Removal of Pb(II) by adsorption onto Chinese walnut shell activated carbon
Zheng-ji Yi, Jun Yao, Yun-fei Kuang, Hui-lun Chen, Fei Wang and Zhi-min Yuan

ABSTRACT
The excessive discharge of Pb(II) into the environment has increasingly aroused great concern. Adsorption is considered as the most effective method for heavy metal removal. Chinese walnut shell activated carbon (CWSAC) was used as an adsorbent for the removal of Pb(II) from aqueous solution. Batch experiments were conducted by varying contact time, temperature, pH, adsorbent dose and initial Pb(II) concentration. Adsorption equilibrium was established within 150 min. Although temperature effect was insignificant, the Pb(II) adsorption was strongly pH dependent and the maximum removal was observed at pH 5.5. The Pb(II) removal efficiency increased with increasing CWSAC dosage up to 2.0 g/L and reached a maximum of 94.12%. Langmuir and Freundlich adsorption isotherms were employed to fit the adsorption data. The results suggested that the equilibrium data could be well described by the Langmuir isotherm model, with a maximum adsorption capacity of 81.96 mg/g. Adsorption kinetics data were fitted by pseudo-first- and pseudo-second-order models. The result indicated that the pseudo-first-order model best describes the adsorption kinetic data. In summary, CWSAC could be a promising material for the removal of Pb(II) from wastewater.

Key words | adsorption, Chinese walnut shell activated carbon, isotherm, kinetics, Pb(II)

INTRODUCTION
Lead contamination is attracting wide attention because of its poisonous effects on human health and living organisms. Lead as an important industrial raw material is widely used in storage battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass industry printing, painting, dying, and other industries (Wang et al. 2007). As is well known, lead is listed with mercury, cadmium, chromium and arsenic in the group of most serious hazardous heavy metals (Bulut & Baysal 2006). Once released into air, soil and water bodies, lead can cause environmental pollution. Lead as one of the most toxic heavy metals is easy to accumulate in living organisms but hard to degrade into nontoxic end products (El-Ashtoukhy et al. 2008). Lead toxicity in humans leads to serious damage to the kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead causes sterility, abortion, and even neo-natal deaths (Liu et al. 2015). The permissible limit of lead is 0.05 mg/L in drinking water (Goel et al. 2005). In this context, recovery and removal of Pb(II) from wastewater has become a major topic of research in water treatment.

There are many reported and established technologies for the recovery and removal of metals from wastewater, which include ion exchange, chemical precipitation, coagulation, membrane filtration, reverse osmosis, and solidification/stabilization (Fu & Wang 2011). In actual fact, each of these methods has its own disadvantages, such as high operating cost, low selectivity, incomplete removal, high energy requirement and production of toxic sludge, thereby limiting their practical use (Omar & Al-Itawi 2007). Thus, environmental researchers face severe challenges in the development of efficient and cheap separation processes for Pb(II) removal.

In recent years, many researchers have made great efforts to look for low-cost materials with good Pb(II) adsorption performance. It is noted that many agricultural and forestry byproducts and biomass residues have been extensively investigated for the removal of various heavy metals from
wastewater. These byproducts or residues include peat, wood, pine bark, banana seed hulls, peanut shells, coconut shell, hazelnut shell, rice husk, sugarcane, wool, orange peel, compost and plant leaves (Chopra & Pathak 2010). In addition, some of them can be processed into activated carbon (AC) with high surface area and excellent adsorption performance.

The shell of Chinese walnut (Carya hunanensis W. C. Cheng & R. H. Chang ex Chang & Lu) is an agricultural residue with excellent durability. It is now widely used as polishing and cleaning material for trimming, removal of adhered objects, and for deburring of critical and fragile parts without etching, scratching or marking the cleaned areas. It can also be made into AC through high temperature steam activation and refining. Nutshell AC often has high porosity, large surface area and high surface reactivity, thereby making it possible to use Chinese walnut shell activated carbon (CWSAC) as a superior adsorption material. It should also be pointed out that the price of CWSAC (ca. USD600 per ton) is very low. Many experiments have been carried out on the adsorption of Pb(II) by various carbonaceous materials (Shi et al. 2011; Hamid et al. 2012). However, as far as we know, little investigation has focused on the application of CWSAC in the removal of Pb(II). In the present study, adsorption of Pb(II) from aqueous solution using CWSAC was examined. The effects of pH, contact time, adsorbent dosage and Pb(II) concentration were investigated and experimental data were evaluated and fitted using adsorbent equilibrium isotherms and kinetic models.

**MATERIALS AND METHODS**

**Adsorbents and chemical reagents**

CWSAC powder was purchased from Guoqing Water Purification Material Co. Ltd in China and used as an adsorbent for the following metal adsorption experiments. The quality testing indexes of CWSAC were determined (Table 1) according to the GB/T 7702-1997 (Chinese National Standard for Nut Shell Activated Carbon Test).

A stock solution of Pb(II) (1,000 mg/L) was prepared by dissolving 1.598 g of Pb(NO₃)₂ in 1,000 mL distilled water. This stock solution was then diluted to required concentrations and the pH values of resulting solutions were adjusted to desired values with 1.0 mol/L NaOH or HCl. The pH of the solutions was determined using a pHS-3C digital pH meter (Shanghai Leici Device Works, Shanghai, China) with a combined glass-calomel electrode. All chemicals and reagents were of analytical grade and were used as received without any further purification.

**Batch adsorption experiments**

Batch adsorption experiments were carried out in a series of 250 mL conical flasks to examine the effects of aforementioned process variables on the Pb(II) removal. Pretrial experiments were also performed to determine the minimum and maximum levels of each variable. Briefly, 100 mL of Pb(II) solution was mixed with a certain amount of CWSAC powder. Thereafter, the flasks were agitated at 140 rev/min on a thermo-controlled rotary shaker. Finally, the equilibrated solutions were withdrawn and the adsorbent was separated from them by centrifugation. The concentration of the Pb(II) in the residual solution was determined using a standard method by microtitration using EDTA standard solution (Li et al. 2002). All the experiments were repeated thrice to confirm the results and average values are presented.

The Pb(II) removal efficiency and adsorption capacity of CWSAC powder were calculated by using the following equations:

\[
Ad\% = \frac{(C_0 - C_f)}{C_0} \times 100
\]

\[
q_t = \frac{(C_0 - C_f) \times V}{W}
\]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granularity diameter</td>
<td>10–325 mesh</td>
<td>True density</td>
<td>2–2.2 g/cm³</td>
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<tr>
<td>Phenol adsorption</td>
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<td>Packing density</td>
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<tr>
<td>Strength</td>
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<td>Total pore volume</td>
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<tr>
<td>Iodine value</td>
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<td>Specific surface area</td>
<td>590–1,500 m²/g</td>
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<tr>
<td>Methylene blue value</td>
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<td>pH</td>
<td>8–10</td>
</tr>
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<td>≤5 cm</td>
<td>Ash</td>
<td>≤8–12%</td>
</tr>
<tr>
<td>Moisture</td>
<td>≤3%</td>
<td>Specific heat</td>
<td>–1.00 J/(g °C)</td>
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</table>
where $q_e$ is the Pb(II) removal efficiency; $q_e$ and $q_t$ are the adsorption capacity (mg/g) at equilibrium and at time $t$ (min), respectively; $C_0$, $C_t$ and $C_e$ are the initial Pb(II) concentration, liquid-phase Pb(II) concentration at time $t$, and equilibrium Pb(II) concentration (mg/L), respectively; $V$ is the volume of the aqueous solution (L); $W$ is the mass of the adsorbent (g).

Equilibrium and kinetic modeling

The experimental data for Pb(II) adsorption on CWSAC at different initial Pb(II) levels were fitted using Langmuir and Freundlich isotherm models (Ozacar 2003). The non-linear form of the Langmuir and Freundlich equations can be given as the following Equations (4) and (5):

$$q_e = \frac{bq_{\text{max}}C_e}{1 + bC_e}$$  \hspace{0.5cm} (4)

where $q_{\text{max}}$ represents the maximum monolayer adsorption capacity (mg/g), and $b$ represents the affinity constant related to the free energy of adsorption (L/mg):

$$q_e = K_F C_e^{1/n}$$  \hspace{0.5cm} (5)

where $K_F$ is the Freundlich constant indicative of the adsorption capacity of the adsorbent [(mg/g)(L/mg)$^{1/n}$], and $n$ is the Freundlich exponent depicting adsorption intensity (dimensionless).

To define the adsorption kinetics of heavy metal ions, the kinetic parameters for the adsorption process were studied for the contact time ranging between 0 and 150 min. The kinetic data were fitted using pseudo-first-order and pseudo-second-order kinetic models (Ho & McKay 1999). The non-linear form of the two models can be expressed as the following Equations (6) and (7):

$$q_t = q_e(1 - e^{-k_1t})$$  \hspace{0.5cm} (6)

where $k_1$ is the rate constant of the pseudo-first-order sorption (min$^{-1}$):

$$q_t = \frac{k_2q_e^2t}{1 + k_2q_e^2t}$$  \hspace{0.5cm} (7)

where $k_2$ is the rate constant of pseudo-second-order adsorption [g/(mg-min)].

RESULTS AND DISCUSSION

Effect of contact time

A series of contact time experiments for the adsorption of Pb(II) onto CWSAC were conducted at a fixed dose of adsorbent (2.0 g/L) and three different initial Pb(II) concentrations (50, 100, and 200 mg/L). The effects of contact time on the adsorption process are given in Figure 1. Apparently, the uptake of Pb(II) from aqueous solution by CWSAC increased with time and reached equilibrium in 150 min for all the concentrations studied. As far as CWSAC was concerned, the equilibrium time required for the adsorption reaction was relatively long, which may be a drawback of this adsorbent. It can also be seen from Figure 1 that equilibrium time was independent of the initial Pb(II) concentration. Based on these results, 150 min was selected as the standard contact time in the following adsorption experiments.

Effect of temperature

The effect of temperature on the Pb(II) adsorption by CWSAC was investigated at four different temperatures (Figure 2). From 25 to 55 °C, the Pb(II) removal efficiency did not significantly change. The adsorption of Pb(II) on the CWSAC seems to be temperature independent over the temperature range tested. It has been also reported that change of
wastewater temperature has little effect on the overall Pb(II) removal by common wood AC (Payne & Abdel-Fattah 2004). However, a significant effect of temperature on the adsorption of Pb(II) onto AC prepared from Enteromorpha prolifera and Eucalyptus camaldulensis Dehn. bark was reported (Patnukao et al. 2010; Li et al. 2013).

**Effect of pH**

Wastewater purification using non-traditional and traditional adsorbents is highly dependent on the acidity of wastewater under treatment since it could influence the surface charge of adsorbents and the degree of ionization of various contaminants. Therefore, pH is one of the most important parameters controlling adsorption of metals from wastewater. Generally, Pb(II)-bearing industrial wastewater is in the acidic range. In this study, precipitation of Pb(OH)₂ occurred when the pH is higher than 5.7. So the effect on the removal of Pb(II) was investigated between the pH range from 2.0 to 5.5.

Obviously, the minimum adsorption of 18.62% was found at pH 2.0 and the Pb(II) removal efficiency increased with increasing pH over the studied pH range from 2.0 to 5.5 (Figure 3). In addition, a remarkable increase in Pb(II) removal was observed in the pH range from 3.0 to 4.0. The optimum pH for Pb(II) adsorption was found to be 5.5 with 90.25% of Pb(II) removed. These results suggested that acidic pH is unfavorable to the adsorption, and the pH shift toward neutral enhances the Pb(II) removal. Several other investigators have studied the pH effect on the adsorption of heavy metals by using other carbonaceous materials and similar findings were reported (Imamoglu & Tekir 2008; Mondal 2010; Gupta et al. 2011). Generally, the CWSAC surface tends to be protonated and positively charged at acidic pH values, which will block the active adsorption sites and make metal cations more difficult to be adsorbed. Contrarily, when the pH value increased, the positive density on the CWSAC surface gradually decreased and some active adsorption sites could be liberated. The electrostatic attraction between Pb(II) and those active adsorption sites was enhanced, thereby increasing the Pb(II) removal (Zaini et al. 2009).

**Effect of CWSAC dose**

The Pb(II) removal efficiency profile versus adsorbent dose is shown in Figure 4. The adsorbent dose varied from 0.5 to 3.0 g/L keeping all of the other experimental parameters constant.

![Figure 3: Effect of pH on Pb(II) adsorption by CWSAC (temperature: 25 °C; contact time: 150 min; CWSAC dosage: 2.0 g/L; Pb(II): 100 mg/L; solution volume: 100 mL).](image)

![Figure 4: Effect of CWSAC dosage on Pb(II) adsorption by CWSAC (contact time: 150 min; temperature: 25 °C; pH: 5.0; Pb(II): 200 mg/L; solution volume: 100 mL).](image)
constant. As shown in Figure 4, the Pb(II) removal efficiency increased from 37.68 to 94.12% with an increase in the dose of adsorbent from 0.5 to 2.5 g/L. This may be attributed to increased adsorbent surface area and availability of more sorption sites resulting from the increased dose of the adsorbent. The Pb(II) removal changed little with further increase of dose of adsorbent above 2.5 g/L. One other study has reported that the increase in the metal removal efficiency with increasing adsorbent dosage is due to the increase of the number of adsorption sites (Singanan 2011).

**Effect of initial Pb(II) concentration**

The effect of initial Pb(II) concentration ranging from 25 to 250 mg/L on the Pb(II) removal efficiency and amount of Pb(II) adsorbed on the CWSAC was studied. The result is shown in Figure 5. As can be seen from Figure 5, the Pb(II) adsorption capacity increased and removal efficiency decreased as the initial metal concentration. This result is similar to that reported by other research (Lu et al. 2013). The increasing amount of Pb(II) adsorbed on CWSAC with the elevation of initial metal concentration may be explained by higher Pb(II) gradient providing an important driving force toward active sites and increasing the probability of collision between the adsorbent and Pb(II).

**Adsorption isotherms**

Experimental data obtained from Figure 5 were fitted with Langmuir and Freundlich isotherm equations and all parameters are shown in Table 2. By comparing the correlation coefficients of two isotherms, it is shown that the Langmuir ($R^2 > 0.99$) adsorption model was fitted better to the experimental results. Furthermore, the calculated value of $q_{\text{max,cal}}$ (81.96 mg/g) from the Langmuir equation was very close to the experimental value of $q_{\text{max,exp}}$ (77.16 mg/g). These results suggested the Pb(II) adsorption process can be well described using the Langmuir model, implying monolayer coverage of Pb(II) on the surface of the adsorbent.

In addition, the essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor $R_L$ (Singh et al. 2012):

$$R_L = \frac{1}{1 + b \times C_0}$$  \hspace{1cm} (8)

where $C_0$ and $b$ are defined as previously mentioned, and $R_L$ parameter is the separation factor for predicting whether the adsorption is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). In fact, $R_L$ values vary between the range of 0.0257 and 0.2093 for all selected Pb(II) concentrations (25–250 mg/L). These $R_L$ values always lie between 0 and 1.0, indicating that the adsorption of Pb(II) onto CWSAC was greatly favorable. Meanwhile, the $q_{\text{max}}$ in this study is much higher than those of other carbonaceous materials, such as AC from precursor hazelnut husk (13.05 mg/g) (Imamoglu & Tekir 2008), AC from coconut (4.38 mg/g) (Gueu et al. 2007), and AC from peanut shell (35.5 mg/g) (Xu & Liu 2008). Therefore, CWSAC could be considered as a promising adsorbent for lead removal from wastewater.

**Kinetic modeling**

In the present study, pseudo-first-order and pseudo-second-order models were used to fit the experimental data on Pb(II) adsorption by CWSAC. The kinetic model parameters derived from the fitting of Figure 1 data, including the

<table>
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<tr>
<th>Table 2</th>
<th>Adsorption equilibrium constants obtained from Langmuir and Freundlich isotherms</th>
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<tr>
<td>Langmuir</td>
<td>Freundlich</td>
</tr>
<tr>
<td>$q_{\text{max,cal}}$ (mg/g)</td>
<td>$b$ (L/mg)</td>
</tr>
<tr>
<td>81.96</td>
<td>0.1511</td>
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kinetic constant ($k$), square of correlation coefficient ($R^2$) and equilibrium adsorption capacity ($q_{e,cal}$), are presented in Table 3. Besides, $q_{e,exp}$ and the theoretical values of equilibrium adsorption capacity ($q_{e,cal}$) were also compared in Table 3.

Obviously, the $R^2$ values of the pseudo-first-order model are not only much closer to 1.0, but also greater than those of the pseudo-second-order model. In addition, the adsorption capacity calculated from the pseudo-first-order model ($q_{e,cal}$) is much closer to the experimental values ($q_{e,exp}$), and yet it is not the case for the equilibrium adsorption capacity derived from the pseudo-second-order model ($q_{e,cal}$). Based on these findings, it can be concluded that the adsorption of Pb(II) onto CWSAC was better fitted to the pseudo-first-order kinetic model. Although this result is in agreement with similar studies on Pb(II) adsorption by AC from coconut and seed hull of palm tree (Gueu et al. 2011), it is different from a previous report on Pb(II) adsorption by AC developed from apricot stone which followed pseudo-second-order kinetics (Mouni et al. 2011).

### CONCLUSIONS

In this study, the equilibrium and kinetics of Pb(II) adsorption onto CWSAC were investigated. The influence of temperature, pH, contact time, adsorbent dosage and initial Pb(II) concentration was examined. Based on the present research, the following conclusions could be drawn:

1. The effect of temperature on the Pb(II) adsorption is negligible, but the Pb(II) removal efficiency increased with increasing pH in the pH range of 2.0–5.5.
2. The adsorption capacity for Pb(II) was increased with an increase in the initial concentration of Pb(II). The adsorption isotherm can be much better defined by the Langmuir equation over the initial Pb(II) concentration range studied. The maximum Pb(II) adsorption capacity calculated from the Langmuir model was 81.96 mg/g.
3. The adsorption of Pb(II) was rapid and reached equilibrium within 150 min. The pseudo-first-order kinetic model was found to correlate the experimental data well. The high adsorption capacity suggested that CWSAC exhibited highly potent for applications for the removal of Pb(II) from wastewater.

### ACKNOWLEDGEMENTS

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### REFERENCES


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