Kinetics and equilibrium adsorption study of p-nitrophenol onto activated carbon derived from walnut peel
Xiaohong Liu, Fang Wang and Song Bai

ABSTRACT

An original activated carbon prepared from walnut peel, which was activated by zinc chloride, was modified with ammonium hydroxide or sodium hydroxide in order to contrast the adsorption property of the three different activated carbons. The experiment used a static adsorption test for p-nitrophenol. The effects of parameters such as initial concentration, contact time and pH value on amount adsorbed and removal are discussed in depth. The thermodynamic data of adsorption were analyzed by Freundlich and Langmuir models. The kinetic data of adsorption were measured by the pseudo-first-order kinetics and the pseudo-second-order kinetics models. The results indicated that the alkalized carbon samples derived from walnut peel had a better performance than the original activated carbon treated with zinc chloride. It was found that adsorption equilibrium time was 6 h. The maximum removal rate of activated carbon treated with zinc chloride for p-nitrophenol was 87.3% at pH 3, whereas the maximum removal rate of the two modified activated carbon materials was found to be 90.8% (alkalized with ammonium hydroxide) and 92.0% (alkalized with sodium hydroxide) at the same pH. The adsorption data of the zinc chloride activated carbon were fitted to the Langmuir isotherm model. The two alkalized activated carbon samples were fitted well to the Freundlich model. The pseudo-second-order dynamics equation provided better explanation of the adsorption dynamics data of the three activated carbons than the pseudo-first-order dynamics equation.

Key words | adsorption, modified activated carbon, p-nitrophenol, walnut peel

INTRODUCTION

The presence of p-nitrophenol in the aquatic environmental has been a big concern to advocates for the environment due to its increased discharge, toxic nature, persistence and other adverse effects on receiving waters. It is an important contaminant discharged from plenty of industries such as pesticides, medicines and dyes. There are many methods for p-nitrophenol removal, which include chemical methods, physical methods and biological methods. Physical methods consist of adsorption, membrane separation, extraction, etc (Deniz & Karaman 2011; Dubey & Shiwani 2012). Adsorption is an attractive process, in view of its efficiency and easy operation, which can be applied to the treatment of wastewater with ease and does not release any other pollution into the environment.

The uses of adsorbents have been reported, such as activated carbon, activated carbon fiber, macroporous resin, fly ash, bentonite and bamboo charcoal. Among all the adsorbing substances, activated carbon has been widely used as a powerful adsorbent because of its well-developed pore structure, high surface area, high mechanical strength, chemical stability, easy regeneration, and insolubility in water and organic solvents (Julinova & Slavik. 2012; Kumar et al. 2012).

Recently, some investigators have carried out the feasibility of using many agricultural byproducts or wastes to make activated carbon (Han et al. 2011; Mehrizad et al. 2012; Cerino-Cordova et al. 2013; Lang et al. 2013); nevertheless walnut peel has been infrequently used to prepare activated carbon, in the literature searches. There are large areas of walnut trees in Shaanxi province in China, amounting to about 252 thousand hm² 2. The discarded peel not only is a waste of resource, but pollutes the ecological environment. In this work, firstly, activated carbons were prepared with walnut peel which was activated by zinc...
chloride, and then modified by ammonium hydroxide or sodium hydroxide. The three different activated carbon materials were used to explore their adsorptive properties. The aim of this study is to investigate walnut peel as a new material for the adsorption process and find some new ideas about the adsorption of p-nitrophenol with activated carbon derived from walnut peel, with or without modification by the action of alkaline matter.

**EXPERIMENTAL**

**Preparation of adsorbents**

The preparation of zinc chloride has been infrequently used activated carbon (AC1)

The collected walnut peel was washed with distilled water to remove sand and other impurities. Dried in shade, the materials were then impregnated in 25 mL of zinc chloride solution and held in a thermostatic water bath at 80 °C for 24 h, and then again dried at 105 °C. After activation in a muffle furnace at 500 °C for 2.5 h, the materials was cooled down, and washed with deionized water until a neutral pH was obtained. The resulting material was named as AC1. Characteristics of the sample AC1 are given in Table 1.

Activated carbon modified by sodium hydroxide (AC2)

AC1 (10 g) was alkalized with sodium hydroxide (100 mL, 17%), and held in a thermostatic water bath oscillator at 60 °C for 2 h, followed by filtering and drying in a muffle furnace at 500 °C for 2.5 h. The final material was designated the code AC2.

Activated carbon modified by ammonium hydroxide (AC3)

AC1 (5 g) was soaked in ammonium hydroxide (50 mL, 10%), held in a thermostatic water bath oscillator at 60 °C for 2 h, and after that the sample was filtered and placed in a muffle furnace at 500 °C for 2.5 h. Finally, the material was taken out and named as AC3.

**Batch adsorption studies**

These experiments were carried out by adding a fixed quantity of activated carbon into nitrophenol solution with a known volume and concentration; then the sample was oscillated at a fixed temperature and pH value. The treated samples were filtered and the supernatant was analyzed for p-nitrophenol using ultraviolet spectroscopy and the absorbance was measured. Then the mass concentration of the solution was calculated. The following formulae were used to calculate adsorption capacity and removal rate:

\[
q_t = \frac{(c_0 - c_t)}{m} V, \quad \beta = \frac{c_0 - c_t}{c_0} \times 100\%
\]

where \( \beta \) is the removal rate (%), \( c_0 \) is the initial concentration (mg L\(^{-1}\)), \( c_t \) is the concentration of treated solution (mg g\(^{-1}\)), \( q_t \) is the amount of p-nitrophenol adsorbed by unit weight of adsorbent at time \( t \) (mg g\(^{-1}\)), \( V \) is the volume of the solution (L), \( m \) is the quality of the activated carbon (g) (Behera et al. 2012; Chi & Yang 2012; Mendez-Diaz et al. 2012; Ozer et al. 2012).

At room temperature, adsorption experiments were carried out at increasing oscillation times (1, 2, 3, 4, 5, 6, 7, 8 h) with 0.05 g adsorbent (every solution with different contact time was in separate conical flasks). The carbon was separated from the solution by filtering, and the supernatant was analyzed for p-nitrophenol using ultraviolet spectroscopy. Then the absorbance was obtained, as well as the adsorption capacity and removal rate of p-nitrophenol onto activated carbon at different oscillation time. The adsorption process described above was repeated for the three activated carbon materials (AC1, AC2, AC3).

Adsorption experiments were performed at room temperature by adding the adsorbents into a known volume of solution of different initial pH (2, 3, 4, 5, 6, 7, 8, 9) separately and keeping all the other experimental variables, viz. adsorbents dose (0.05 g), initial concentration (100 mL, 50 mg/L),

### Table 1 | The specific BET (Brunauer–Emmett–Teller) surface area, pore volume and average aperture distributions of the sample AC1

<table>
<thead>
<tr>
<th>BET surface area (m(^2) g(^{-1}))</th>
<th>Internal surface area</th>
<th>External surface area</th>
<th>Total pore volume (mL g(^{-1}))</th>
<th>Mesopore volume (mL g(^{-1}))</th>
<th>Micropore volume (mL g(^{-1}))</th>
<th>Mesopore ratio (%)</th>
<th>Average aperture (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1258.05</td>
<td>963.67</td>
<td>294.38</td>
<td>0.6399</td>
<td>0.2059</td>
<td>0.4340</td>
<td>32.18</td>
<td>2.15</td>
</tr>
</tbody>
</table>
and shaking time (6 h) constant, adding the adsorbent into every nitrophenol solution with different pH value. The reaction mixture was shaken, after then filtered and the absorbance was determined using ultraviolet spectroscopy. Finally, the concentration in the filtrate, adsorption capacity and removal rate of p-nitrophenol onto activated carbon at various pH value were valued. The adsorption process described above was repeated for the three activated carbon materials (AC1, AC2, AC3).

For the assessment of the effect of nitrophenol concentration on adsorption, nitrophenol solutions (100 mL, pH 3) ranging from 10 to 150 mg/L were used at room temperature, to which was added fixed dose of activated carbon adsorbents of 0.05 g separately (every solution with different concentration was in separate conical flask). The reaction mixture was shaken for 6 h. Then the supernatant liquids were filtered and the absorbance in each flask was determined using ultraviolet spectroscopy. Adsorption capacity and removal rate of p-nitrophenol onto activated carbon at various nitrophenol concentration were calculated. The adsorption process described above was repeated for the three activated carbon materials (AC1, AC2, AC3).

RESULTS

Effect of contact time

The removal rate and the adsorption capacity increased with increase of contact time, and the rate of adsorption became slower gradually after 2 h and reached a saturation state at 6 h. Therefore, 6 h was selected as the optimum contact time for all further experiments. Results are presented in Figure 1 and Figure 2. The removal rate of the three adsorbents was determined as 85.96%, 92.24% and 86.39% for AC1, AC2 and AC3, respectively. The concentration of p-nitrophenol retained in the adsorbent phase (AC1, AC2, AC3) were 85.62 mg g\(^{-1}\), 91.87 mg g\(^{-1}\) and 86.05 mg g\(^{-1}\). Among the three adsorbents studied, the two alkalized activated carbons (AC2, AC3) were found to be more effective than the other adsorbent (AC1). This may be due to the sharply increasing alkaline oxygen-containing groups at the outer surface offered by the adsorbents after the alkalization. Therefore the special adsorbent presented a great removal potential of phenol organic matter are ascribed to increase of its hydrophobicity (Qureshi et al. 2012; Ren et al. 2012).

Effect of pH

The pH is an important an variable in the adsorption process. The binding of p-nitrophenol by surface functional groups was strongly pH dependent (Figures 3 and 4). In the pH range of 2.0–6.0, the removal rate of the three
absorbents (AC1, AC2 and AC3) decreased from 85% to 80%, 91% to 84.5% and 88.8% to 85.8%, respectively, and the negative changes in value were 5%, 6.5% and 3%. In the pH range of 6.0–9.0, the removal rate of the three absorbents (AC1, AC2 and AC3) decreased from 80% to 58%, 85% to 74%, and 85% to 69%, viz., the negative changes in value were 22, 11 and 16%. With the increase of pH from 2.0 to 6.0, the adsorption capacity of the three activated carbons decreased from 84.78 mg g\(^{-1}\)/C0\(^{1}\) to 80.17 mg g\(^{-1}\)/C0\(^{1}\), 93.74 mg g\(^{-1}\)/C0\(^{1}\) to 84.17 mg g\(^{-1}\), and, 88.43 mg g\(^{-1}\) to 83.94 mg g\(^{-1}\), a decrease of 4.61%, 9.57% and 4.49%, respectively. With the increase of pH from 6.0 to 9.0, the adsorption capacity of the three activated carbons decreased from 80.17 to 57.80 mg g\(^{-1}\), 84.17 to 73.41 mg g\(^{-1}\), and 83.94 to 69.05 mg g\(^{-1}\), viz., the negative changes in value were 22.37, 10.76 and 14.89%. Thus, the more acidic the medium, the higher the removal percentage. The effect of pH on the adsorption could be explained by considering the ionization degree of the adsorbate. There is a lower degree of ionization for \(p\)-nitrophenol in acidic condition (Shaikh et al. 2012).

**Effect of initial concentration**

It is evident from Figures 5 and 6 that AC2 and AC3 have a better removal behavior; the percentage removal of \(p\)-nitrophenol decreased and adsorption capacity increased with increasing initial concentrations. It was clear that, when the initial concentration changed from 10 mg/L to 150 mg/L, the removal rate of \(p\)-nitrophenol decreases approximately from 86% to 45% for AC1, from 94.7% to 73% for AC2 and from 92% to 57.7% for AC3, respectively. Simultaneously, the adsorption capacity of the three absorbents (AC1, AC2 and AC3) ranged from 17.2 mg g\(^{-1}\) to 133.36 mg g\(^{-1}\), 18.87 mg/g to 219 mg g\(^{-1}\), and 18.32 mg g\(^{-1}\) to 172.46 mg g\(^{-1}\), respectively. This could be due to the known quantity of dosage with fixed number of surface functional groups which give rise to the certain amount of removal. At lower concentration, the uptake amount of \(p\)-nitrophenol at equilibrium is nearly the same as the total amount, and hence there is a higher removal rate. In contrast, at higher concentration, the adsorbed amount of \(p\)-nitrophenol is invariably less than the initial amount in solution; hence the smaller removal rate is generated. The total adsorbed amount of \(p\)-nitrophenol increased with the increasing initial concentration. So it can be concluded that the amount adsorbed increased with the increase of initial concentration.

**Adsorption isotherms**

The analysis of the isotherm data is important to develop an equation which can be used for describing the reaction mechanism between adsorbate and adsorbents. And it is
responsible for moving forward a single step in the conditions of the adsorption process. The isotherm is described by the following equations (Shaikh et al. 2012).

Langmuir model:
\[
\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b}
\]

Freundlich model:
\[
\lg q_e = \lg k_f + \frac{\lg c_e}{n}
\]

It can be seen from Table 2 and Figures 7 and 8 that the experimental data of AC1 fit well with the Langmuir adsorption isotherm and the values of correlation coefficients \(R^2\) whereby \(R^2_1 > R^2_2\), but the data of AC2 and AC3 are similar in shape to the Freundlich model, as \(R^2_1 < R^2_2\).

Sorption kinetics

Kinetic modeling of the \(p\)-nitrophenol data was studied using the pseudo-first-order kinetics equation and the pseudo-second-order kinetics equation. They are represented as
\[
\ln (q_e - q_t) = \ln q_e - k_1 t \quad \text{and} \quad \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}
\]
(Zhang & Ren 2013).

Table 3 and Figures 9 and 10 show that, when the data are analyzed using the second-order dynamic model, the values of \(R^2\) for the three adsorbents are all above 0.999, and the theoretical ‘\(q\)’ values are very close to the actual values (Figure 2). The results show that the experimental data about adsorption dynamics of the three adsorbents are more likely to be adjusted to the second-order rate kinetics model.

CONCLUSION

These experimental studies have indicated that activated carbons obtained by walnut peel have the potential to act
as an adsorbent for the removal of p-nitrophenol. The percentage removal and the adsorption capacity increase with the increase of time, and the optimum adsorption appears at 6 h. The acidic condition plays an important role in the adsorption. The adsorption capacity and removal rate increase with decrease of pH value and it is clear that the optimum pH conditions for removal of p-nitrophenol by adsorption onto all the three adsorbents studied was 5.0. Above and below this pH, the extent of adsorption was found to be quite low. The adsorption capacity increases and removal efficiency decreases with an increase in the initial concentration. The adsorption data of the carbon activated by zinc chloride (AC1) fit the Langmuir adsorption isotherm. The data of AC2 and AC3 are given a good explanation by the Freundlich model. The experimental values about adsorption dynamics of the three kinds of activated carbon are more likely to be adjusted to the pseudo-first-order kinetics equation. The alkaline modification of activated carbon has an obvious positive influence on the adsorption capacity and removal efficiency.

Zhou Shan and colleagues reported that the adsorption ratio of p-nitrophenol and adsorption amount could reach 82.5% and 2.06 mg g\(^{-1}\), respectively, under the conditions of 10 °C, p-nitrophenol concentration of 50 mg L\(^{-1}\), bamboo-carbon size of 0.106-0.090 mm, bamboo-carbon dosage of 20.0 g L\(^{-1}\), and adsorption time of 120 min (Zhou et al. 2008). Dou and colleagues discovered that a dosage of 2.1 g L\(^{-1}\) of active carbon derived from peanut hull was required to attain the removal rate of 95% of p-nitrophenol for its initial concentration of 200 mg L\(^{-1}\) (Dou et al. 2011). In comparison with above adsorbents, the three kinds of activated carbon derived from walnut peel have a higher removal efficiency of p-nitrophenol at a lower dosage.

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