Preparation, adsorptive properties and chemical regeneration studies of high-porous activated carbon derived from *Platanus orientalis* leaves for Cr(VI) removal

Xiaowei Liu, Lihui Huang, Lisha Wang, Chuang Wang, Xueyuan Wu, Guihua Dong and Yangyang Liu

**ABSTRACT**

Activated carbon (AC) was prepared from *Platanus orientalis* leaves by H$_3$PO$_4$ activation using a microwave heating method and characterized by SEM (scanning electron microscopy), Brunauer–Emmett–Teller (BET) surface area analysis and FTIR (Fourier transform infrared spectroscopy) techniques. AC exhibited a surface area of 1089.67 m$^2$/g and a relatively high pore volume of 1.468 cm$^3$/g. Utilization of AC for the removal of Cr(VI) from aqueous solution was researched. The adsorption efficiency was highly pH dependent and adsorption capacity of AC for Cr(VI) could reach up to 135.24 mg/g. Adsorption equilibrium could be quickly reached within 2 h. A kinetic study indicated that the adsorption of Cr(VI) conformed to the pseudo-second-order model ($R^2 > 0.99$). An intraparticle diffusion model was applied to describe the adsorption kinetics, and the results showed that there are other factors that affect the rate. Chemical regeneration for AC saturated with Cr(VI) was performed and HNO$_3$ displayed the best regeneration performance among the four chemical regeneration agents (HNO$_3$, H$_2$SO$_4$, NaOH, NaCl). The regeneration performance increased at first and then decreased with the rise of HNO$_3$ concentration, and regeneration reaction could reach equilibrium within 4 h in the first cycle. The FTIR spectra revealed that HNO$_3$ successfully introduced N-H bonds onto the AC surface in the regeneration process.

**Key words** | activated carbon, Cr(VI), microwave heating, *Platanus orientalis* leaves, regeneration

**INTRODUCTION**

Chromium is widely used in various industries, including metallurgy, mineral, electroplating, tanning, dye and so on. Herein, large amounts of waste-water containing chromium, which is degradation-resistant, highly toxic and highly carcinogenic, is being produced annually. Both of the two forms of chromium, hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)), are oxidation states in aqueous systems (Ihsanullah *et al.* 2016), but the former is much more toxic than the latter; thus Cr(VI) has always gained more attention from researchers. Because of the high surface area, developed porosity, abundant functional groups and stable physicochemical properties of activated carbons (ACs), adsorption by ACs has been one of the most frequently used methods among the numerous technologies to remove Cr(VI) from waste-water. However, as a result, a mass of AC saturated with Cr(VI) has been abandoned, which will bring about a waste of resources and secondary pollution. Therefore, it is imperative to explore the regeneration (desorption) technologies of ACs containing high concentrations of Cr(VI).

There are mainly two mechanisms for the regeneration of spent AC: (1) destroying the interaction force between
adsorbate molecule and AC surface; and (2) destroying the porous structure of AC so as to remove the adsorbate. Traditional regeneration technologies of spent AC include thermal regeneration, chemical regeneration (Li et al. 2015), biologic regeneration (Oh et al. 2015), ultrasonic regeneration (Liu et al. 2017), etc., while microwave regeneration (Mao et al. 2015), photocatalytic regeneration (Chen et al. 2016), etc., are new-style regeneration methods. Each of the above-mentioned regeneration methods has pros and cons; thermal and chemical regeneration are the most frequently used regeneration methods. Yet there is a shortage of relevant information on chemical regeneration of Cr(VI) saturated AC in the literature.

Many kinds of low-cost waste biomass have been used as precursors for AC preparation, such as sugarcane bagasse (Kaushik et al. 2017), coconut husk (Aljeboree et al. 2017) and orange peel (Köseoglu & Akmil- Başar 2015), but the adsorption capacity of these ACs is not ideal. Platanus orientalis is widely planted in Eurasia, especially in China, as an important ornamental and economic plant. In China, Platanus orientalis spreads almost all over every city and town; thereby a tremendous quantity of Platanus orientalis dead leaves (POLs) are produced annually. However, quite a large number of the POLs are not disposed of properly, such as in the vast rural areas of China; most of them are simply burned up in winter. Herein, there is a special and practical significance to find a preferable disposal method for POLs in China. POLs consist of ample leaf vascular cylinders and developed stomata, which are beneficial for preparing efficient ACs. However, as far as we know, few works have been carried out to employ POLs to prepare AC thus far. In the present study, POLs were employed as precursor, H3PO4 as activator, and microwave heating as calcination craft to produce AC. Compared with conventional heating methods, microwave thermal treatment has the advantages of fast temperature rise, homogeneous temperature distribution and saving of energy (Yang et al. 2010). The carbon was characterized by means of scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area analysis and Fourier transform infrared spectroscopy (FTIR). Then batch adsorption experiments toward Cr(VI) were conducted and sorption isotherm and kinetics were studied. Additionally, the regeneration processes were carried out using four different types of chemical regeneration agents to explore the regeneration rates, and the best one was chosen to discuss the regeneration mechanism. Eventually, the Cr(VI) in regeneration solution was converted to barium chromate precipitate.

**MATERIALS AND METHODS**

**Reagents**

H3PO4 (85%, China), potassium dichromate (K2Cr2O7, 99.8%), H2SO4, HCl, HNO3, NaOH, NaCl, BaCl2, and 1,5-diphenylcarbazide were purchased from Shanghai Hushi Laboratorial Equipment Co., Ltd (Shanghai, China).

All the reagents were analytical grade, and all the water used in the experiment was distilled water.

**Preparation and characterization of POLs-based activated carbon**

POLs collected from Jinan city (Shandong, China) were mixed with 40 wt% H3PO4 with the optimum mass ratio of 1:3, and heated to 450 °C in a microwave oven (MKX-M1-Q, Qingdao) for 20 min. Afterwards the material was washed with distilled water repeatedly until the pH of supernatant was constant, then it was dried at 105 °C for 12 h; ultimately it was ground and sieved using standard mesh to particles with sizes between 0 and 0.15 mm. The obtained AC was characterized by BET analysis using a surface area analyzer (JW-BK122 W, China), a scanning electron microscope (SEM, Hitachi S4800, Japan) and FTIR spectroscopy (Perkin-Elmer “Spectrum BX” spectrometer).

**Adsorption experiments**

The original solution containing 1.000 g/L of Cr(VI) was prepared by dried K2Cr2O7 in a 1,000 mL volumetric flask. According to the demand, it was diluted to acquire standard solutions containing 10, 20, 30, 40 and 50 mg/L of Cr(VI), respectively. The pH of the solution was adjusted to the wide range of 2.5–8 by adding an appropriate amount of...
0.1 M HCl or 0.1 M NaOH solutions, which were measured by the Model pHS-3C (pH meter, Shanghai).

Experiments on the effect of adsorbent dosage were carried out by dropping different amounts of AC into Cr(VI) solution with a fixed concentration of 50 mg/L at pH = 2.5. The samples were shaken at room temperature (25 ± 1°C) at 150 rpm for 48 h to ensure that sorption equilibrium was reached. Duplicate samples were prepared for all sorption experiments. After equilibrium, the samples were filtered through a 0.45 μm millipore membrane filter. The ion content of Cr(VI) was determined by the UV-5100 spectrophotometer (Shanghai Metash Instruments Co., Ltd, Shanghai, China) at the wavelength of 540 nm, using 1,5-diphenylcarbazide as chromogenic reagent, and H2SO4 and H3PO4 as buffering agents.

Batch sorption experiments were performed by adding 50 mg carbon into 50 mL Cr(VI) solution to investigate the impact of initial Cr(VI) concentration and initial pH on the sorption. Adsorption kinetic experiments were performed by dispersing a known dose (0.2 g/L) of adsorbents into 1 L Cr(VI) solution with a concentration of 50 mg/L and pH of 2.5 in a glass beaker. The beaker was then agitated on a magnetic stirrer (HJ-3, Jintan Medical Instrument Corporation) at a constant speed of 150 rpm at a temperature of 25 ± 1°C. The samples were drawn out using an injector at the desired time and filtered with a 0.45 μm membrane filter for analysis, applying the same method described above.

Regeneration studies

The regeneration studies were conducted by batch experiments. Firstly, the optimum initial conditions of Cr(VI) adsorption experiments were implemented as follows: concentration of Cr(VI) solution was 50 mg/L, dosage of adsorbent was 1.0 g/L, temperature was 25°C, vapour-bathing vibrator was at a rotating speed of 150 rad/min, pH = 2.5 and sorption reaction time was 24 consecutive hours. The AC saturated with Cr(VI) (AC-Cr) was taken out by filtering the reaction solution and dried at 105°C for 12 h. Although in theory the Cr(VI) ions were probably reduced to Cr(III) ions at low pH, it has been reported that the amount of total chromium is almost the same as that of Cr(VI) under acidic conditions at low pH (Kumar et al. 2007). The results show that the existence of Cr(III) is negligible in the final solution (Gupta & Babu 2009). Therefore, the amount of Cr(III) is not considered in this research.

Four kinds of chemical regeneration agents (RAs) and two concentrations for each RA were selected to conduct the first regeneration cycle (RAs: HNO3, H2SO4, NaOH, NaCl; concentrations: 0.1 and 1.0 mol/L). AC-Cr was divided into several parts, and these parts were added into different RAs with different concentrations at a dosage of 1.0 g/L. Next the samples were shaken at a rotate speed of 150 rad/min for 8 h, then filtrated using vacuum filtration, washed with distilled water for 8–10 times and dried at 110°C for 12 h. The obtained materials were identified as AC-R, and secondary adsorption experiments were conducted for AC-R by means of the above mentioned procedure. The adsorption-regeneration-adsorption (A-R-A) processes were repeated using the RA which presented the best regeneration performance in the initial adsorption with detailed RA concentrations and regeneration times to explore the effects of RA concentration and regeneration time on regeneration efficiency. The whole experimental procedure is summarized and presented in Figure 1. Each A-R-A procedure with the best RA in the initial adsorption was continued for five cycles using 10% (w/w) HCl as eluent.

The amount of Cr(VI) absorbed at equilibrium by the ACs ($q_e$, mg/g), the removal rate of Cr(VI) and the percentage of regeneration were calculated respectively by Equations (1)–(3), as follows:

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

$$ \%\text{Removal} = \frac{100(C_0 - C_i)}{C_0} \quad (2) $$

$$ \%\text{Regeneration} = \frac{100(C_0 - C_{e2})}{(C_0 - C_{e1})} \quad (3) $$

where $C_0$, $C_i$ and $C_e$ are the initial, effluent and equilibrium concentrations (mg/L) of Cr(VI), $C_{e1}$ and $C_{e2}$ are the equilibrium concentration (mg/L) of the initial adsorption and secondary adsorption, $V$ is the volume of Cr(VI) aqueous solution (mL) and $W$ is the amount of AC (g).
RESULTS AND DISCUSSION

Characterization of AC

Figure 2 and Table 1 display the characterization results of AC, including SEM images, pore size distribution, N₂ adsorption/desorption isotherms, surface area and pore volume parameters. From the SEM images we can see that the carbon surface was extremely rugged and thickly dotted with irregular pores, indicating that porosity had been well developed during the activation process. Figure 2(a) shows that the distribution of the pores was concentrated and chiefly distributed in the narrow aperture range dimension of 0–1.5 and 2–4 nm. N₂ adsorption/desorption isotherms show a representative type II curve and a type H₄ N₂ hysteresis loop, suggesting the coexistence of micropores and mesopores. The $S_{\text{mic}}/S_{\text{BET}}, V_{\text{mic}}/V_{\text{tot}}$ values and average pore diameter were 48.2%, 31.1%, 5.442 nm, respectively, demonstrating that AC contained mostly mesopores. The surface area of AC was 1089.67 m²/g while total pore volume was 1.468 cm³/g. Compared with those ACs whose $S_{\text{BET}}$ is similar, its pore volume is quite high (Liu et al. 2012) and is beneficial for enhancing its adsorptive capacity.

Effect of adsorbent dosage on adsorption

The study of the influence of the dosage of adsorbent on Cr(VI) removal was significant enough to give rise to the most appropriate amount of AC, which was guided by an apparent trade-off between the adsorptive capacity and the removal efficiency of Cr(VI) (Gupta & Babu 2009). Figure 3(a) shows the impact of dosage of AC on the adsorption of Cr(VI) when the other adsorption conditions were as follows: concentration of Cr(VI) solution was 50 mg/L, temperature was 25 °C, vapour-bathing vibrator was at a rotating speed of 150 rad/min, pH = 2.5, and sorption reaction time was 24 consecutive hours. The percentage removal increased drastically from 31.39 to 87.94% by increasing the amount of the adsorbent from 0.2 to 1.0 g/L, while the surface adsorption ability reduced from 71.17 to 40.59 mg/g, respectively.

The increase in percentage removal of Cr(VI) with the rise in AC dosage may be due to the increase in
total surface area and pore volume, namely adding bonding of the Cr(VI) ions to AC. The corresponding mass of Cr(VI) adsorbed per unit mass of adsorbent is referred to as adsorption capacity. The amount of Cr(VI) adsorbed per unit mass of adsorbent consequentially decreased with the increased adsorbent amount on account of the lower available number of Cr(VI) ions under the constant Cr(VI) solution concentration. The unsaturated adsorption sites in the process of physiosorption were generated resulting from the increasing of the AC adsorbent dosage; therefore, adsorption capacity decreased.

Table 1 | Surface area and pore volume parameters of AC

<table>
<thead>
<tr>
<th></th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>( S_{\text{ext}} ) (m(^2)/g)</th>
<th>%</th>
<th>( S_{\text{mic}} ) (m(^2)/g)</th>
<th>%</th>
<th>( V_{\text{mic}} ) (cm(^3)/g)</th>
<th>%</th>
<th>( V_{\text{tot}} ) (cm(^3)/g)</th>
<th>( D_p ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>1089.67</td>
<td>564.62</td>
<td>51.8</td>
<td>525.05</td>
<td>48.2</td>
<td>0.456</td>
<td>31.1</td>
<td>1.468</td>
<td>5.442</td>
</tr>
</tbody>
</table>

\( S_{\text{BET}} \), BET surface area; \( S_{\text{ext}} \), external surface area; \( S_{\text{mic}} \), micropore surface area; \( V_{\text{mic}} \), micropore volume; \( V_{\text{tot}} \), total pore volume; \( D_p \), average pore diameter.
Effect of pH and initial Cr(VI) concentration on adsorption

The effect of initial pH of the solution on the adsorption process is displayed in Figure 3(b), and the experimental conditions were: pH varied from 2.5 to 8, concentration of Cr(VI) solution was 50 mg/L, temperature was 25 °C, rotating speed was 150 rad/min and sorption reaction time was 24 consecutive hours. The adsorption of metal ions from aqueous solution was influenced by one of the principal elements, which is the value of pH. As can be obviously seen from Figure 3(b), the percentage of Cr(VI) removal decreased keenly with the increased value of pH; in other words, it was strongly pH dependent. When the pH value changed from 2.5 to 8.0, the percentage of Cr(VI) removal was found to decrease from 87.94 to 3.28%, which can be explained as follows: at low pH (2.5–4.0), the dominant species of Cr(VI) in aqueous solution was HCrO$_4^-$ while the superficies of AC were highly protonated and, as a consequence, a forceful attraction existed between HCrO$_4^-$ and the surface of the adsorbent carrying positive charges. As the pH value increased in the range of 4.0–8.0, the metal uptake further decreased, which may be due to the fact that the surface of the substrate is negatively charged at higher pH. This is by virtue of one or both of the following factors. One possibility is the adsorption of hydroxyl ions on the substrate, and another possibility is that the weak acidic functional groups of the adsorbent are ionized (Giri et al. 2012). There is a repulsive force generated between the negatively charged surface and the dichromate ions (Cr$_2$O$_7^{2-}$) or chromate ions (CrO$_4^{2-}$).

The experimental conditions for the study on the effect of initial concentration of Cr(VI) were: pH = 2.5, concentrations of Cr(VI) solution were from 10 to 100 mg/L, temperature was 25 °C, rotating speed was 150 rad/min and sorption reaction time was 24 consecutive hours. The
adsorption capacity was obtained from the isotherm study which applied the Langmuir and Freundlich isothermal adsorption models, shown in Figure 3(c), and the Langmuir model was the best to represent the records with high $R^2 (>0.99)$. The fitted constants are shown in Table 2. Therefore, the uptake of Cr (VI) by AC may involve a monolayer adsorption with interactions between the adsorbed molecules. The calculated adsorption capacity was 135.24 mg/g. Table 3 displays a comparison of the maximum adsorption capacities and the preparation process of different adsorbents for Cr(VI). Compared with other adsorbents, the survey consequences of the current research manifest that the POLs-based AC has a better adsorption capacity and can be used as a preferable adsorbent for the removal of Cr(VI) from liquid waste.

Effect of contact time on adsorption and kinetics

Effect of contact time on adsorption was investigated with the conditions as follows: concentration of Cr(VI) solution was 50 mg/L, dosage of adsorbent was 0.2 g/L, pH = 2.5, temperature was 25 °C, rotating speed was 150 rad/min, and the results are shown in Figure 4. As can be seen from the figure, the concentration of Cr(VI) reduced rapidly in the first 20 min, then the reduced rate slowed down gradually, and the concentration became near constant after 100 min. Eventually, equilibrium was achieved in 2 h. The mechanism of Cr(VI) shifting to the adsorbent included two stages: diffusing through the fluid membrane around the AC particles and diffusing through the pore structure to the interior active sites. In the first step, the gradient concentration for Cr(VI) ions between the available surface active sites and the fluid film was large, so the transfer of Cr(VI) was faster. The removal rate of Cr(VI) decreased in the later stage because the intraparticle diffusion became dominant, and this may be due to the slow pore diffusing of Cr(VI) into the bulk of the adsorbent. Herein, Cr(VI) particles took more time to move from the surface of the solid to the interior adsorption sites through the pores.

For the purpose of studying the adsorption dynamics mechanism of Cr(VI) ions on AC, three dynamical models, pseudo-first order kinetic model, pseudo-second order kinetic model and intraparticle diffusion model, were applied in this study. Figure 5 displays the equation fitting diagrams of the above three models. The kinetic parameters of those three models for Cr(VI) adsorption on the surface of AC were counted and are summarized in Table 4. The gained coefficients of correlation ($R^2$) imply that the experimental data is more consistent with the pseudo-second order dynamics model, in which $R^2$ can reach up to 0.9987. Moreover, the calculated adsorption amount $q_{e,cal}$ (mg/g) fits well with experimental $q_{e,exp}$. These results imply that the process of adsorption was

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_{max}$ (mg/g)</th>
<th>Temperature (°C)</th>
<th>Heating time</th>
<th>Optimum pH</th>
<th>Agent</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugarcane bagasse carbon</td>
<td>103</td>
<td>180</td>
<td>2 h</td>
<td>3.0</td>
<td>DMDHEU and choline chloride</td>
<td>Wartelle &amp; Marshall (2005)</td>
</tr>
<tr>
<td>Sawdust activated carbon</td>
<td>65.8</td>
<td>364</td>
<td>1 h</td>
<td>2.0</td>
<td>H₃PO₄</td>
<td>Karthikeyan et al. (2005)</td>
</tr>
<tr>
<td>Rice husk carbon</td>
<td>48.31</td>
<td>150</td>
<td>24 h</td>
<td>2.0</td>
<td>H₂SO₄</td>
<td>Bansal et al. (2009)</td>
</tr>
<tr>
<td>Activated tamarind seeds</td>
<td>29.7</td>
<td>150</td>
<td>24 h</td>
<td>2.0</td>
<td>H₂SO₄</td>
<td>Gupta &amp; Babu (2009)</td>
</tr>
<tr>
<td>Ficus carica fibre AC</td>
<td>44.84</td>
<td>700</td>
<td>5 min</td>
<td>3.0</td>
<td>H₃PO₄</td>
<td>Gupta et al. (2015)</td>
</tr>
<tr>
<td>Corn cob AC/magnetite</td>
<td>57.37</td>
<td>500</td>
<td>2 h</td>
<td>2.0</td>
<td>FeSO₄</td>
<td>Nethaji et al. (2013)</td>
</tr>
<tr>
<td>Acrylonitrile-divinylbenzene</td>
<td>80</td>
<td>850</td>
<td>–</td>
<td>2.0</td>
<td>Air</td>
<td>Duranoglu et al. (2012)</td>
</tr>
<tr>
<td>AC</td>
<td>135.24</td>
<td>450 °C</td>
<td>20 min</td>
<td>2.5</td>
<td>H₃PO₄</td>
<td>This study</td>
</tr>
</tbody>
</table>

Table 3 | Maximum adsorption capacities and the preparation process of different carbon adsorbents for Cr(VI)
affected and controlled by chemisorption (Hameed 2009) and electrostatic interactions (Huang et al. 2011).

For the purpose of carrying out further research on the mechanisms and adsorption rate controlling steps influencing the kinetics, the model of intraparticle diffusing was used in this study about the steps of rate controlling. Figure 5(c) shows that the data of adsorption presents multi-linear plots with two steps. The first portion of the curve does not pass through the original point, which illustrates that the speed is not only controlled by particle internal diffusion but also by other different mechanisms such as boundary layer diffusion.

As can be seen from the intraparticle diffusion plot, the first linear part of the curve implies that Cr(VI) adsorption is controlled by external film resistance or external mass transfer. For the second section of the curve, intraparticle diffusing was limited by rate, and eventually the state of equilibrium was approached. The intraparticle diffusion rate began to decrease as a result of the following points: (a) the Cr(VI) concentration was decreasing; (b) the pore diameter for diffusion was smaller; (c) the electrostatic repulsion on the surface of AC was intensified (Liu et al. 2011).

The $k_{int}$ and $C_{int}$ values can reveal the rate of the adsorption process and the boundary layer thickness. The $k_{int}$ value severely decreased and the $C_{int}$ value increased as time passed in the process of adsorption. Taking the effect of time into consideration, it was put forward that intraparticle diffusion plays a critical part in the process of adsorption (Liu et al. 2011).

Regeneration studies

For the sake of a sustainable adsorption process, the adsorbents should have the potential of superb desorption and reusability. Regeneration studies help to determine the
adsorption mechanism and to evaluate the feasibility of reusing the spent AC (Liu et al. 2010).

Regeneration performances of four kinds of RAs

HNO₃, H₂SO₄, NaOH and NaCl were selected to perform the first round of the A-R-A procedure. The regeneration performances of the four chemical RAs are illustrated in Figure 6(a).

From the results displayed in Figure 6(a), NaOH and NaCl were not suitable for the regeneration of AC-Cr due to their poor regeneration performances. Meanwhile, H₂SO₄ and HNO₃ exhibited relatively high percentages of regeneration but the latter was better; therefore, acidic RAs were adaptive for the regeneration of ACs saturated with chrome. Herein HNO₃ was chosen to conduct the A-R-A procedure again to explore the optimum regeneration conditions and mechanism.

Regeneration of AC-Cr by HNO₃ and regeneration mechanism

Figure 6(b) and 6(c) demonstrate the influence of HNO₃ concentration and regeneration time on the percentage of regeneration. The regeneration performance for AC-Cr increased at the initial stage and then decreased with the rise of HNO₃ concentration; the culminating point appears at the 20% concentration with a 55.42% regeneration. This phenomenon may be explained as follows: the regeneration effect of HNO₃ for AC-Cr can be assigned to three aspects: (a) a number of new functional groups (such as N-H bond, see below under FTIR analysis of AC, AC-Cr, AC-R, AC-R-Cr and adsorption mechanism) were introduced onto the surface of AC by molecules of HNO₃, which accordingly increased the surface activation sites; (b) due to the strong oxidizing property and acidity of HNO₃, it can corrode and drill plenty of new pores and holes inside the carbon; (c) HNO₃ reacts chemically with Cr(VI), which was adsorbed onto the AC surface, promoting the desorption process. When the concentration of HNO₃ increased from 0 to 20%, the above mentioned three aspects all resulted in positive roles, but with the rise of the concentration, excessive HNO₃ was added into the system, the (a) and (c) effects tended to approach an equilibrium state and no longer increased, the (b) effect took advantage, the porosity of AC was overly corroded and partly destroyed, and therefore the regeneration performance accordingly degraded. It can be clearly seen from Figure 6(c) that the regeneration reaction mainly arose in the first 1.5 h and could reach equilibrium within 4 h. The %regeneration-regeneration time curve can provide information on the optimum regeneration time, which was 4 h in the present case.

However, in general, the regeneration rate was not ideal, with a maximum value of 55.42%; these findings imply that the mechanism of Cr(VI) adsorption onto AC is predominantly chemisorption, and the Cr(VI) ions may have formed strong bonds with the adsorbent surface, which was in keeping with the results of the aforementioned kinetic study.

In addition, the major problem of the regeneration process is the disposition of the regeneration solution acquired, which contains Cr(VI) in high concentration. Gupta & Babu (2009) suggested a method to address this issue which uses barium chloride to produce one precipitation of Cr(VI) from the aqueous solution. The bright yellow barium chromate precipitate was generated by adding a barium chloride solution to the Cr(VI) solution, which can be reused by the industries.

Table 4 | Kinetic parameters of pseudo-first order model, pseudo-second order model and intraparticle diffusion model for the removal of Cr(VI) by AC

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Parameters</th>
<th>Values</th>
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<tbody>
<tr>
<td>Pseudo-first order model</td>
<td>qₑₑₑₑ (mg/g)</td>
<td>79.65</td>
</tr>
<tr>
<td></td>
<td>qₑₑₑₑ (mg/g)</td>
<td>56.70</td>
</tr>
<tr>
<td></td>
<td>k₁ (mg/g min)</td>
<td>0.06130</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.9258</td>
</tr>
<tr>
<td>Pseudo-second order model</td>
<td>qₑₑₑₑ (mg/g)</td>
<td>79.65</td>
</tr>
<tr>
<td></td>
<td>qₑₑₑₑ (mg/g)</td>
<td>81.96</td>
</tr>
<tr>
<td></td>
<td>k₂ × 10⁻³ (mg/g min)</td>
<td>2.300</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.9987</td>
</tr>
<tr>
<td>Intraparticle diffusion model</td>
<td>K₁₁</td>
<td>6.0022</td>
</tr>
<tr>
<td></td>
<td>C₁₁</td>
<td>31.88</td>
</tr>
<tr>
<td></td>
<td>R₁</td>
<td>0.9821</td>
</tr>
<tr>
<td></td>
<td>K₁₂</td>
<td>0.1380</td>
</tr>
<tr>
<td></td>
<td>C₁₂</td>
<td>77.65</td>
</tr>
<tr>
<td></td>
<td>R₁</td>
<td>0.4681</td>
</tr>
</tbody>
</table>

k₁ (1/h) and k₂ (g/(mg h)) are the rate constants of pseudo-first order and pseudo-second order model, respectively; K₁₁ (mg(g h⁻¹/²)/C₀) and K₁₂ are the intraparticle diffusion rate constants of the first and second stage in intraparticle diffusion model, C₁₁ and C₁₂ are the slopes of the first and second stage in intraparticle diffusion model.
FTIR analysis of AC, AC-Cr, AC-R, AC-R-Cr and adsorption mechanism

The FTIR spectra (400–4,000 cm\(^{-1}\)) of ACs are shown in Figure 7. The broad bands at around 3,416, 1,619, 1,181 and 492 cm\(^{-1}\) are the results of the stretching vibration of \(\text{–OH, } C = \text{C or C = O, C–C or C–O and S–S functionalities, respectively. Noteworthily, the peak was located at 2,922 cm\(^{-1}\), which is attributed to the N-H bond on the AC-Cr sample’s spectrum being larger than that of other samples, suggesting that HNO\(_3\) successfully introduced the N-H bond onto the AC surface in the regeneration process.}

![Figure 6](image1.png)  
**Figure 6** | (a) Regeneration performances of HNO\(_3\), 1/2H\(_2\)SO\(_4\), NaOH and NaCl after one regeneration cycle, (b) influence of concentration of HNO\(_3\) on the percentage of regeneration with five regeneration cycles and (c) influence of regeneration time on the percentage of regeneration after one regeneration cycle.

![Figure 7](image2.png)  
**Figure 7** | FTIR spectra of AC, AC-Cr, AC-R and AC-R-Cr.
The obtained FTIR spectra (400–4,000 cm\(^{-1}\)) of ACs also reveal that the species of functional groups of AC did not change obviously during the A-R-A process, but the quantities of most groups reduced markedly after initial adsorption, indicating that the disappeared functional groups were occupied by Cr(VI) and chemisorption.

Figure 8 | Graphical representation of the adsorption and regeneration mechanism.
occurred, which corresponds with the results of the kinetic study; see above under Effect of contact time on adsorption and kinetics. The dominant species of Cr(VI) in the aqueous solution is HCrO$_4$ at low pH. There are three stages in the mechanism of the adsorption: the absorption and loading of chromate on the AC surface, the Cr reduced from Cr(VI) to Cr(III), and the ionic exchange of Cr(III) with oxygen functional groups which are original or newly formed on the AC surface, just as shown below (Huang et al. 2014):

HCrO$_4$ + 7H$^+$ + 5e$^-$ ↔ Cr$^{3+}$ + 4H$_2$O  
(4)

CrO$_4^{2-}$ + 8H$^+$ + 3e$^-$ ↔ Cr$^{3+}$ + 4H$_2$O  
(5)

Sur − C − e$^-$ ↔ Sur − CO$_3$H  
(6)

Cr$^{3+}$ + H$_2$O + Sur − CO$_3$H ↔ (Sur − CO$_3$H − [Cr(OH)]$^{2+}$) + 2H$^+$  
(7)

in which Sur-C stands for the C bond on the surface of AC, and Sur-CO$_3$H is characteristic of the newly formed oxygenic functional groups. To further understand the process as well as to realize the characteristics of the material which contribute to designing a new adsorbent for future applications, the mechanism of any adsorption process is a significant constituent part (Giri et al. 2012). A brief graphical representation of the adsorption and regeneration mechanism is shown in Figure 8.

**CONCLUSIONS**

In this study, AC was prepared from Platanus orientalis leaves by H$_3$PO$_4$ activation using a microwave heating method; this carbon exhibited a surface area of 1089.67 m$^2$/g and a relatively high pore volume of 1.468 cm$^3$/g. Utilization of this carbon for the Cr(VI) ions removal from aqueous solution is surveyed in the current research. It was discovered that the adsorption was strongly pH dependent and equilibrium could be reached in 2 h. The maximum adsorption of Cr(VI) calculated from the isotherm study can reach the relatively high value of 135.24 mg/g. In the kinetic study, it is found that the adsorption of Cr(VI) obeyed the pseudo-second order model ($R^2 > 0.99$), which implies that chemisorption had control of the adsorption process. The intraparticle diffusion model was applied to inquire into the adsorption rate controlling step, and the results show that intraparticle diffusion is not the only rate controlling procedure. HNO$_3$ displayed the best regeneration performance of the four chemical RAs; the regeneration performance increased at first and then decreased with the rise of HNO$_3$ concentration, and regeneration reaction can reach equilibrium within 4 h. The FTIR spectra reveal that HNO$_3$ successfully introduced an N-H bond onto the AC surface in the regeneration process.

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**COMPLIANCE WITH ETHICAL STANDARDS**

The authors declare that they have no conflict of interest.

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