Preparation of activated carbon from corn cob and its adsorption behavior on Cr(VI) removal
Shuxiong Tang, Yao Chen, Ruzhen Xie, Wenju Jiang and Yanxin Jiang

ABSTRACT

Operation experiments were conducted to optimize the preparation of activated carbons from corn cob. The Cr(VI) adsorption capacity of the produced activated carbons was also evaluated. The impact of the adsorbent dosage, contact time, initial solution pH and temperature was studied. The results showed that the produced corn cob activated carbon had a good Cr(VI) adsorptive capacity; the theoretical maximum adsorption was 34.48 mg g\(^{-1}\) at 298 K. The Brunauer–Emmett–Teller and iodine adsorption value of the produced activated carbon could be 924.9 m\(^2\) g\(^{-1}\) and 1,188 mg g\(^{-1}\), respectively. Under the initial Cr(VI) concentration of 10 mg L\(^{-1}\) and the original solution pH of 5.8, an adsorption equilibrium was reached after 4 h, and Cr(VI) removal rate was from 78.9 to 100% with an adsorbent’s dosage increased from 0.5 to 0.7 g L\(^{-1}\). The kinetics and equilibrium data agreed well with the pseudo-second-order kinetics model and the Langmuir isotherm model. The equilibrium adsorption capacity improved with the increment of the temperature.

Key words | activated carbon, adsorption, chromium (VI), corn cob, isotherms, kinetics modeling

INTRODUCTION

Chromium exists in both trivalent and hexavalent forms in an aqueous environment. Cr(VI) is very dangerous due to its toxicity and non-biodegradation. Cr(VI) has been proved to be a primary contaminant to humans, animals, and microorganisms, which will accumulate in living organisms, causing various diseases and disorders, and now it is a well-known carcinogen and mutagen. Chromium is widely used in a variety of industries, such as electroplating, printing, dying and finishing, tanning, and mining (Bhattacharya et al. 2008). A large quantity of chromium is discharged into our environment. Therefore, chromium in aqueous effluents must be controlled by appropriate methods. Treatment processes for those heavy metal-contaminated wastewaters include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation, etc. Adsorption by activated carbon is by far the most common and effective method for wastewater contaminants removal.

In past decades, several raw materials have been utilized to get the low-cost absorbents to remove the Cr(VI) ion in wastewaters and many investigations have been undertaken in this field. Hai Liu et al. (Liu et al. 2014) studied the Cr(VI) removal from aqueous solution by activated carbon prepared from Zizania caduciflora with tartaric acid modification. The results indicated that the Cr(VI) removal by this specific activated carbon was fully attributed to its high surface amount of oxygen-containing functional groups. Weifeng Liu et al. (Liu et al. 2010) made the Trapa natans husk into activated carbon to remove Cr(VI) from aqueous solutions. The maximum theoretic adsorption capacity was 11.83 mg g\(^{-1}\) at room temperature, calculated by the Langmuir equation. Furthermore, from industrial wastes to agriculture byproducts or biological materials, i.e. bagasse and wood charcoal (Mukherjee et al. 2007), coffee grounds (Namane et al. 2005), coconut shell (Radhika & Palanivelu 2006), bamboo (Cheung et al. 2012), Eichhornia crassipes root (Giri et al. 2012), peanut shell (AL-Othman et al. 2012), Lemna minor (Huang et al. 2014), wood apple shell (Doke & Khan 2012), bael fruit (Gottipati & Mishra 2010), leaves of vetiver grass (Le et al. 2015) and Terminalia arjuna nuts (Mohanty et al. 2005), etc., all can be used to prepare the low-cost activated carbon for Cr(VI) removal.

Corn cob, residual of corn production, is a typical agricultural waste and abundant in the southwest of China. The huge amount of corn cob residue is usually discarded or burned without any beneficial use. The utilization of this new
biomass-based activated carbon can avoid the secondary pollution caused by the corn cob disposal and also obtain a kind of low-cost adsorbent. In the past few years, several studies have been carried out using corn cob to get activated carbon and some applications are reported about this biomass precursor. Bagheri and Abedi (Bagheri & Abedi 2011) got an activated carbon prepared from corn cob for methane adsorption, using potassium hydroxide (KOH) as the chemical activating agent. It has been proved that corn cob is an excellent starting material to produce nano-porous carbon. Min Song’s research (Song et al. 2015) indicated that the chemical activation could produce good performance adsorbent with larger Brunauer–Emmett–Teller (BET) surface areas and bigger microporous structures than the steam physical activation under optimum conditions. Although previous studies have proven the feasibility of corn cob to be an effective precursor in activated carbon production, the information of Cr(VI) removal by this new biomass-based activated carbon is limited. Its adsorption behavior, operation, kinetics and thermodynamics on Cr(VI) removal still need further investigation. Thus, in the present study, corn cob-based activated carbon was synthesized using a chemical activation agent, ZnCl2, and provided an accessible work to remove Cr(VI) ion from aqueous solution by employing this new biomass-based adsorbent. In addition, kinetics and equilibrium studies of the Cr(VI) adsorption process were performed. The impacts of pH, contact time, and adsorbent dosage on Cr(VI) removal from aqueous solutions were also investigated.

**METHODS**

**Materials and equipments**

The corn cob used as the raw material to prepare the activated carbon was collected from Leshan city, which is located in south central Sichuan province. All the chemicals used in our experiments were analytical grade.

The equipments used are as follows: tubular furnace (KXG-2-13A, Shanghai, China), atomic absorption spectrometer (AAS, SpectraAA220FS, USA), thermostirker (HY-5), laboratory pH meter (PHS-3C), and KQ-100E-type ultrasonic cleaner.

**Analytical methods**

The morphologies of the produced activated carbons are obtained by JSM-5900LV scanning electron microscopy (SEM, Japan). BET surface areas are measured by Micromeritics (SSA-4200, China) using nitrogen adsorption at 77 K. The iodine number method of China National Standards (GB/T12496.8-1999) is applied to characterize the adsorption capacity of the produced carbon. X-ray photo-electronic spectroscopy (XPS) analysis is performed on XSAM800 spectrometer (KRATOS, UK). A Fourier transform infrared spectrometer (FTIR 6700 NEXUS Nicolet, USA) is used for qualitative estimation of the surface functional groups. The spectra are recorded from 4,000 to 400 cm \(^{-1}\) using KBr window.

**Preparation of activated carbon**

Similar to our previous research (Chen et al. 2011; Xie et al. 2015), the dried corn cob was crushed and passed through a 60-mesh sieve for further use. The sample was impregnated with ZnCl2 and NH4Cl solution mixture (activating agent) in a sonic oscillation (50 kHz) for a certain time and then dried in the oven. The precursor was then put into a quartz crucible, heated in the tubular furnace at a constant heating rate of 10 C min \(^{-1}\) to the carbonization temperature in N2 atmosphere. After adequate carbonization and pyrolysis time, the activated product was cooled down to room temperature under N2 flow. The product was then washed several times with HCl (3M) and hot deionized water to remove any residual chemicals, dried in a vacuum oven and stored in the desiccators for further use.

Orthogonal array testing with three levels and seven factors, L21(37), was designed in this study to determine the optimum conditions for preparation of corn cob activated carbons. (The orthogonal array is omitted here.)

**Adsorption experiments**

Stock solution of Cr(VI) was prepared by dissolving Cr(NO3)6 in deionized water. Adsorption experiments with the produced activated carbons were performed by batch tests to learn the effects of contact time, pH, adsorbent dosage on Cr(VI) removal from aqueous solutions. The batch experiments were carried out in a series of 150-mL Erlenmeyer flasks with magnetic stirring (180 rpm) and maintained at the designed temperature in a thermostatic bath. The samples were collected, filtered and analyzed for the Cr(VI) concentration by AAS after different reaction times.
The amount of adsorption capacity at time $t$, $q_t$, and removal rate of Cr(VI), $\varphi$ (%) was obtained as follows:

$$q_t = \frac{C_0 - C_t}{V}$$

$$\varphi(\%) = \frac{C_0 - C_t}{C_0} \times 100$$

where $C_0$ (mg L$^{-1}$) and $C_t$ (mg L$^{-1}$) are the liquid-phase concentrations of solutes at initial and time $t$, respectively, $V$ is the volume of the Cr(VI) ion solution, and $w$ is the mass of the activated carbon (g).

**RESULTS AND DISCUSSION**

**Preparation of corn cob activated carbon**

According to the results of our orthogonal array tests, among those seven factors: activating time, activating agent ZnCl$_2$ and the impregnated ratio of raw material to activating agent had the most significant impact on the preparation of this new biomass-based activated carbon. Thus, the optimal preparation of corn cob activated carbon from the orthogonal tests was to impregnate the raw materials with activating agent (volume ratio of ZnCl$_2$ to NH$_4$Cl is 3:1) in a solid-to-liquid ratio of 1:2 (g:mL), and then after 20 min sonic oscillation, pyrolysis under 450°C for 50 min to get the finished one.

The produced corn cob activated carbon had a remarkable BET surface area of 924.9 m$^2$ g$^{-1}$ and a total nitrogen adsorption volume of 0.55 cm$^3$ g$^{-1}$, including 0.21 cm$^3$ g$^{-1}$ micropore volume and 0.34 cm$^3$ g$^{-1}$ mesopore volume based on nitrogen adsorption/desorption isotherms. The average pore diameter was 1.17 nm. Also, its iodine adsorption value was high, up to 1,188.5 mg g$^{-1}$, and methylene blue adsorption value was 369.69 mg g$^{-1}$.

**Characterization of activated carbon**

Figure 1 shows the SEM micrograph of the raw material and the produced activated carbon. As shown in Figure 1, pores of different sizes and shapes could be observed on the adsorbent’s surface. After carbonization and activation processes, the corn cob-based adsorbent’s surface exhibits a relatively uneven and rough surface morphology compared to the raw material.

XPS has been demonstrated to be a useful tool for analyzing the surface groups of activated carbons. It was used to

<table>
<thead>
<tr>
<th>Author</th>
<th>Preparation methods</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Iodine number (mg g$^{-1}$)</th>
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<td>Cao, Q.</td>
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<td>2,720</td>
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<td>1,262.25</td>
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<td>–</td>
<td>Tsai et al. (1998)</td>
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<td>980</td>
<td>665.23</td>
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<tr>
<td>This study</td>
<td>Chemical, ZnCl$_2$</td>
<td>924.9</td>
<td>1,188.5</td>
<td>This study</td>
</tr>
<tr>
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<td>630</td>
<td>–</td>
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<tr>
<td>Milenković, D. D.</td>
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<td>431</td>
<td>456</td>
<td>Milenković et al. (2013)</td>
</tr>
<tr>
<td>Nethaji, S.</td>
<td>Physical, CO$_2$</td>
<td>143</td>
<td>–</td>
<td>Nethaji et al. (2015)</td>
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</table>
study the elemental information of activated carbon and semi-quantitative analysis of functional groups. As shown in Figure 2(a) (the XPS wide-scan spectra), distinct peaks of carbon, oxygen, and nitrogen were observed with contents of 85.0%, 12.3%, and 2.7%, respectively, while the other elements with weak peaks could be ignored.

The main functional groups were characterized using high-resolution XPS spectra of C1 s. The chemical nature of those functional groups presented on the adsorbent surface is vitally important in understanding the adsorption process and the capacity of the adsorbent (Fan et al. 2011). The abundant oxygen-containing functional groups on the surfaces of adsorbents can provide numerous chemical adsorption sites and thus increased the ion-exchange capacities towards heavy metal cations such as Cr(VI). As shown in Figure 2(b), deconvolution of the C1 s spectra displayed four peaks: the carbon skeleton (C–C, 284.8 ± 1 eV), ether (C–OH, C–O–C, 286 ± 1 eV), carbonyl (C=O, 287.6 eV), carboxylate (–COOH, 289.7 eV). Their peak areas are calculated in Table 2. As shown in Table 2, the carbon-containing functional groups were produced on the activated carbon, and the functional groups’ contents were sorted as: C–C > C–OH > C=O > COO.

Infrared spectroscopy was used to record the chemical changes occurring on the surface of the adsorbent. The FTIR spectra of the raw material corn cob and the produced activated carbon are shown in Figure 3(a) and 3(b), respectively. The most distinct changes were the disappearance of wavelength bands at 2,919 cm⁻¹ and 1,042 cm⁻¹, also the band at the 3,410 cm⁻¹ became narrow in Figure 3(a). The band observed at 2,919 cm⁻¹ represented the C–H stretching vibration of aliphatic –CH₃ groups in the cellulose and

| Table 2 | Summarization of peak numbers and areas of corn cob-based activated carbon |
| Sample | Carbon-containing functional groups | C-C | C-OH/ C-O-C | C=O | COO |
| Corn cob-based AC | Peak (eV) | 284.54 | 285.33 | 286.56 | 288.89 |
| | Peak area (CPS) | 2,798.26 | 2,157.47 | 1,097.24 | 673.08 |
hemicellulose, and the one at 1,042 cm\(^{-1}\) reflected the stretching vibration of C—O groups in the cellulose. The disappearance of these bands indicated that cellulose and hemicellulose of the raw material were mostly decomposed during carbonization and activation. The intense bands in Figure 3(b) observed at 1,064 cm\(^{-1}\) could be assigned to stretching vibration of C—O groups. C—O groups on the produced activated carbon increased obviously compared with the raw materials, thus could provide numerous chemical adsorption sites for heavy metal ions. The peak at 2,362 cm\(^{-1}\) and 883 cm\(^{-1}\) could be assigned to CO\(_2\) on the activated carbon, and the stretching vibration of Si—O—Si, respectively.

In conclusion, the changes during carbonization and activation could result in abundant functional groups (C—OH, C—H, C=O). The observation of FTIR fitted well with XPS analysis.

**Adsorption studies**

Various amounts of the corn cob-based activated carbons from 0.2 to 2.0 g L\(^{-1}\) were added in a series of 50-mL Cr(VI) solution (10 mg L\(^{-1}\)) to study the effect of adsorbent dosage. The original pH kept ca. 5.8. After 12 h agitating (180 rpm) at room temperature, the supernatant was filtered and analyzed by AAS to determine the Cr(VI) concentration. As shown in Figure 4(a), the removal rate of Cr(VI) was increased with the increment of adsorbent dosage. This can be due to the increase of adsorbent surface area and the availability of more adsorption sites. An adsorbent dosage of 0.7 g L\(^{-1}\) was enough to achieve 100% removal rate of Cr(VI) from the aqueous solution, while the removal rate was only 78.9% with 0.5 g L\(^{-1}\) adsorbent dosage.

To investigate the effect of contact time, 25 mg carbon was mixed with 50 mL 10 mg L\(^{-1}\) Cr(VI) solution. The samples were collected and analyzed for Cr(VI) ion removals at different time intervals. Figure 4(b) shows the effect of contact time on adsorption of Cr(VI). The removal rate of Cr(VI) increased rapidly in the first 2 h, and gradually increased from 2 to 4 h, then slightly changed after 4 h reaction. It takes a relatively long contact time to reach equilibrium (4 h).

The pH of the aqueous solution is an important factor in adsorption studies because it affects both the surface functional groups presented on the adsorbent and the metal ions’ form in solution. Figure 4(c) shows the influence of pH on the removal of Cr(VI) from aqueous solution. As shown in Figure 4(c), the removal rate of Cr(VI) decreased sharply when pH varied from 2 to 9 (\(q_e = 19.97 \text{ mg g}^{-1}\), pH = 2; \(q_e = 0.6 \text{ mg g}^{-1}\), pH = 9). It was concluded that low solution pH was in favor of the Cr(VI) ion adsorption. The Cr(VI) species existed in various forms, including H\(_2\)CrO\(_4\), HCrO\(_4\)\(^-\), CrO\(_4\)\(^{2-}\), and Cr\(_2\)O\(_7\)\(^{2-}\) in the solution. In the acid condition, the carbon surface became positively charged due to protonation. With a large quantity of H\(_3\)O\(^+\) in the solution, it would lead to an electrostatic
attraction with negatively charged Cr(VI) anions (HCrO$_4^-$, Cr$_2$O$_7^{2-}$, CrO$_4^{2-}$) on the positively charged carbon surface. As pH increased, the increasing amount of OH$^-$ would compete strongly with anions (CrO$_4^{2-}$) for binding sites on the carbon surface and resulted in deprotonation and lower adsorption capacity (Rashid et al. 2014).

**Adsorption kinetics**

Kinetic studies are generally carried out to determine the uptake rate of metal ions, which controls the residual time of the whole process. In this study, the kinetic models, the pseudo-first-order and pseudo-second-order models, were used to investigate the adsorption process.

The pseudo-first-order rate equation can be expressed in a linear form as:

$$\ln(q_e - q_t) = \ln q_e - k_1t$$

(3)

The linear form of the pseudo-second-order rate equation can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t$$

(4)

where $q_t$ and $q_e$ are the amounts of Cr(VI) absorbed (mg g$^{-1}$) onto activated carbon at time $t$ and equilibrium, respectively, and $k_1$ (h$^{-1}$), $k_2$ (g mg$^{-1}$ h$^{-1}$) are the adsorption rate constants for the models.

The adsorption kinetics was investigated by fitting the experimental data with pseudo-first-order and pseudo-second-order models. The calculation results showed that the pseudo-second-order model fitted those data much better than the pseudo-first-order did ($R^2 = 0.998 > 0.952$), and the calculated $q_e$ of pseudo-second-order (14.493 mg g$^{-1}$) was closer to the experimental $q_e$ (15.13 mg g$^{-1}$) than that of the pseudo-first-order (8.855mg·g$^{-1}$). The adsorption rate constants $k_1$, $k_2$ were 0.757 (h$^{-1}$), 2.654(mg g$^{-1}$ h$^{-1}$), respectively, of two kinetic models. It suggested that the adsorption process was controlled by chemisorptions (Sadhukhan et al. 2009).

**Adsorption isotherms**

The Cr(VI) adsorption isotherms under initial pH value at 298 K, 308 K, 318 K, respectively, are shown in Figure 5, using 0.5 g L$^{-1}$ corn cob activated carbon mixed with Cr(VI) concentration ranging from 8 mg to 20 mg L$^{-1}$.

Two isotherms models, Langmuir and Freundlich isotherms, were used to fit the experimental data for Cr(VI)
adsorption in aqueous solution by corn cob-based activated carbon. The forms of the two isotherms are:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \]  
\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]

where \( q_m \) is theoretical maximum adsorption capacity when the carbon surface is completely covered with metal ions (mg g\(^{-1}\)), \( C_e \) is the equilibrium concentration of metal ions in the solution (mg L\(^{-1}\)), \( q_e \) is the amount of metal ion adsorbed at specified equilibrium (mg g\(^{-1}\)), \( K_L \) (L mg\(^{-1}\)), \( K_F \) (mg g\(^{-1}\)), \( 1/n (L mg\(^{-1}\)) \) are the constants for Langmuir and Freundlich, respectively.

Table 3 shows the experimental adsorption data fitted by the Langmuir and Freundlich isotherms models. As shown in Table 3, the Langmuir model fitted very well with the activated carbon adsorption under different temperatures \((R^2 > 0.995)\). From Table 3, it was found that the adsorption capacity of activated carbon increased gradually with increments of temperature, which showed that the adsorption of Cr(VI) on activated carbon was not only a physics process, but also involved a chemical ion-exchange process. Because of the free energy caused by the increasing temperature, the adsorption binding sites increased and enhanced the adsorptive capacity of the produced carbons (Xie et al. 2015).

### CONCLUSION

In this study, the produced corn cob activated carbon has a good Cr(VI) adsorptive capacity; the theoretical maximum adsorption is 34.48 mg g\(^{-1}\) at 298 K.

As shown by the orthogonal tests, the optimal preparation of the new biomass-based activated carbon was to impregnate the raw materials with activating agent (volume ratio of ZnCl\(_2\) to NH\(_4\)Cl = 3:1) in a solid-to-liquid ratio of 1:2, and then after 20 min sonic oscillation, pyrolysis under 450°C for 50 min. The BET and iodine adsorption value of the produced activated carbon were 924.9 m\(^2\) g\(^{-1}\) and 1,188 mg g\(^{-1}\), respectively.

FTIR and XPS revealed that the produced activated carbon was mainly composed of carbon, oxygen, nitrogen, and the formation of carbon-containing functional groups like C–C, C–O–C, and C–OH groups was mostly produced by the carbonization and activation in comparison with raw materials.

The adsorbent dosage had significant impact on the adsorption capacity of Cr(VI). For the initial Cr(VI) concentration of 10mg L\(^{-1}\) and the original solution pH of 5.8, an adsorption equilibrium could be reached after 4 h, the removal rate of Cr(VI) was 78.9% with 0.5 g L\(^{-1}\) adsorbent addition and high, up to 100%, with 0.7 g L\(^{-1}\) adsorbent dosage. The results also showed that the lower the pH, the better Cr(VI) adsorption.

The experimental data fitted very well with pseudo-second-order kinetic model under 298 K, and the experimental \( q_e \) and the theoretical calculated \( q_e \) were with high correlation coefficient \((R^2 = 0.998)\). The equilibrium adsorption process fitted well by Langmuir isotherm model under 298 K, 308 K, and 318 K, respectively. The increasing adsorption of Cr(VI) with the increase of temperature showed that the adsorption of Cr(VI) was endothermic.

### ACKNOWLEDGEMENT

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