52.6	2	Yong et al. 2006
Activated kraft lignin	75.75	2	This work
Sugar-cane bagasse	13.4	2	Sharma and Forster 1994

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CONCLUSIONS

Lignin produced from alfa grass sulfate cooking was converted successfully to activated lignin, a low-cost adsorbent. This activated lignin was characterized and utilized for removal of Cr (VI) from aqueous solution. The sorption data were better fitted by the Langmuir adsorption isotherm model as compared to the Freundlich model. The monolayer capacity (q_m) was calculated using a Langmuir adsorption isotherm for activated lignin and was found to increase with increasing temperature, confirming the spontaneous and exothermic nature of the process. The maximal removal efficiency of Cr(VI) was found at pH = 2 - 3. Also, the adsorption capacity was found to be comparable to those of commercially available low-cost adsorbents used for removal of Cr(VI) from aqueous solution. The best correlation coefficient was obtained using the pseudo-second-order kinetic model, indicating that the chromium removal process followed the pseudo-second-order rate expression. The studies presented here reveal that the activated lignin could be fruitfully employed as an adsorbent for removal of chromium from aqueous solution without any sludge production. Studies with actual electroplating wastewater are in progress.

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