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Full Length Research Paper

Optimization of key parameters for chromium (VI) removal from aqueous solutions using activated charcoal

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Commercial activated charcoal was investigated for removal of Cr(VI) from aqueous solutions. The effects of altering the initial Cr(VI) concentration, pH, contact time and amount of activated charcoal were studied. Maximum adsorption of Cr(VI) was achieved between pH 1 - 3 and after a contact time of 120 min. The percentage of Cr(VI) removed decreased from 99.99 - 90.83 % when the initial Cr(VI) concentration was increased from 0.05 - 0.5 mg ml^{-1} at pH 2 and 26 ± 2°C. Various kinetic models such as pseudo first-order, pseudo second-order and Elovich models were used to evaluate the mechanism of Cr(VI) adsorption on activated charcoal. The Cr(VI) removal process was found to be governed by second-order kinetics and the rate constant of the adsorption (k_2) was 0.1800 g kg^{-1} min^{-1} for an initial Cr(VI) concentration of 0.1 mg ml^{-1}. The adsorption of Cr(VI) was evaluated using Langmuir, Freundlich, and Temkin isotherms and their constants were determined. The maximum adsorption capacity obtained using the Langmuir isotherm model was 45.24 g kg^{-1} at pH 2.

Key words: Key parameters, activated charcoal, adsorption, aqueous solutions, Cr(VI).

INTRODUCTION

Chromium (Cr), a group 6 transition metal, is the 21st most abundant element in the Earth's crust, with an average concentration of 100 ppm (Emsley, 2001). Its concentrations ranges are 0.001 - 3 mg g^{-1} in soil, 5 × 10^{-6} - 0.8 × 10^{-3} mg ml^{-1} in seawater, 2.6 × 10^{-5} - 5.2 × 10^{-3}mg ml^{-1} in rivers and lakes (Kota and Stasicka, 2000) , and 5 × 10^{-4} - 270 mg ml^{-1} in industrial wastewater (Patterson, 1985). Cr (0) has an electronic configuration of $4s^1 3d^5$, due to the lower energy of the high spin configuration. Cr has a wide range of possible oxidation states (+2, +3, and +6), with +3 being the most stable; +1, +4 and +5 are rare. The proportion of Cr(III) and Cr(VI) strongly depends on the pH and oxidative properties of the location but in most cases Cr(III) is the dominating species (Kota and Stasicka, 2000). However, in some areas the ground water can contain up to µg of total chromium of which 30 µg is present as Cr(VI) (Emsley, 2001; Kota and Stasicka, 2000). Historically, Cr compounds were used in dyes and paints and the tanning of leather, and these compounds are often found in the soil and groundwater at abandoned industrial sites. These sites are regarded as brownfield land and require environmental cleanup and remediation. Primer paint containing hexavalent chromium is still widely used for aerospace and automobile refinishing applications. Chromate poisoning can cause skin disorders and liver damage, and there is some evidence that chromates are oncogenic (carcinogenic) (Sawyer et al., 2004). Due to this, the World Health Organization has recommended a maximum allowable chromium (VI) concentration in drinking water (5 × 10^{-5} mg mL^{-1}) . For this reason, its pollution in water is becoming a worrying situation for scientists. The methods applied for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption(Martins and Martins,1993; Mahvi et al., 2005; Oke and Okuofu, 2000). Most of these methods suffer

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Table 1. Physical properties.

Alcohol dissolved	0.2%
Acid dissolved	0.8%
Residue on ignition	2%
Dry weightlessness	10.0%
Cl	0.025%
Sulfur compounds	0.10%
Fe	0.02%
Zn	0.05%
Pb	0.005%

from disadvantages such as high capital and operational costs or the disposal of the residual metal sludge which further poses problem for environment (Weng et al., 2008; Shama et al., 2007). Amongst these techniques, adsorption seems to be one of the most effective methods because of simple operation and easy handling. The objective of this study was to investigate the use of activated charcoal as an adsorbent material for removing Cr(VI) from wastewater.

Batch experiments were carried out for kinetic studies on the removal of Cr(VI) from aqueous solutions. The influence of various important parameters such as the pH, contact time, adsorbent amount, and initial Cr(VI) concentration were investigated by varying any one of the process parameters and holding the other parameters constant. The Langmuir, Freundlich, and Temkin equations were used to fit the equilibrium isotherm models. Pseudo first-order, second-order and Elovich kinetic models were used to evaluate the mechanism of adsorption.

EXPERIMENTAL

Commercial activated carbon in granular form (CAC) (Table 1) was obtained from Sinopharm Chemical Reagent Co. Ltd (Beijing, China) and crushed and sieved to a particle size of 450 µm. A Cr(VI) stock solution (1 mg ml^{-1}) was prepared by dissolving 99.9% $K_2Cr_2O_7$ (2.8287 g) in distilled water (1 L). This solution was diluted as required to obtain 0.05 - 0.5 mg ml^{-1} Cr(VI) standard solutions. The initial pH of the solution was adjusted using either 0.5 M NaOH or 0.5 M H_2SO_4. The batch experiments were carried out in 100 ml conical flasks by agitating a pre-weighed amount of the activated charcoal with 50 ml of the aqueous Cr(VI) solution for a predetermined period of time (based on prior kinetic studies) at 26 ± 2°C on a water bath-mechanical shaker (198 rpm). The effect of altering the initial pH was studied with 0.05 mg ml^{-1} Cr(VI) . The effect of altering the contact time was studied with 0.1 - 0.4 mg ml^{-1} Cr(VI) solutions at pH 2.

Experiments were also conducted to investigate the effect of varying the amount of activated charcoal from 2 - 24 g L^{-1} with a Cr(VI) concentration of 0.250 mg ml^{-1} at pH 2. Adsorption isotherm studies were carried out with the different standard solutions (0.05 - 0.5 mg ml^{-1} Cr(VI)) while maintaining the adsorbent dosage at 10 g L^{-1} and the pH at 2. An UV-visible spectrophotometer was employed with 1,5-diphenylcarbazide in acid medium to determine the concentrations of Cr(VI) remaining in the sample. The absorbance of the purple-violet colored solution was recorded at 540 nm. The filtrate was analyzed for the remaining Cr(VI) concentration. The amount of Cr(VI) adsorbed (g kg^{-1}) at time *t* was calculated using Equation (1):

$$q_t = \frac{C_o - C_t}{m_S} \times V \qquad (1)$$

Where C_o and C_t are the Cr(VI) concentrations in g L^{-1} at time 0 and time *t*, respectively, *V* is the volume of the Cr(VI) solutions in *L*, and m_s is the weight of activated charcoal in kg.

RESULTS AND DISCUSSION

Effect of initial pH

The percentage of Cr(VI) adsorbed by activated charcoal decreased from 99.9 - 39.54% when the pH was increased from 1 - 7 (Figure 1) . The maximum percent removal of Cr(VI) was obtained between pH 1 - 3, and therefore pH 2 was selected for the rest of the experiments. Chromium exists mostly in two oxidation states which are Cr(VI) and Cr(III) and the stability of these forms is dependent on the pH of the system (Cimino et al., 2000; selomulya et al., 1999; Sharma and Forster, 1994a). It is well known that the dominant form of Cr(VI) at pH 2 is $HCrO_4^-$. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms; CrO_4^{2-} and $Cr_2O_7^{2-}$. Maximum adsorption at pH 1.0 indicates that it is the $HCrO_4^-$ form of Cr(VI), which is the predominant species between pH 1 and 4, which is adsorbed preferentially on the activated carbon.

Cr(VI) in aqueous solution can be present in different ionic forms, which are closely related to the pH of the solution. The existence of these different forms and their dependence on the pH can be described by the following reactions at 25°C (Weng et al., 2008).

$$H_2CrO_4 = HCrO^-_4 + H^+ \qquad \log\frac{(HCrO_4^-)}{(H_2CrO_4)} = -0.75 + pH \qquad (I)$$

$$HCrO^-_4 = CrO^{2-}_4 + H^+ \qquad \log\frac{(CrO_4^{2-})}{(HCrO_4^-)} = -6.45 + pH \qquad (II)$$

$$Cr_2O_7^{2-} + H_2O = 2HCrO_4 \qquad \log\frac{(HCrO_4^-)^2}{(Cr_2O_7^{2-})} = -1.68 \qquad (III)$$

$$Cr_2O_7^{2-} + H_2O = 2CrO_4^{2-} + 2H^+ \qquad \log\frac{(CrO_4^-)^2}{(Cr_2O_7^{2-})} = -14.59 + 2pH$$

(IV)

Reaction (III) is a dimerization that in a particular pH range, occurs independently of the presence of H$^+$ ions but depends on the initial concentration as can be seen in the corresponding classical Pourbaix (potential/pH) diagram (Deltombe et al., 1963).

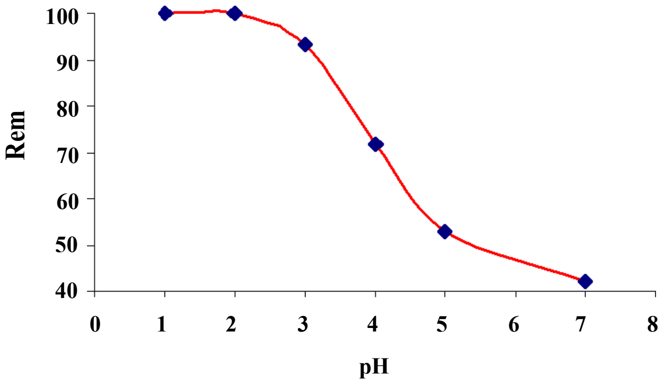

Figure 1. Effect of initial pH on the percentage of Cr(VI) adsorbed by activated charcoal (10 g l^{-1}) at a Cr(VI) concentration of 0.05 mg ml^{-1}.

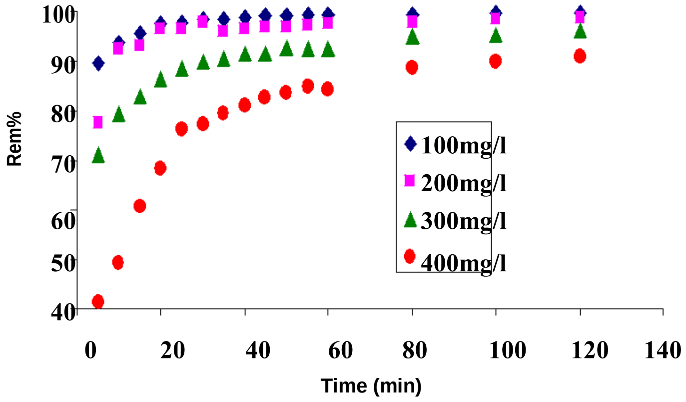

Figure 2. Effect of contact time on the percentage of Cr(VI) adsorbed by activated charcoal (10 g L^{-1}) at pH 2 for solutions with different initial Cr(VI) concentrations (0.1 - 0.4 mg ml^{-1}).

Effect of contact time

The contact time was found to be an important parameter for the adsorption of Cr(VI) on activated charcoal (Figure 2). Over the first 20 min the percent removal of Cr(VI) from the aqueous solution increased rapidly and reached 60.21 - 97.43% (for 0.4 - 0.1 mg ml^{-1} Cr(VI) solutions. After this the percent removal tapered off until at 120 min it reached 99.76% and 90.83% for solutions containing 0.1 and 0.4 mg ml^{-1} of Cr(VI), respectively. Further increase in the contact time had a negligible effect on the percent removal. Therefore, a contact time of 120 min was used for Cr(VI) adsorption on activated charcoal in all the batch studies.

Effect of initial Cr(VI) concentration

When the initial Cr(VI) concentration was varied from 0.05 - 0.5 mg ml^{-1}, the percentage of Cr(VI) removed decreased from 99.99 - 88.21% (Figure 3) . However, the absolute amount of Cr(VI) removed per unit mass of activated charcoal (or absorption capacity) significantly increased from 4.99 - 44.10 g kg^{-1} with the increase in initial Cr(VI) concentration.

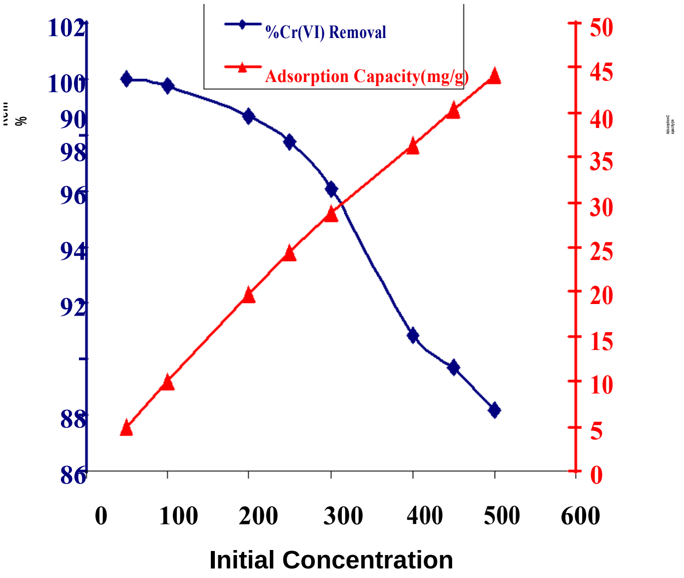

Figure 3. Effect of initial Cr(VI) concentration (0.05 - 0.5 mg ml^{-1}) on the absorption capacity an d percentage of Cr(VI) adsorbed by activated charcoal (10 g l^{-1}) at pH 2 with a contact time of 120 min.

Effect of adsorbent amount on Cr(VI) removal

When the amount of activated charcoal was increased from 2 - 24 g L^{-1}, the percentage of Cr(VI) removed increased from 56 - 99.44% (Figure 4). The amount of activated charcoal selected for subsequent experiments was 10.0 gL^{-1} as above this amount the removal of Cr(VI) remained stable.

Adsorption isotherm

The equilibrium of adsorption is an important physico-chemical parameter for evaluation of the adsorption process. The adsorption isotherm (q_e versus C_e) obtained in this study showed that the adsorption capacity (g kg^{-1}) increased with increasing equilibrium Cr(VI) concentrations and eventually attained a constant value (Figure 5).

To model the adsorption behavior, three adsorption isotherms were studied and their correlation with the experimental data was assessed. These included the Freundlich and Langmuir isotherms, which are the earliest and simplest known relationships describing the adsorption equation (Muhamad et al., 1998; Jalali et al., 2002), and the Temkin isotherm. Table 2 shows the

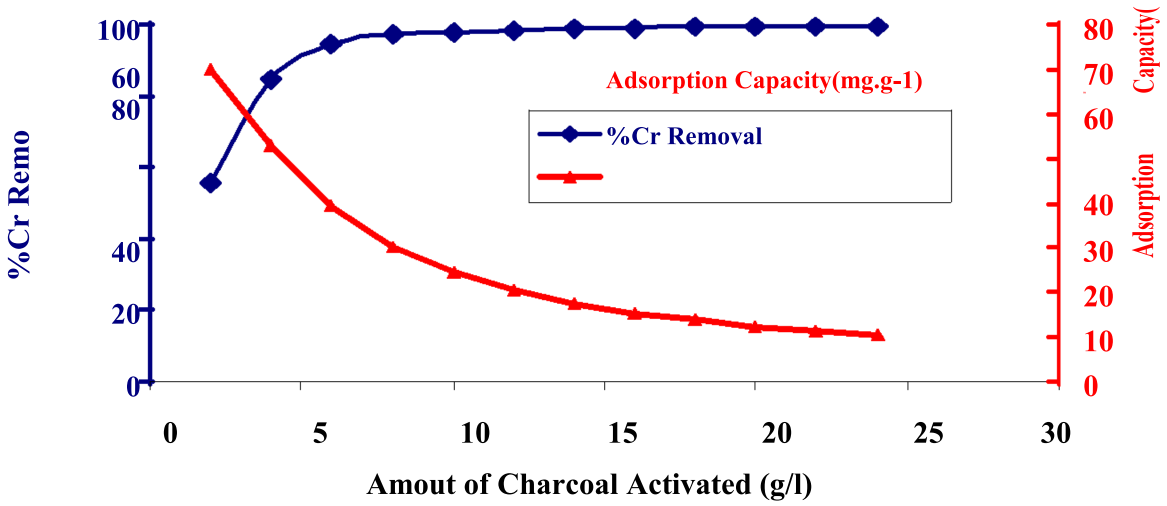

Figure 4. Effect of the amount of activated charcoal on the percentage of Cr(VI) adsorbed at an initial Cr(VI) concentration of 0.250 mg ml^{-1}, a contact time of 120 min, and pH 2.

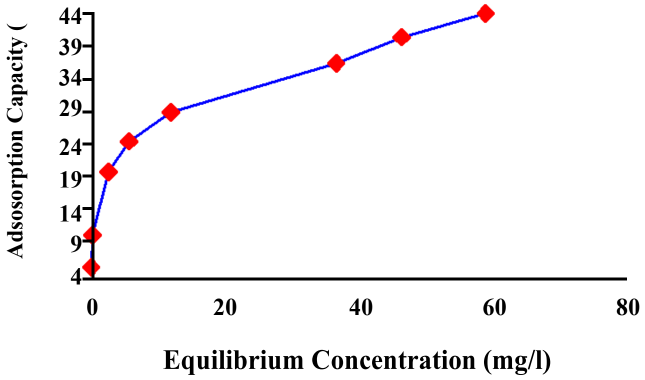

Figure 5. Adsorption isotherm obtained for Cr(VI) absorption by activated charcoal(10 g/l) at initial concentrations(0.05, 0.1, 0.2, 0.25, 0.3, 0.4, 0.45, 0.5 mg ml), pH 2 and contact time 120 min.

Table 2. Linear regression equations, coefficients of determination (R^2) and isotherm constants for the Freundlich, Langmuir and Temkin isotherm models for adsorption of Cr(VI) by activated charcoal.

Langmuir isotherm			
Linear regression equation	q_m	b	R^2
Ce = 0.0221Ce + 0.0727	45.25	0.3039	0.9800
Freundlich isotherm			
Linear regression equation	K_f	n_f	R^2
$\log q_e = 0.2259 \log C_e + 1.2139$	16,364	0.2259	0.9886
Temkin isotherm			
Linear regression equation	a_T	b_T	R^2
$q_e = 9.0917 \log Ce + 21.409$	226.35	274.48	0.8710

adsorption capacities of various adsorbents. It is clear from this table that the adsorption capacity of the commercial activated carbon used in this study far exceeded that of other activated carbons prepared from different materials.

Langmuir isotherm

The linear form of the Langmuir equation is shown in Equation (2) (Ravikumar et al., 2007; Langmuir, 1916; Bulut and Aydin, 2006):

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (2)$$

Where *b* and q_m are constants related to the apparent energy of adsorption and the adsorption capacity, respectively; and q_e is the amount adsorbed per unit mass of the adsorbent (g kg^{-1}) with an equilibrium concentration of C_e (mg ml^{-1}). A plot of (Ce/q_e) vs. *Ce* was linear (Figure 6) and the constants q_m and *b* were determined from the slope and intercept of the plot (Table 3). The correlation coefficient obtained with the Langmuir equation was high (R^2 = 0.98), which indicated a good fit between the parameters. The dimensionless parameter ($R_L = 1/1+bC_0$), which is a measure of adsorption favorability, was found to be in the range of 0.00653 - 0.06174 ($0 < R_L < 1$) and confirmed that Cr(VI) removal using activated charcoal at pH 2 and 26 ± 2°C was a favorable adsorption process.

Freundlich isotherm

The Freundlich isotherm is expressed by Equation (3)

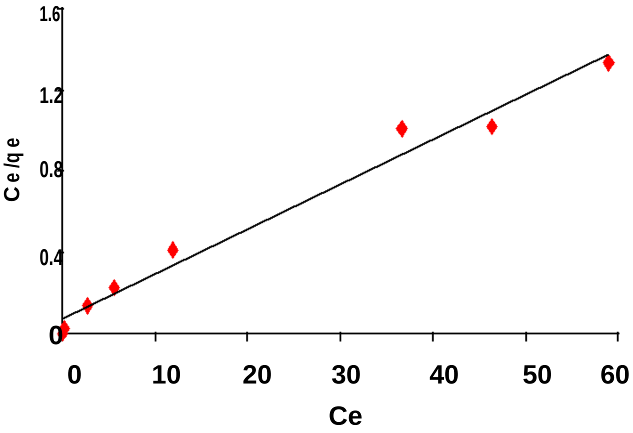

Figure 6. Langmuir isotherm for adsorption of Cr(VI) by activated charcoal (10g/l)at initial concentrations(0.05, 0.1, 0.2, 0.25, 0.3, 0.4, 0.45, 0.5 mg ml^{-1}), pH 2 and contact time 120 min.

(Freundich, 1906):

$$q_e = K_f C_e^{n_f} \qquad (3)$$

Where K_f (g$^{1-1/n}$ l$^{1/n}$ kg^{-1}) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n_f is the heterogeneity factor representing how the absorption deviates from linearity. Values of n_f less than one are an indication that significant adsorption takes place at low concentration, while high K_f values indicate greater adsorption intensity. The linear form of the Freundlich isotherm is Equation (4):

$$\log q_e = \log K_f + n_f \log C_e \qquad (4)$$

The Freundlich coefficients were determined from a plot of log q_e versus log Ce (Figure 7) and are given in Table 2. The Freundlich model clearly agreed very well with the experimental data.

Temkin isotherm

The Temkin isotherm is expressed by Equation (5) (Temkin and Pyzhev, 1940):

$$q_e = \frac{RT}{b_T} \log(a_T C_e) \qquad (5)$$

The linear form of this is Equation (6):

$$q_e = B_T \log a_T + B_T \log C_e \qquad (6)$$

where B_T = (RT)/b_T, T is the absolute temperature in Kelvin and R is the universal gas constant, 8.314 J K^{-1} mol^{-1}. The constant b_T is related to the heat of adsorption, and a_T is the equilibrium binding constant (l min^{-1}) corres-ponding to the maximum binding energy (Akkaya and Ozer, 2005). The isotherm constants a_T and b_T (Table 3) were determined from the slope and intercept of a q_e versus log C_e plot (Figure 8). The regression correlation coefficient for the Temkin isotherm model was 0.871, which indicates that the Temkin isotherm model does not fit well with the experimental data.

In summary, the regression coefficients (R^2) were 0.986 for the Freundlich isotherm, 0.980 for the Langmuir iso-therm, and 0.871 for the Temkin isotherm. The R^2 values indicate that while each isotherm has its own merits in describing the removal of Cr(VI) ions by activated char-coal, the Freundlich isotherm is the best followed by the Langmuir isotherm. The Temkin isotherm does not agree well with the adsorption process.

Adsorption kinetics

Pseudo first-order kinetics

Kinetic modeling of the removal of Cr(VI) by activated charcoal was carried out using the well known Lagergren model (ATabak et al., 2009; Hameed , 2009):

$$\log(q_e - q_t) = \log q_e - k_{ad}\, t / 2.303 \qquad (7)$$

Where q_e and q_t are the amounts of Cr(VI) adsorbed (g kg^{-1}) at equilibrium and time t, respectively, and k_{ad} (L min^{-1}) is the rate constant of the pseudo first-order adsorption operation.

A plot of log $(q_e – q_t)$ versus t (Figure 9) was linear and represents the pseudo first-order kinetics for the removal of Cr(VI) using activated charcoal. The first-order rate constants k_1 and q_e were calculated for a range of initial Cr(VI) concentrations (0.1 - 0.4 mg L^{-1}) with a constant amount of activated charcoal (10 g L^{-1}) (Table 3). The regression correlation coefficient was in the range 0.97 - 0.982, which is good and shows the applicability of the pseudo first-order kinetic model to the removal of Cr(VI) using activated charcoal. The experimental values of q_e obtained using initial Cr(VI) concentrations of 100, 200, 300, and 400 mg L^{-1} were 9.97, 19.73, 28.81, and 36.33 g kg^{-1}, respectively, which do not agree with the values predicted by the pseudo first-order model (Table 4).

Pseudo second-order kinetics

The pseudo second-order adsorption kinetic rate equation is expressed as Equation (8) (Ho et al., 2000).

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (8)$$

Table 3. Kinetic constants for pseudo first-order, pseudo second-order, and Elovich models of the Cr(VI) adsorption by activated charcoal.

Co (mg/L)	qe (g kg^{-1})	Pseudo first-order kinetics model			Pseudo second-order kinetics model			Elovich kinetic model		
	(experimental)	k_1	q_e	R^2	k_2	q_e	R^2			R^2
100	9.97	0.0199	0.77	0.9652	0.1800	10.02	1.000	6.39×10^9	2.82	0.9041
200	19.73	0.0159	2.23	0.8456	0.0451	19.88	1.000	1.43×10^5	0.81	0.7966
300	28.81	0.0155	7.06	0.9751	0.0141	29.32	0.9999	6.15×10^3	0.43	0.9569
400	36.33	0.0172	21.2	0.9815	0.0032	38.75	0.9998	20.83	0.16	0.9772

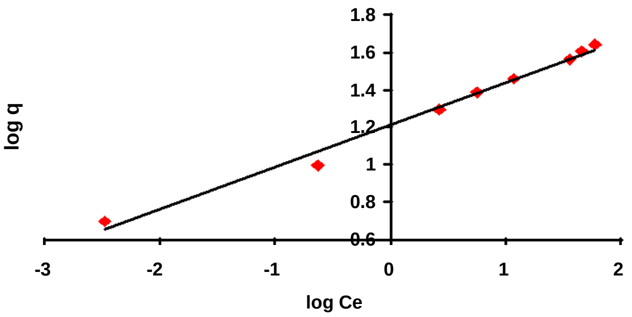

Figure 7. Freundlich isotherm for adsorption of Cr(VI) by activated charcoal(10 g/l) at initial concentrations(0.05, 0.1, 0.2, 0.25, 0.3, 0.4, 0.45, 0.5 mg ml^{-1}), pH 2 and contact time 120 min.

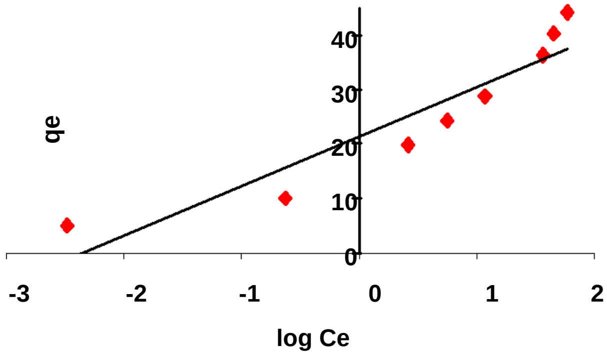

Figure 8. Temkin isotherm for Cr(VI) adsorption by activated charcoal (10g/l) at initial concentrations (0.05, 0.1, 0.2, 0.25, 0.3, 0.4, 0.45, 0.5 mg ml^{-1}), pH 2 and contact time 120 min.

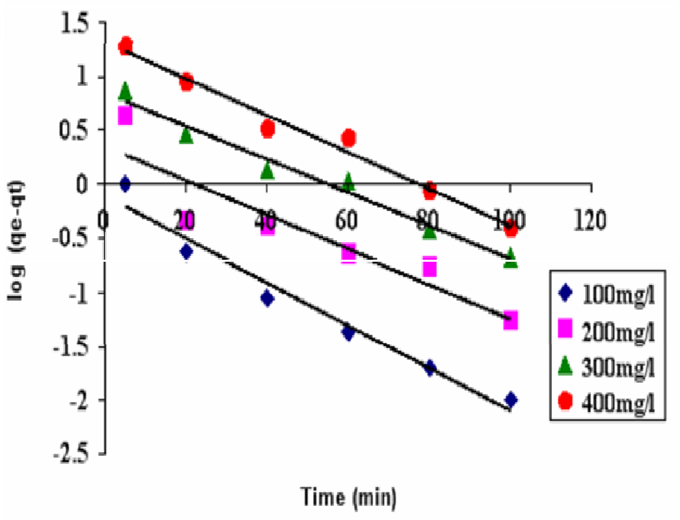

Figure 9. Lagergren's plot for kinetic modeling of the adsorption of Cr(VI) by activated charcoal(10g/l) at initial concentrations(0.1, 0.2, 0.3, 0.4 mg mL^{-1}), pH 2 .

Where k_2 is the rate constant of pseudo second-order adsorption (kg g^{-1} min^{-1}).

Equation (8) can be rearranged to obtain Equation (9), which has the linear form:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{9}$$

With h (g kg^{-1} min^{-1}), the initial adsorption rate, expressed by: Equation (10)

$$h = k_2 q_e^2 \tag{10}$$

The plot of (t/q_t) and t of Eq. (9) was linear (Figure 10), and q_e and k_2 (Table 4) were determined from the slope and intercept, respectively. Because pseudo first-order kinetics were not applicable to the adsorption of Cr(VI) on activated charcoal, the second-order kinetic model was evaluated. The calculated q_e values agreed with the experimental values, and the values obtained for the regression correlation coefficients were more than 0.9998. These results indicate that the kinetics of Cr(VI) adsorption using activated charcoal are explained better by a second-order kinetic model than a first-order one.

Elovich kinetic equation

The Elovich equation is a rate equation based on the adsorption capacity, and is commonly expressed as Equaton (11) (Chien and Clayton, 1980):

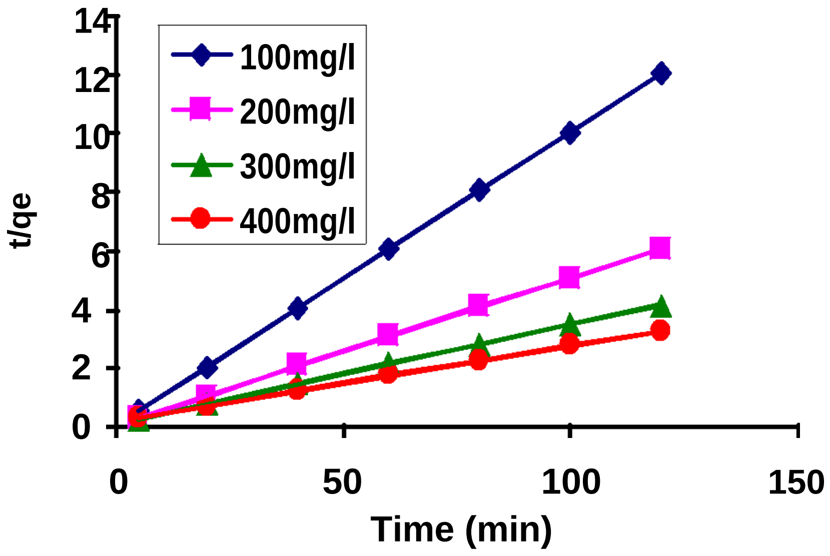

Figure 10. The pseudo second-order kinetic modeling plot of the adsorption of Cr(VI) by activated charcoal (10 g/l) at initial concentrations(0.1, 0.2, 0.3, 0.4 mg ml), pH 2.

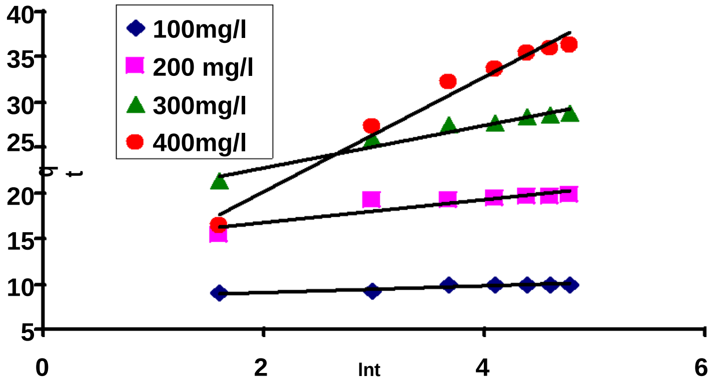

Figure 11. Elovich's plot for kinetic modeling of the adsorption of Cr(VI) by activated charcoal(10g/l) at initial concentrations (0.1, 0.2, 0.3, 0.4 mg ml^{-1}), pH 2.

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \qquad (11)$$

Where α (g kg^{-1} min^{-1}) is the initial adsorption rate and β (kg g^{-1}) is the desorption constant. Equation (11) is simplified by assuming $\alpha\beta >> t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, as given by by: Equation (12):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (12)$$

The slope and intercept of the plot of q_t versus ln t (Figure 11) were used to determine the kinetic constants α andβ, respectively, and the regression correlation coefficients were calculated (Table 4).

It is evident from Table 4. that the regression correlation coefficients for the second-order kinetic model are greater than those for the pseudo first-order and Elovich kinetic model for all initial Cr(VI) concentrations. This indicates that the second-order kinetic model can be applied to the removal of Cr(VI) using activated charcoalas an adsorbent.

Conclusion

Activated charcoal has been successfully used to remove Cr(VI) from aqueous solution. The adsorption of Cr(VI)

Table 4. Regression equations and R^2 values for the pseudo first-order, pseudo second-order, and Elovich rate equation plots for the adsorption of Cr(VI) by activated charcoal.

Co (mg/ml)	Pseudo first-order kinetics	Pseudo second-order kinetics	Elovich kinetic
0.1	Y = -0.0199X - 0.1098 R^2 = 0.9652	Y= 0.0998X + 0.0553 R^2 = 1.0000	Y= 0.3546X + 8.3739 R^2 = 0.9041
0.2	Y= -0.0159X + 0.3499 R^2 = 0.8456	Y = 0.0503X + 0.0561 R^2 = 1.0000	Y = 1.2293X +14.344 R^2 = 0.7966
0.3	Y= -0.0155X + 0.8493 R^2 = 0.9751	Y = 0.0341X + 0.0825 R^2 = 0.9999	Y = 2.3160X + 18.261 R^2 = 0.9569
0.4	Y = -0.0172X + 1.3264 R^2 = 0.9815	Y = 0.0258X + 0.2056 R^2 = 0.9998	Y =6.3064 + 7.5378 R^2 = 0.9772

was best at low pH values, and the percentage of Cr(VI) removed depended on the initial concentration, contact time and amount of activated charcoal. The Freundlich and Langmuir isotherm models agreed with the experimental data. Cr(VI) adsorption obeyed a second-order rate equation, and the rate constant was found to be 0.0032 kg g^{-1} min^{-1} with an initial Cr(VI) concentration 0.4 mg ml^{-1}.

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