Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes

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Abstract

The batch removal of Cr(VI) from aqueous solution using low-cost adsorbents such as cornelian cherry, apricot stone and almond shell under different experimental conditions was investigated in this study. The influences of initial Cr(VI) ion concentration (20 to 300 mg·L⁻¹), pH (1 to 4) and particle size (0.63 to 1.60 mm) have been reported. Adsorption of Cr(VI) is highly pH-dependent and the results indicate that the optimum pH for the removal was found to be 1 for all types of carbon. A comparison of kinetic models applied to the adsorption of Cr(VI) ions on the adsorbents was evaluated for the pseudo first-order, the pseudo second-order, Elovich and intraparticle diffusion kinetic models, respectively. Results show that the pseudo second-order kinetic model was found to correlate the experimental data well.

Keywords: adsorption; Cr(VI); adsorption kinetics; low-cost adsorbents; aqueous solution

Introduction

Hexavalent chromium is present in the effluents produced during the electroplating, leather tanning, cement, mining, dyeing and fertilizer and photography industries and causes severe environmental and public health problems. Hexavalent chromium has been reported to be toxic to animals and humans and it is known to be carcinogenic (Raji and Anirudhan, 1998). Its concentrations in industrial wastewaters range from 0.5 to 270.000 mg·L⁻¹ (Raji and Anirudhan, 1998). Its concentrations in industrial public health problems. Hexavalent chromium has been reported to and photography industries and causes severe environmental and electroplating, leather tanning, cement, mining, dyeing and fertilizer hexavalent chromium is present in the effluents produced during the

Many reports have appeared on the development of low-cost activated carbon adsorbents developed from cheaper and readily available materials (Babel et al., 2003; Bailey et al., 1999; Pollard et al., 1992). Activated carbons with their large surface area, microporous character and chemical nature of their surface have made them potential adsorbents for the removal of heavy metals from industrial wastewater.

The adsorption of Cr(VI) by a number of materials such as leaf mould (Sharma and Forster, 1994a), activated groundnut husk carbon (Srinivasan et al., 1991; Periasamy et al., 1991), coconut husk and palm pressed fibres (Tan et al., 1993), coconut shell activated carbon (Alaerts et al., 1989), coconut shell, wood and dust coal activated carbons (Selomulya et al., 1999), coconut jute carbon (Chand et al., 1994), coconut tree sawdust carbon (Selvii et al., 2001), sawdust and used tyres carbon (Hamadi et al., 2001), phosphate treated sawdust (Ajmal et al., 1996), cactus, olive stone/cake, wool, charcoal and pine needles (Dakiki et al., 2002), rice husk carbon (Low et al., 1999; Srinivasan et al., 1988), moss (Lee et al., 1995), sphagnum moss peat (Sharma and Forster, 1993), coconut fibre compost, maize cob, sugar beet pulp and cane bagasse (Sharma and Forster, 1994b), hazelnut shell carbon (Kobyas, 2004), almond shell carbon (Candela et al., 1995), corn cob (Bosinco et al., 1996), quaternized wood (Low et al., 2001), cow dung carbon (Das et al., 2000), waste slurry (Srivastava et al., 1989) and carbon slurry (Singh and Tiwari, 1997) have been reported in the literature.

In this study, three activated carbons prepared from agricultural wastes are used to remove Cr(VI) from aqueous solution. A kinetic study was carried out using pH, concentration and particle size as parameters.

Material and methods

Adsorbent

Cornelian cherry (CC), apricot stone (AS) and almond shells (ASC) were obtained from various regions of Turkey. These materials are low-value agricultural waste products. Each material was ground in a micro-hammer cutter mill (Glen Mills) and sieved to a 2.0 mm x 0.5 mm particle size prior to activation. Chemical activation using H2SO4 at moderate temperatures produces a high surface area and high degree of micro-porosity (Demirbas et al., 2002). The materials were mixed in a 1:1 wt ratio with concentrated H2SO4 and allowed to soak for 24 h at room temperature. The samples were then washed with distilled water and soaked in

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1% NaHCO₃ solution to remove any remaining acid. The samples were then washed with distilled water until pH of the activated carbon reached 6, dried at 105°C for 5 h and sieved to the particle size 0.63 to 1.60 mm. The surface area of the activated carbons was measured by BET (Brunauer-Emmett-Teller nitrogen adsorption technique). Characteristics of the carbon were presented in Table 1. The adsorbents made in this study were characterised by scanning electron microscopy (SEM, Philips XL30S-FEG) (Figs. 1(a) to(c)). Samples were gold coated prior to SEM observation. These figures showed that the three adsorbents had an irregular and porous surface, which indicated high surface areas.

**Batch adsorption studies**

Batch experiments with various activated carbons were conducted to investigate the parametric effects of initial adsorbate concentration on Cr(VI) adsorption. All reagents used were of AR grade (Sigma-Aldrich, Germany). Chromium samples were prepared by dissolving a known quantity of potassium dichromate (K₂Cr₂O₇) in double-distilled water and used as a stock solution and diluted to the required initial concentration (range: 20 to 300 mg·l⁻¹). 50 ml of Cr(VI) solution of known concentration (C₀) and initial pH was taken in a 100 ml screw-cap conical flask with a required amount of adsorbent and was agitated at a speed of 200 r·min⁻¹ in a thermostatic shaker bath at 25ºC for a specified period of contact time. Then, the solution was filtered through a 0.45 µm membrane filter. The initial pH of the solution was adjusted by using either 0.1 N NaOH or 0.1 N H₂SO₄. Perkin-Elmer UV-visible spectrophotometer (model 550S) was employed with 1,5-diphenylcarbazide in acid medium to determine the remaining concentrations of Cr(VI) in the sample. The filtrate was analysed for the remaining Cr(VI) concentration. The amount of Cr(VI) adsorbed in mg·g⁻¹ at time t was computed by using the following equation:

\[ q_t = \frac{(C_0 - C_t)V}{m_s} \]  

where:
- \( C_0 \) and \( C_t \) are the Cr(VI) concentrations in mg·l⁻¹ initially and at a given time t, respectively
- \( V \) is the volume of the Cr(VI) solutions in ml
- \( m_s \) is the weight of activated carbon in g.

The percentage of removed Cr(VI) ions (\( R_{\text{rem}} \% \)) in solution was calculated using Eq. (2):

\[ R_{\text{rem}} (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \]  

\[ \text{Table 1: The characteristics of the adsorbents} \]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CC</th>
<th>AS</th>
<th>ACS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g·ml⁻¹)</td>
<td>0.46</td>
<td>0.43</td>
<td>0.51</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>2.08</td>
<td>2.21</td>
<td>2.14</td>
</tr>
<tr>
<td>pH</td>
<td>6.20</td>
<td>6.25</td>
<td>5.80</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>6.48</td>
<td>7.18</td>
<td>7.21</td>
</tr>
<tr>
<td>Surface area (m²·g⁻¹)</td>
<td>449</td>
<td>369</td>
<td>412</td>
</tr>
<tr>
<td>Solubility in water (%)</td>
<td>0.81</td>
<td>0.85</td>
<td>0.82</td>
</tr>
<tr>
<td>Solubility in 0.25M HCl (%)</td>
<td>1.18</td>
<td>1.22</td>
<td>1.24</td>
</tr>
<tr>
<td>Decolorising power (mg·g⁻¹)</td>
<td>40.4</td>
<td>22.8</td>
<td>30.5</td>
</tr>
<tr>
<td>Iodine number (mg·g⁻¹)</td>
<td>214</td>
<td>164</td>
<td>192</td>
</tr>
</tbody>
</table>

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Adsorption dynamics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Cr(VI) adsorption on the activated carbons were analysed using pseudo first-order (Lagergren, 1898), pseudo second-order (Ho et al., 2000), Elovich (Chien and Clayton, 1980; Sparks, 1986) and intraparticle diffusion (Srivastava et al., 1989; Weber and Morris, 1963) kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients ($r^2$, values close or equal to 1). A relatively high $r^2$ value indicates that the model successfully describes the kinetics of Cr(VI) adsorption.

The pseudo first-order equation

The pseudo first-order equation (Lagergren, 1898) is generally expressed as follows:

$$ \frac{dq}{dt} = k_1 (q_e - q_t) $$

where:

- $q_t$ and $q_e$ are the adsorption capacity at equilibrium and at time $t$, respectively (mg·g⁻¹).
- $k_1$ is the rate constant of pseudo first-order adsorption (g·mg⁻¹·min⁻¹).

After integration and applying boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_e$, the integrated form of Eq. (3) becomes:

$$ \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} \cdot t $$

(4)

The values of $\log(q_e - q_t)$ were linearly correlated with $t$. The plot of $\log(q_e - q_t)$ vs. $t$ should give a linear relationship from which $k_1$ and $q_e$ can be determined from the slope and intercept of the plot, respectively.

The pseudo second-order equation

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

$$ \frac{dq}{dt} = k_2 (q_e - q_t)^2 $$

(5)

where:

- $k_2$ is the rate constant of pseudo second-order adsorption (g·mg⁻¹·min⁻¹).

For the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_e$, the integrated form of Eq. (5) becomes:

$$ \frac{1}{q_e - q_t} = \frac{t}{q_e} + k_2 t $$

(6)

which is the integrated rate law for a pseudo second-order reaction. Equation (6) can be rearranged to obtain Eq.(7), which has a linear form:

$$ \left( \frac{t}{q_e} \right) = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} $$

(7)

if the initial adsorption rate, $h$ (mg·g⁻¹·min⁻¹) is:

$$ h = k_2 q_e^2 $$

(8)

then Eqs. (7) and (8) become:

$$ \left( \frac{t}{q_e} \right) = \frac{1}{h} + \frac{1}{q_e} $$

(9)

The plot of $t/q_e$ vs. $t$ and of Eq.(7) should give a linear relationship from which $q_e$ and $k_2$ can be determined from the slope and intercept of the plot, respectively.

The Elovich equation

The Elovich model equation is generally expressed as (Chien and Clayton, 1980; Sparks, 1986):

$$ \frac{dq}{dt} = \alpha - \beta q_t $$

(10)

where:

- $\alpha$ is the initial adsorption rate (mg·g⁻¹·min⁻¹)
- $\beta$ is the desorption constant (g·mg⁻¹)

To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha t > \beta t$ and by applying the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_e$ at $t=t$ Eq.(10) becomes:

$$ q_e = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t) $$

(11)

If Cr(VI) adsorption fits the Elovich model, a plot of $q_t$ vs. $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha \beta)$.

The intraparticle diffusion model

The intraparticle diffusion model is expressed as (Weber and Morris, 1963; Srivastava et al., 1989)

$$ R = k_i d \pi^2 $$

(12)

A linearised form of the equation is followed by

$$ \log R = \log k_i + \alpha \log(t) $$

(13)

where:

- $R$ is the per cent Cr(VI) adsorbed
- $t$ is the contact time (h)
- $a$ is the gradient of linear plots
- $k_i$ is the intraparticle diffusion rate constant (h⁻¹)
- $\alpha$ depicts the adsorption mechanism
- $d$ may be taken as a rate factor, i.e., per cent Cr(VI) adsorbed per unit time.

The values of $k_i$ were calculated from the slope of such plots (plots not shown here) and the $r^2$ values led to the conclusion that the intraparticle diffusion process is the rate-limiting step. Higher values of $k_i$ illustrate an enhancement in the rate of adsorption, whereas larger $k_i$ values illustrate a better adsorption mechanism, which is related to an improved bonding between Cr(VI) ions and the adsorbent particles (Tables 2 to 4).

Results and discussion

Effect of pH

The removal of Cr(VI) by three types of carbon (CC, AS and ASC) at different pH at an initial Cr(VI) concentration of 105 mg·L⁻¹, a temperature of 25°C, particle size of 1.00 to 1.25 mm and agitation

Available on website http://www.wrc.org.za
The adsorption of Cr(VI) occurred in two stages. The first stage was solute uptake i.e. the immediate solute uptake achieved within a few hours, followed by the second stage, i.e. the subsequent uptake of solute, which continued for a long time period. For CC, the amount adsorbed increased from 4.21 to 20.98 mg·g⁻¹ as the pH decreased from 4 to 1. While for AS, the amount adsorbed increased from 11.44 to 20.98 mg·g⁻¹ as the pH decreased from 4 to 1. For ASC, the amount adsorbed increased from 14 to 19.98 mg·g⁻¹ as the pH decreased from 4 to 1. The variation in adsorption capacity in this pH range is largely due to the influence of pH on the adsorption characteristics of the carbon which indicates that the adsorption capacity of the adsorbent is clearly pH dependent. The optimum pH was observed with 99.9 % Cr(VI) removal at pH 1.0.

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 HCrO₄⁻. Increasing the pH will shift the concentration of HCrO₄⁻ to other forms, CrO₄²⁻ and Cr₂O₇²⁻. Maxi-

### Table 2

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial pH</th>
<th>Pseudo first-order</th>
<th>Pseudo second-order</th>
<th>Elovich model</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>k₁</td>
<td>r²</td>
<td>k₂</td>
<td>h</td>
</tr>
<tr>
<td>CC</td>
<td>1.0</td>
<td>0.218</td>
<td>0.989</td>
<td>0.0081</td>
<td>11.661</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.107</td>
<td>0.992</td>
<td>0.0047</td>
<td>6.408</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>0.045</td>
<td>0.948</td>
<td>0.029</td>
<td>1.577</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.181</td>
<td>0.825</td>
<td>0.034</td>
<td>1.057</td>
</tr>
<tr>
<td>AS</td>
<td>1.0</td>
<td>0.093</td>
<td>0.976</td>
<td>0.0018</td>
<td>0.952</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.093</td>
<td>0.884</td>
<td>0.0035</td>
<td>0.852</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>0.031</td>
<td>0.985</td>
<td>0.0026</td>
<td>0.813</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.051</td>
<td>0.764</td>
<td>0.0024</td>
<td>0.631</td>
</tr>
</tbody>
</table>
mum 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 adsorbents.

Results also show that the adsorption reaction can be approximated with the pseudo second-order kinetic model. The smallest value of correlation coefficient was $> 0.991$ (Table 2). The rate constants are represented in Table 2. It can be observed that $h$ is generally higher for AS than that of CC and ASC.

**Effect of initial chromium ion concentrations**

The removal of Cr(VI) by adsorption on CC, AS and ASC was shown to increase with time and attained a maximum value at 72 h, and thereafter, it remained almost constant. On changing the initial concentration of Cr(VI) solution from 20 to 300 mg·ℓ$^{-1}$, the amount adsorbed increased from 10.60 mg·g$^{-1}$ (99.99% removal) to 59.40 mg·g$^{-1}$ (99.0% removal) at 25°C, pH 1.0 and particle size of 1.25 to 1.40 mm for CC (Fig. 3(a)). While for AS, the amount adsorbed increased from 10.59 mg·g$^{-1}$ (99.90% removal) to 58.86 mg·g$^{-1}$ (98.10% removal) (Fig. 3(b)). For ASC at the same conditions, the amount adsorbed increased from 10.59 mg·g$^{-1}$ (99.99% removal) to 59.64 mg·g$^{-1}$ (99.41% removal) as the Cr(VI) concentration increased from 50 to 100 mg·ℓ$^{-1}$ (Fig. 3(c)).

It is evident from Figs. 3(a) to (c) that the amount of adsorbate on the solid phase with lower initial concentration of adsorbate was smaller than the amount when higher initial concentrations were used. AS appeared to be the least influenced by these initial concentrations and the process is slower than that for ASC. It was clear that the removal of Cr(VI) was dependent on the concentration of Cr(VI) because the decrease in the initial Cr(VI) concentration increased the amount of Cr(VI) adsorbed. The data also showed that the adsorption capacity increased for the higher Cr(VI) ion concentrations.

The experimental points shown together with the theoretically generated curves (Figs. 3(a) to (c)) reflect the extremely high correlation coefficients shown in Table 3. The data showed good compliance with the pseudo second-order kinetic model ($r^2 > 0.989$). The values of the rate constants, $k_2$, were found to increase from 48.10$^{-5}$ to 58.10$^{-3}$ (ℓ·mg$^{-1}$·min$^{-1}$) for a decrease in the initial Cr(VI) ion concentration from 300 to 20 mg·ℓ$^{-1}$.

**Effect of particle size**

The batch adsorption experiments were carried out by using various particle sizes of the adsorbent (0.63 to 1.60 mm) at pH 1, 25°C, 200 r·min$^{-1}$ and initial concentration of 105 mg·ℓ$^{-1}$. The removal of Cr(VI) ions at different particle sizes showed that the removal rate increased better with a decrease in particle diameter (plots not shown here).

The relatively higher adsorption with smaller adsorbate particle may be attributed to the fact that smaller particles yield large surface areas. There is a tendency that a smaller particle produces shorter time to equilibration. The data obtained separately for each of the kinetic models from the slopes of plots show a good compliance with the pseudo second-order equation, the $r^2$ values for the linear plots being $> 0.991$ showed that kinetic data fitted the pseudo second-order adsorption kinetic equation (Table 4).

**Conclusion**

Removal of Cr(VI) from aqueous solution was possible using several abundantly available low-cost adsorbents. ASC was the most effective, for which the removal reached 99.99% Cr(VI) at 25°C. Adsorption of Cr(VI) was highly pH-dependent and the results available on website [http://www.wrc.org.za](http://www.wrc.org.za)

showed that the optimum pH for the removal was found to be 1, at which Cr(VI) exists mostly as the most easily adsorbed form, HCrO$_4$$. Increasing the initial Cr(VI) concentration and contact time were found to increase the percentage removal of Cr(VI). The kinetics of the Cr(VI) adsorption on the different adsorbents was found to follow a pseudo second-order rate equation.

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