Study of Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ adsorption onto activated carbons prepared from glycyrrhiza residue by KOH or H$_3$PO$_4$ activation

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ABSTRACT

The activated carbons (ACs) were prepared from glycyrrhiza residue by KOH or H$_3$PO$_4$ activation and were used for removing Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ from simulated wastewater. The changes of the physical structure and chemical properties of the glycyrrhiza residue before and after activation were characterized by using a variety of analytical instruments and methods. Kinetics and equilibrium isotherms were obtained and the effects of solution pH value and adsorbent dosage were studied in batch experiments. The results indicated that after activation, the surface structure of glycyrrhiza residue changes and surface area, micropore volume also increase accordingly. Kinetic studies showed that the adsorption followed a pseudo-second-order reaction. The Freundlich model fitted the equilibrium data better than the Langmuir isotherm. According to the Langmuir equation, the maximum adsorption capacities of ACs prepared from glycyrrhiza residue by KOH and H$_3$PO$_4$ activation for Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ are 2.170 mmol/g, 2.617 mmol/g, 3.741 mmol/g and 2.654 mmol/g, 3.095 mmol/g, 3.076 mmol/g, respectively, which are much higher than ACs prepared from other raw materials.

Key words | adsorption, glycyrrhiza residue, H$_3$PO$_4$, heavy metals, KOH

INTRODUCTION

In recent years, with rapid economic development, the environmental problems from water pollution become more and more important; in particular heavy metal pollution (such as Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$) becomes increasingly serious. Heavy metal residues in the environment affect not only the ecosystem, but also human life via bioconcentration, bioaccumulation and biomagnification in the food chain (Lu et al. 2013). Excessive ingestion of these metals by humans can cause accumulative poisoning, cancer, nervous system damage and ultimately death. For these reasons, removal of heavy metal from wastewater is of great importance. Consequently, many treatment processes have been applied for the removal of heavy metal from wastewater. These processes include extraction, precipitation, ion exchange, adsorption and membrane filtration. Furthermore, among the aforementioned treatment technologies, adsorption has low operational costs, and no secondary pollution has been reported, making it an efficient and economic option. A number of adsorbent materials have been studied for their ability to remove heavy metals and they have been sourced from natural materials and biological wastes of industrial processes, for example: activated carbon (AC), orange peel, wheat straw, peanut shell, lignite, kaolinite, ballclay, chitosan, carrageenan, coconut fiber and limestone. So far, adsorption by AC has been reported as a technically and economically viable technology for heavy metal removal (Papageorgiou et al. 2009; Belgacem et al. 2014).

As a strong-performing type of adsorbent, AC is widely used in the treatment of wastewater due to its exceptionally developed pore structure, large specific surface area, stable chemical properties, high mechanical strength, acid and alkali resistance, heat resistance, and its insolubility in water and organic solvents. In addition, it can be used with recycling. So, AC has been widely used not only in environmental protection, but also in the chemical industry, food industry, and other aspects (Baccara et al. 2009; Demirbas et al. 2009).
Materials includes wood (Ma et al. 2014), nut shells (Hernández-Montoya et al. 2012), pitch coke, petroleum coke (Zhu et al. 2013), coal (Kopac & Toprak 2009), etc.

Residues from Traditional Chinese Medicine (TCM) consist of many carbons, which result from the production process of TCM. Currently, they are disposed of through combustion or land filling, which produces secondary pollution and waste resources, which has created some difficult problems for the manufacturer, society and the environment. Therefore, comprehensive utilization of residue resources has important practical significance, and has become an important topic for current research. It is necessary to find a new method to use TCM processing residues efficiently. Preparing ACs from TCM residues is an excellent way to utilize these residues. Many researchers have investigated ACs produced from agricultural waste using both chemical and physical activation methods (Kim 2004; Shang et al. 2004), but only a few have been studied for AC preparation from TCM residues (Yang & Qiu 2022).

Glycyrrhiza is a plant used in TCM. Its main active constituents are glycyrrhizic acid and glycyrrhetic acid. After extracting glycyrrhizin and licorice extract, a large amount of solid waste – glycyrrhiza residue – is also an output. According to a report by Chen & Jia (2009), more than 100,000 tones of solid waste – glycyrrhizic residue – are produced annually in China. Zhao et al. studied the process of extracting alkaline lignin from residues of glycyrrhiza (Zhao et al. 2021); Chen and Tian studied the application of glycyrrhiza residue in reconstituted tobacco paper-base papermaking method (Chen & Tian 2021). However, no research has yet reported the chemical activation of glycyrrhiza residue with KOH or H3PO4. Therefore, in the present study, the ACs were prepared from glycyrrhiza residue by chemical activation using KOH or H3PO4 and the adsorption characteristics of the ACs on Pb2+, Cd2+ and Ni2+ adsorption are also discussed in this work. The main objective was to make full use of glycyrrhiza residue in wastewater treatment, so that it can improve the utilization rate of resources and reduce environmental pollution.

MATERIALS AND METHODS

Materials and reagent

Glycyrrhiza residues were collected from the pharmaceutical factory in Ningxia, China; all chemicals used (H3PO4, KOH, I2, methylene blue, Na2S2O3·2H2O, NaOH, HCl, Pb(NO3)2, Cd(NO3)2 and NiCl2) were of analytical grade; solutions were prepared by dissolving the corresponding reagent in doubly distilled water.

Preparation of the ACs

Glycyrrhiza residue was pulverized, sieved to particle size (40 mesh), washed with distilled water, then dried at 80°C in a conventional oven and reserved; these materials were called GR.

The preparation of ACs by KOH activation

A certain amount of GR was mixed with a saturated KOH solution (weight ratio of GR and KOH is 1:10) and allowed to soak for 24 hours at room temperature. The resulting chemical-loaded sample was then heated in a muffle furnace (Carbolite HVT-1200, Tianjin, China), to the carbonization temperature of 700°C, at a heating rate of 10°C/min, and held at that temperature for 60 minutes. The resultant AC was cooled to room temperature, soaked with 0.1 mol/L hydrochloric acid to remove the residual KOH and washed sequentially several times with distilled water until neutral pH, then dried at 80°C and stored for subsequent use. The obtained samples were denoted as CAC.

The preparation of ACs by H3PO4 activation

An amount of GR was weighed then mixed with a concentrated phosphoric acid solution (70%) at a ratio of 1:12 (GR/H3PO4) and allowed to soak for 24 hours in a 90°C water bath. These samples were carbonized in a muffle furnace with a heating rate of 10°C/min to reach the desired temperature of 500°C and maintained for 90 minutes. After being heated, samples were naturally cooled to room temperature and washed several times with distilled water to remove the phosphoric acid until the pH value of the filtered liquid was neutralized. The H3PO4-treated GR (PAC) was then dried in an oven for 24 hours at 80°C.

Instruments and methods used for AC characterization

The surface morphology was observed by scanning electron microscopy (SEM; JSM-6 700 F Tokyo, Japan); surface area and pore volume were calculated by nitrogen adsorption isotherms (Micromeritics Instrument Corporation, Model ASAP-2020, Atlanta, GA, USA); the iodine adsorption number (iodine number) and methylene blue number of the ACs were determined according to GB/T7702.7-2008 from China (Luo et al. 2013); structural parameters were detected with powder...
X-ray diffraction (XRD; Rigaku P/max 2200VPC, Toshiba, Tokyo, Japan) using Cu Kα radiation; Fourier transform infrared (FTIR) spectrometry was obtained using pressed KBr pellets (Thermo Scientific, Waltham, MA, USA); the surface functional groups were measured using Boehm’s method.

Batch adsorption experiments

Batch adsorption experiments were conducted by mixing CAC and PAC with 25 mL of Pb²⁺, Cd²⁺ and Ni²⁺ ion solutions of desired concentrations in 100 mL sealed conical flasks using a shaking thermostat machine at a speed of 150 rpm at 25 °C. The effect of solution pH on the equilibrium adsorption of Pb²⁺, Cd²⁺ and Ni²⁺ was investigated by mixing 0.100 g of CAC/PAC with 25 mL of Pb²⁺, Cd²⁺ and Ni²⁺ ion solutions of 1 mmol/L between pH 2.0 and 6.0. In kinetic experiments, 1 mmol/L Pb²⁺, Cd²⁺ and Ni²⁺ ion solutions were used; the adsorption time varied from 0 to 180 minutes. The effect of the dosage of CAC/PAC was also varied between 1 and 10 g/L with 25 mL of Pb²⁺, Cd²⁺ and Ni²⁺ ion solutions of 1 mmol/L. In isotherm experiments, 0.100 g of CAC/PAC was added in 25 mL of Pb²⁺, Cd²⁺ and Ni²⁺ ion solutions at various concentrations (1–10 mmol/L). After the pre-set contact time was reached, the samples were withdrawn and then solutions were filtered through 0.45 μm filter paper. The concentration of metal ions was determined by flame atomic absorption spectrometry (Persee A3 Atomic Absorption Spectrophotometer, Beijing, China). All experiments were conducted in triplicate, and average values were used in the data analysis.

The amount of adsorbed metal ions at equilibrium, \( q \) (mmol/g) and the percentage of adsorption (\( E \% \)) was calculated as follows:

\[
E\% = \frac{c_0 - c_e}{c_0} \times 100\%
\]

\[
q = \frac{(c_0 - c_e)V}{W}
\]

where \( c_0 \) (mmol/L) and \( c_e \) (mmol/L) are the initial metal ion concentrations and equilibrium ion concentrations, respectively, \( V \) (L) is the volume of the solution and \( W \) (g) is the weight of the dry ACs.

Desorption and reuse

Desorption experiments were carried out by suspending the Pb²⁺, Cd²⁺ and Ni²⁺ ion-loaded CAC and PAC in 0.1 mol/L HCl and shaking with a rotary shaker for 3 hours. The ACs were separated and washed with distilled water. Regeneration of CAC and PAC was carried out by treating with 1% (m/V) \( \text{Na}_2\text{CO}_3 \) for 12 hours, followed by washing, filtering and drying before use in further experiments. The adsorption–desorption cycles were repeated five times; in every cycle, the initial Pb²⁺, Cd²⁺ and Ni²⁺ ion concentration was 1 mmol/L. The desorption ratio was calculated from the following equation:

\[
\text{Desorption ratio}(D\%) = \frac{\text{amount of } M^{2+} \text{ desorbed}}{\text{amount of } M^{2+} \text{ adsorbed}} \times 100
\]

\((M^{2+} = \text{Pb}^{2+}, \text{Cd}^{2+} \text{ and } \text{Ni}^{2+})\)

RESULTS AND DISCUSSION

Characterization of AC

The surface structures of the GR, CAC and PAC are shown in Figure 1. The surface of GR was quite smooth without any porous structure, except for some occasional cracks or curves. In contrast, it can be seen from the micrographs of CAC and PAC (Figure 1(b) and 1(c)) that their external surfaces are full of spaces, channels and cavities, which are helpful for the mass transfer of metal ions to CAC and PAC.

The physical properties of all samples are summarized in Table 1. It can be seen that the BET surface area and micropore volume of the CAC and PAC increase significantly after activation, while the GR sample exhibits only a small pore volume and a low \( S_{\text{BET}} \). The iodine and methylene blue number of CAC and PAC are 505.6 mg/g, 147.5 mg/g and 500.8 mg/g, 136.9 mg/g, respectively, which is higher than the number of GR (55.41 mg/g, 38.63 mg/g). These confirm that KOH-activated or H₃PO₄-activated porous carbon has lots of micropores, as shown in Figure 1(b) and 1(c). It can also be concluded that ACs may adsorb both small and large molecules, which is relatively clear from large amounts of iodine and methylene blue (Gundogdu et al. 2012; Zhang et al. 2014). The difference in BET surface area value between CAC and PAC is 70 m²/g. The main reason for this is likely to be the difference between the reaction mechanisms of these two chemicals acting on the carbonaceous structure.

In comparison, the BET surface area and micropore volume values from Table 1 of CAC and PAC were
comparable to, or even larger than, those reported in the literature in which KOH, ZnCl₂, or CO₂ were used as the activation agents to produce the AC from waste tire-derived char (Suuberg & Aarna 2011; Zhi et al. 2014); they were much higher than the previously reported mesoporous AC produced by chemical activation with ZnCl₂ by Gorzin & Ghoreyshi (2015) and Liu et al. (2013).

Boehm titration results for CAC and PAC are also shown in Table 1. It is clear that the number of acidic surface functional groups increases after activation with both KOH and H₃PO₄ to varying degrees. These acidic function groups (such as carboxylic, lactone, and phenol groups) are very useful in adsorption. The more these groups exist on the CAC and PAC surface, the better removal of metal ions via adsorption from the wastewater.

The XRD patterns of CAC and PAC are shown in Figure 2. There are two broad diffraction peaks at around 2θ = 25° and 44° in each spectrum, corresponding to the diffraction of (002) and (100) of graphite, respectively, showing that CAC and PAC prepared by KOH and H₃PO₄ direct activation have the predominantly amorphous structure of carbons (Xiao et al. 2014).

From patterns on the surface of the XRD, diffractograms of carbons activated by KOH, H₃PO₄ look quite similar. However, according to the present study, as inferred from the XRD (Figure 2(a)) peaks at 2θ = 28.2, 31.66, and 42.64°, the compounds formed were probably K₂O and K₂CO₃; K₂CO₃ is formed by the reaction of KOH and CO₂. At the end of the reaction, K₂O is left as a residual compound. For the above compounds, typical graphitic layers and stakes of plane were formed during carbonization (Sun et al. 2014). In the XRD patterns of PAC (Figure 2(b)), the carbon also shows a peak at 2θ = 37.47° which indicates the presence of phosphate, assigned by the authors, and it also has characteristic peaks created from general ACs by H₃PO₄ activation (Anirudhan et al. 2009).

<table>
<thead>
<tr>
<th>samples</th>
<th>GR</th>
<th>CAC</th>
<th>PAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_BET (m²/g)</td>
<td>0.799</td>
<td>583.1</td>
<td>513.7</td>
</tr>
<tr>
<td>Micropore volume (cm³/g)</td>
<td>0.005</td>
<td>0.194</td>
<td>0.141</td>
</tr>
<tr>
<td>Iodine number (mg/g)</td>
<td>55.41</td>
<td>505.6</td>
<td>500.8</td>
</tr>
<tr>
<td>Methylene blue number (mg/g)</td>
<td>38.63</td>
<td>147.5</td>
<td>136.9</td>
</tr>
<tr>
<td>Lactonic groups (mmol/g)</td>
<td>0.437</td>
<td>2.324</td>
<td>2.717</td>
</tr>
<tr>
<td>Phenolic hydroxyl groups (mmol/g)</td>
<td>0.651</td>
<td>0.524</td>
<td>3.377</td>
</tr>
<tr>
<td>Carboxylic acid groups (mmol/g)</td>
<td>0.332</td>
<td>1.661</td>
<td>1.533</td>
</tr>
</tbody>
</table>

Figure 1 | SEM images of ACs: (a) GR; (b) CAC; (c) PAC.
As seen in Figure 3(a), the GR shows an intense band at about 3,405 cm\(^{-1}\) which is attributed to the stretching vibrations of O-H or N-H functional groups. The peaks at 2,924 cm\(^{-1}\) are due to the symmetric and asymmetric C-H stretching of \(-\text{CH}_3, \text{CH}_2\) vibrations and C=O vibration of the ketone group of lignin. The peak observed at 1,737 cm\(^{-1}\) is the stretching vibration of the bond due to non-ionic carboxyl groups (–COOH, –COOCH\(_3\)), and may be assigned to glycyrrhizic acid or glycyrrhizic acid ester. The band centered at 1,643 and 1,153 cm\(^{-1}\) is most likely due to the stretching vibrations of C = O and C-N from the protein amide bond. As the peak appears at 1,452 cm\(^{-1}\) it may be assigned to the bending vibration of \(-\text{CH}_3\) and \(-\text{CH}_2\); the band focused at 1,320 cm\(^{-1}\) may arise from the C-O of benzene hydroxyl in lignin; the bands located around 1,022 cm\(^{-1}\) can be ascribed to the bending vibration of O-H, and the stretching vibration of C-O-C from cellulose.

For the IR of CAC (Figure 3(c)), a very small new peak at 2,369 cm\(^{-1}\) comes out, which may arise from the stretching of CO\(_2^-\) groups as a result of the generation of K\(_2\)CO\(_3\) during KOH activation. The bands centered around 1,630 cm\(^{-1}\) were attributed to C=O stretching vibration. The bands located at 3,405, 2,929, 1,737, 1,643, 1,452, 1,320, 1,153, 1,022 cm\(^{-1}\) were attributed to a stretching vibration, which vanished compared with the GR, probably owing to the H element being removed and the dehydration effect of KOH after carbonization and activation. In summary, the most significant changes by KOH activation are the reduction of hydroxyl groups and the emergence of new peaks, indicating the conceivable formation of irregular amorphous carbon structures (Gao et al. 2013).

Compared with GR, the IR spectra for PAC (Figure 3(b)) showed new bands at 3,416 cm\(^{-1}\) (O-H vibrations), 1,634 cm\(^{-1}\) (C = O vibrations); and the spectra show a broad band between 1,300 and 900 cm\(^{-1}\). The absorption in this region is characterized for phosphorus and phosph-carbonaceous compounds (1,165 cm\(^{-1}\) (P = O) and 993 cm\(^{-1}\) (P–OH)). The reduction and disappearance of peaks (2,929, 1,737, 1,643, 1,452, 1,320, 1,153, 1,022 cm\(^{-1}\)) in PAC indicate the conversion of certain functional groups into volatile matter as a result of high temperature and chemical reaction (Chen et al. 2011).

Adsorption studies

Effect of the pH

It is well known that pH values of the solution could significantly influence adsorption. This is partly due to the fact that the pH of metal solutions strongly influences not only the chemical form of the metals in aqueous solutions but also the properties of the adsorbent (Ibrahim 2011). Figure 4 shows the effect of pH variation on adsorption of Pb\(^{2+}\), Cd\(^{2+}\) and Ni\(^{2+}\) ions by CAC and PAC. When the solution’s
pH was increased from 2.5 to 4.0, the adsorption percentage of CAC and PAC for Pb$^{2+}$ and Ni$^{2+}$ ions rises markedly and quickly; at pH ranges 4.0–6.0, the adsorption percentage rises very slowly or even remains unchanged with increments in pH. It would be plausible to explain that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions (H$^+$), thereby preventing the metal ions from approaching the binding sites of the adsorbents, as a result, leaving metal ions unbound because of the electric repulsion of protons on adsorbent. When the pH gradually increases, the competing effect of hydrogen ions decreases and the positively charged metal ions take up the free binding sites; the metal uptake capacity hence increases (Liu et al. 2009). In the case of Cd$^{2+}$ adsorption (Figure 4(b)), the pH values of the solution have little influence on adsorption, when solution pH increases from 2.5 to 4.0, the adsorption percentage of CAC and PAC for Cd$^{2+}$ ions rarely increased. This may be due to the adsorption of CAC and PAC for Cd$^{2+}$ being mainly dependent on the specific surface adsorption (physical adsorption) the functional groups of ACs had a little influence on Cd$^{2+}$ adsorption (Juan et al. 2013). At higher pH (4.0–6.0), Cd$^{2+}$ ion adsorption is nearly constant throughout.

While it is apparent that Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ ion adsorption onto CAC and PAC under different initial pH show different trends, it can also be observed from Figure (4) that CAC and PAC exhibit higher adsorption efficiencies of Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ within the range of 4.0–6.0. If the pH continues to increase (>6.0), it will result in the formation of M(OH)$^+$ ions and M(OH)$_2$, the solubility of metal ions will be lower, thus leading to the adsorbents achieving little sorption for metal ions (Onundi et al. 2012). To examine the adsorption potential of the adsorbent, and to ensure that the heavy metals exist in their ionic states during adsorption, the pH in subsequent experiments was controlled at 5.0 for Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$.

**Effect of contact time and kinetic studies**

The adsorption processes as a function of time to determine the point of equilibrium were studied from adsorption experiments of Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ ions onto CAC and PAC, respectively. The results are shown in Figure 5. It is clear that adsorption of three metal ions by CAC and PAC increases sharply from 0 to 60 minutes; after 60 minutes, the adsorption rates increase very slowly and adsorption equilibrium is gradually achieved; the amount of metal ions removed almost reached a maximum at 90 minutes. With an increase in contact time from 90 minutes up to 180 minutes, the amount of adsorbed metal ions does not change significantly. According to these results, the shaking time was fixed at 120 minutes.

![Figure 4](https://iwaponline.com/wst/article-pdf/72/3/451/467574/wst072030451.pdf)
for the rest of the batch experiments to make sure that equilibrium was reached.

The kinetics of metal ions sorption is an important parameter for designing sorption systems and is required for selecting the optimum operating conditions for a full-scale batch metal removal process (Olivares-Marín et al. 2008). To examine the rate-controlling step of the adsorption process, pseudo-first-order and pseudo-second-order rate equations are proposed to test the experimental data.

The pseudo-first-order rate equation is expressed as (Lagergren & Svenska 1898):

\[
\ln \left( \frac{q_e}{q_t} \right) = -k_1 t
\]

where \( q_e \) (mmol/g) and \( q_t \) (mmol/g) are the sorption capacities at equilibrium and at any time \( t \), respectively, and \( k_1 \) (min\(^{-1}\)) is the pseudo-first-order rate constant.

The pseudo-second-order rate equation is given as (Ho & McKay 1998):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( k_2 \) (g/(mmol min)) is the pseudo-second-order rate constant.

The kinetic constants evaluated from fitting results, along with the correlation coefficients and the experimental adsorption capacities, are summarized in Table 2. From Table 2, it can be seen that the pseudo-second-order model correlates better with the experimental data, which is a good fit for Pb\(^{2+}\), Cd\(^{2+}\) and Ni\(^{2+}\) ion adsorption onto the CAC and PAC with higher correlation coefficients, in comparison to those of the pseudo-first-order kinetic model. Furthermore, the calculated equilibrium adsorption capacity \( q_e \) of CAC and PAC is more similar to the experimental \( q_e \) values of adsorption equilibrium. Successful fitting of the pseudo-second-order model indicates that chemical sorption is the rate-controlling step. The formation of chemisorptive bonds involved balancing force by sharing or exchange of electrons between the metal ions, and the adsorbents may be regarded as the rate-limiting step of the process (Mohamed Lasheen et al. 2012).

**Effect of adsorbent dosage**

Adsorbent dosage is also a critical parameter in adsorption; the effects of adsorbent dosage on the removal percentage of Pb\(^{2+}\), Cd\(^{2+}\) and Ni\(^{2+}\) ions by CAC and PAC are shown in Figure 6. It can be seen that the removal of Pb\(^{2+}\), Cd\(^{2+}\) and Ni\(^{2+}\) ions increases by increasing the dosage of CAC and PAC, which ranged from 1 to 4 g/L; this is due to the availability of more empty binding sites and larger surface.

![Figure 5](https://iwaponline.com/wst/article-pdf/72/3/451/467574/wst072030451.pdf)
area as compared to lower dosages which have fewer binding sites to adsorb the same amount of Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ ions in the adsorbate solution (Özer et al. 2004). At adsorbent dosage $>4$ g/L for Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ the incremental removal of metal becomes very low, as the amount of sorbate ion concentration decreases per active site available for sorption on the adsorbents. Thus, increased adsorbent dosage did not enhance the removal percentage of the studied metal ions (Ahmaruzzaman & Laxmi Gayatri 2010).

**Isotherm studies**

Figure 7 shows the adsorption isotherms of Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ ions by CAC and PAC. The amount of metal ion sorption on CAC and PAC ($q_e$) is examined by adsorption isotherms. It could be seen that $q_e$ increased initially with an increasing $c_e$ until equilibrium was reached, then the $q_e$ remained almost constant with further increase in $c_e$.

To describe the metal ions adsorption behavior on CAC and PAC, isotherm data obtained were fitted to the Langmuir and Freundlich (Figure 7) adsorption models.

The Langmuir model is based on monolayer, uniform and finite adsorption site assumptions. The Langmuir equation can be expressed as (Allen & Brown 1995):

$$c_e = \frac{1}{q^*_e} + \frac{c_e}{q^*_\text{max}}$$

(6)

where $c_e$ is the equilibrium concentration of the adsorbate in solution after adsorption (mmol/L); $q_e$ is the amount adsorbed per unit weight of adsorbent (mmol/g); and $b$ is Langmuir constants; $q^*_\text{max}$ is the saturation capacity (mmol/g), the value of $q^*_\text{max}$ (mmol/g) and $b$ (L/mmol) can be determined from the slope and intercept of a linear plot of $c_e/q_e$ versus $c_e$.

The Freundlich model is an empirical equation for multilayer, heterogeneous adsorption. The linearized form of the Freundlich equation is (Freundlich 1906):

$$\log q_e = \log K_F + \frac{1}{n} \log c_e$$

(7)

where $K_F$ is the Freundlich equilibrium constant, which is an indication of adsorption capacity, and $1/n$ is an empirical constant related to the efficiency of adsorption: if $1/n > 1$, the adsorption is unfavorable, while if $1/n < 1$, the adsorption is favorable (Vazquez et al. 2002).

The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients are listed in Table 3.

The results calculated above show that both the Langmuir and Freundlich equations can describe the experimental data. A comparison of the $R^2$ values of the linearized form of these equations indicated that the Freundlich model yields a better fit than the Langmuir model. The $1/n$ values obtained from the Freundlich model are in the range of $0 < 1/n < 1$, which demonstrates that the adsorption is favorable. According to the Langmuir equation, the maximum adsorption capacities of CAC and PAC for Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ are 2.171 mmol/g, 2.617 mmol/g, 3.741 mmol/g and 2.654 mmol/g, 3.095 mmol/g, 3.076 mmol/g, respectively, which are much higher than ACs prepared from other raw materials (Kavand et al. 2014) and also higher than commercial AC (Alslaibi et al. 2014). This could be explained since the CAC and PAC had a heterogeneous pore distribution, which could avoid the pore blocking favoring the physisorption (Moreno-Barbosa et al. 2013).

**Desorption and reuse**

To test the suitability and stability of the adsorbent, Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ adsorption capacities by CAC and PAC undergoing five cycles are illustrated in Table 4. It can be found that the Pb$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ adsorption percentage by CAC and PAC gradually decrease from the first cycle, but after five cycles,
the Pb\(^{2+}\), Cd\(^{2+}\) and Ni\(^{2+}\) adsorption percentage of CAC and PAC were also above 80%. In every cycle, more than 85% of the adsorbed Pb\(^{2+}\), Cd\(^{2+}\) and Ni\(^{2+}\) were desorbed. And the adsorbent can be reused almost without any significant loss in adsorption performance. This behavior shows that the CAC and PAC can be used successfully five times.
CONCLUSIONS

The ACs were developed from glycyrrhiza residue through a simple and low-cost chemical activation method (KOH/H₃PO₄) with high S_BET and developed pore structure; XRD also showed that CAC and PAC have the predominantly amorphous structure of carbons. The results of the surface functional group titration proved that the amount of acid carboxyl groups on CAC and PAC increased accordingly. The changes in the IR spectra of the CAC and PAC identified the presence of the acid carboxyl groups and special groups after activation.

The findings in this work indicated that CAC and PAC maximum adsorption capacity for Pb²⁺, Cd²⁺ and Ni²⁺ ions (evaluated based on Langmuir fit) were higher than ACs prepared from other raw materials and also higher than commercial ACs. The kinetics of the adsorption process was found to follow the pseudo-second-order kinetic model and equilibrium was well described by Freundlich isotherm. The CAC and PAC were regenerated using HCl solution and could be used five times with little loss of ions-adsorbing capacity. It can be concluded that CAC and PAC are effective and alternative adsorbents for the removal of Pb²⁺, Cd²⁺ and Ni²⁺ ions from wastewaters in terms of high adsorption capacity and low cost.

ACKNOWLEDGEMENT

This work was supported by the National Natural Science Foundation of China (No. 21266026).

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First received 18 February 2015; accepted in revised form 27 April 2015. Available online 14 May 2015.