Comparisons of porous and adsorption properties of carbons activated by steam and KOH

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Abstract

In this work, fir woods and pistachio shells were used as source materials to prepare porous carbons, which were activated by physical (steam) and chemical (KOH) methods. Pore properties of these activated carbons including the BET surface area, pore volume, pore size distribution, and pore diameter were first characterized by a t-plot method based on N2 adsorption isotherms. Highly porous activated carbons with BET surface area up to 1009–1096 m²/g were obtained. The steam and KOH activation methods produced carbons with mesopore content in the range 9–15 and 33–49%, respectively. The adsorption equilibria and kinetics of tannic acid, methylene blue, 4-chlorophenol, and phenol from water on such carbons at 30°C were then investigated to check their chemical characteristics. The Freundlich equation gave a better fit to all adsorption isotherms than the Langmuir equation. On the other hand, the intraparticle diffusion model could best follow all adsorption processes. In comparison with KOH-activated carbons, it was shown that the rate of external surface adsorption with steam-activated carbons was significantly higher but the rate of intraparticle diffusion was much lower.

Keywords: Activated carbons; Steam activation; KOH activation; Porous properties; Adsorption equilibrium; Kinetics

1. Introduction

Liquid-phase adsorption has been shown to be highly efficient for removal of colors, odors, organic, and inorganic matter from process or waste effluents. Activated carbons (granular or powdered) are the most widely used adsorbents because of their excellent adsorption capability for organic pollutants [1]. The properties of activated carbons depend on the activation process and the nature of the source materials. Moreover, in both physical and chemical activation processes, knowledge of different variables is very important in developing the porosity of the carbons [2]. The high adsorption capacities of activated carbons are related to properties such as surface area, pore volume, and porosity [3]. Particularly, the development of micropores and mesopores is of great importance because it allows the porous carbons to adsorb large amounts and various types of chemical compounds from gas or liquid streams. The recent progress of industrial technology provides new applications fields for porous carbons, such as supercapacitors, and, at the same time, requires the carbons to have a desired pore structure [4].

Activated carbons are important materials, which have been widely used in various industrial applications [5–7]. In general, carbon materials with the unique pore size distribution are due to the differences in precursors and treatments [8]. In addition, activated carbons used in supercapacitors must have highly electrochemically accessible surface areas with mesoporous structures, which are the typical characteristics of wood-derived activated carbons [5]. In our laboratory, a series of studies were conducted to prepare porous carbons from various wood wastes and fruit shells by a physical activation method (steam), in which these carbons have
been evaluated for the possibility of applications in industrial pollution control [5,9,10]. The aim of this work was to prepare porous carbons from fir woods and pistachio shells by physical (steam) and chemical (KOH) activation processes. Physical properties of the carbons including the BET surface area, pore size distribution, and the total pore volume were compared. Their capacities and mechanisms for the adsorption of tannic acid, methylene blue, 4-chlorophenol, and phenol from water are systematically discussed.

2. Materials and methods

2.1. Preparation of the carbons by steam activation

Prior to use, fir wood and pistachio shells were dried at 110 °C for 24 h. Then they were placed in a sealed ceramic oven and heated to 550 °C at a rate of 5 °C/min. In the meantime, steam generated from deionized water (Milli-Q) in a heated tube was poured into the oven by a rate of 3 cm³/min for 3 and 2 h, respectively. The vaporized steam was quickly removed from the oven through the exhaust pipes. Under such oxygen-deficient conditions, fir wood and pistachio shells were thermally decomposed into porous carbonaceous materials and hydrocarbon compounds. This is the carbonization step.

In the subsequent activation process, the oven was continuously heated at the same rate to 900 and 890 °C, respectively. The flow rate of steam remained the same. The time for activation was 5 and 3 h, respectively. The resulting carbons were ground in a mill followed by washing with pure water and drying, and they were finally sieved in the size range 0.12–0.2 mm.

2.2. Preparation of the carbons by KOH activation

After the aforementioned carbonization step, the chars of fir woods and pistachio shells were removed, crushed, and sieved to a uniform size range of 0.833 to 1.65 mm. Equal weights of chars, KOH, and H₂O were mixed in a stainless steel beaker. After being dried at 130 °C for 24 h, the carbons were placed in sealed ceramic oven and heated at a rate of 10 °C/min to 780 °C. In the meantime, N₂ gas in a tube was let into the oven by a rate of 4 dm³/min. The time for activation was 780 °C was 1 h. The activated products were cooled to room temperature and washed with deionized water. Then, the samples were poured to a beaker containing 250 cm³ of 0.1 mol/dm³ HCl and stirred for 1 h. Finally, they were washed with hot water until pH of the washed solution was about 6–7 [11].

2.3. Measurements of physical properties

The yield was calculated as the weight ratio of final carbons to the initial dried raw materials. The BET surface area of the carbons (S_p) was obtained from N₂ adsorption isotherm at 77 K with a sorptimeter (Porous Materials, BET-202A). Prior to measurement, the samples were first dried in an oven at 130 °C overnight and were quickly placed in the sample tube. The tube was then heated at 170 °C and was evacuated for 4 h until the pressure was less than 10⁻⁴ Torr. The manufacturer’s software provided the total pore volume (V_pore) and the pore size distribution by the BJH theory [12], as well as the micropore volume (V_micro) and external surface area (S_ext) using the t-plot method [13,14]. The surface area due to the micropores (S_micro) was obtained by from difference of S_p and S_ext [15]. The points of zero charge of the final carbons were in the range 6.0–6.5 from zeta potential measurements (Malvern, Zetasizer 3000).

2.4. Procedures for adsorption experiments

Four solutes, tannic acid (TA, MW = 1701), methylene blue (MB, MW = 320), 4-chlorophenol (4-CP, MW = 128.5), and phenol (MW = 94) were analytical reagent grade (Merck). The aqueous phase for adsorption was prepared with dissolving TA, MB, 4-CP, and phenol in deionized water without pH adjustment. Under the conditions studied, the initial aqueous pH was about 3.52 with 0.29 mol/m³ of TA, 6.60 with 0.63 mol/m³ of MB, and 6.40 for 1 mol/m³ of phenol and 4-CP.

In the adsorption equilibrium experiments, an amount of carbon (0.1 g) and 0.1 dm³ of an aqueous phase were placed in a 0.25-dm³ flask and stirred for 4 days in a water bath (Haake Model K-F3) at 30 °C. Preliminary tests showed that adsorption was complete after 3 days. After filtration with glass fibers, the concentrations of solutes in aqueous phase were determined with a Hitachi UV/visible spectrophotometer (UV-2000). Each experiment was at least repeated under identical conditions. The amount of adsorption at equilibrium, q_e (mol/kg), was calculated by

\[ q_e = \frac{(C_0 - C_e)V}{W}, \]  

where \( C_0 \) and \( C_e \) are the initial and equilibrium liquid concentrations (mol/m³); \( V \) is the volume of the solution (m³); and \( W \) is the weight of dried carbons used (kg).

The kinetic experiments were made in a Pyrex glass vessel of i.d. 100 mm and height 130 mm, fitted with four glass baffles 10 mm wide. The aqueous solution (0.6 dm³) was agitated at 500 rpm using a Cole–Parmer Servodyne agitator having a six-blade, flat-bladed impeller (12 mm high, 40 mm wide). Stirring speed higher than 500 rpm had little effect on adsorption. An amount of carbon (0.6 g) was added into the vessel and the time recording was started. The vessel was also immersed in a water bath controlled at 30 °C. At pre-set time intervals, aqueous samples (5 cm³) were taken and the concentrations were similarly analyzed. The amount of adsorption at time \( t \), \( q_t \) (mol/kg), was similarly calculated by

\[ q_t = \frac{(C_0 - C_t)V}{W}. \]
where \( C_t \) is the liquid concentration at time \( t \) (mol/m\(^3\)). The reproducibility of the measurements was within 4%.

3. Results and discussions

3.1. Physical properties of steam- and KOH-activated carbons

Identifying pore structure of the adsorbents is an essential procedure for the design and use of adsorption processes. Inert gas adsorption is a good tool for this purpose [1,16]. Fig. 1 shows the isotherms of \( \text{N}_2 \) adsorption/desorption at 77 K onto steam- and KOH-activated carbons. Unlike KOH-activated carbons, the adsorption/desorption isotherms for steam-activated carbons overlap completely at low relative pressures but hysteresis exists at high relative pressures \( (P/P_0 > 0.5) \) [14]. Irrespective of the source materials, hysteresis is mainly due to the presence of inkbottle types of pores [16].

A feature common to hysteresis loops is that the steep region of desorption branch leads to the lower closure point at a relative pressure (for a given adsorption), which depends mainly on the nature of the adsorption rather than the nature of porous adsorbents, e.g., for \( \text{N}_2 \) at its boiling point at \( P/P_0 = 0.42 \) and for benzene at 25 \(^\circ\)C at \( P/P_0 = 0.28 \) [14]. According to the Kelvin equation, the inkbottle types of pores have a large pore size, given that for the samples hysteresis occurs at high relative pressures \( (P/P_0 > 0.5) \) [14]. On the other hand, the isotherms for KOH-activated carbons are of Langmuir type [14]. The initial (steepest) part represents micropore filling (rather than surface coverage) and the low slope of the plateau is due to multilayer adsorption on the small external area. That is, the Langmuir-type isotherms are given for the microporous solids having relatively small external surface area.

According to the definition from IUPAC, adsorbent pores are classified into three groups, i.e., micropore (size <2 nm), mesopore (2–50 nm), and macropore (>50 nm). In general, micropores account for over 95% of the total surface area for common activated carbons [1]. Fig. 2 shows the pore size distributions. Steam-activated carbons have two types of pores, micropores (0–2 nm) and mesopores (3.5–4.5 nm). In contrast, KOH activation produces mainly micropores.

Table 1 shows the pore properties of activated carbons, including \( S_p \), \( S_{micro}/S_p \), \( V_{pore} \), \( V_{micro}/V_{pore} \), \( D_p \), and yield. The \( S_p \) values obtained for the present carbons (1009–1096 m\(^2\)/g) are comparable to those of commercial ones [1], e.g., 300–600 (ICI Hydrodarco 3000), 1044 (Calgon Filtrasorb 400), 1000 (Westvaco Nuchar WL), and 1050 m\(^2\)/g (Witco 517), although some carbons prepared by chemical activation method reach above 2500 m\(^2\)/g [17]. It was reported that activated carbons prepared from apricot stones,

![Fig. 1. Adsorption/desorption isotherms of \( \text{N}_2 \) at 77 K on steam- and KOH-activated carbons derived from fir woods and pistachio shells.](image1)

![Fig. 2. Pore size distribution of the steam- and KOH-activated carbons derived from fir woods and pistachio shells.](image2)

<table>
<thead>
<tr>
<th>Source</th>
<th>Activation</th>
<th>( T_A ) (^a) (°C)</th>
<th>( t_A ) (^b) (h)</th>
<th>( S_p ) (m(^2)/g)</th>
<th>( S_{micro}/S_p )</th>
<th>( V_{pore} ) (cm(^3)/g)</th>
<th>( V_{micro}/V_{pore} )</th>
<th>( D_p ) (nm)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fir woods</td>
<td>Steam</td>
<td>900</td>
<td>5</td>
<td>1016</td>
<td>0.70</td>
<td>0.75</td>
<td>0.51</td>
<td>2.9</td>
<td>10.4</td>
</tr>
<tr>
<td>Pistachio</td>
<td>Steam</td>
<td>890</td>
<td>3</td>
<td>1009</td>
<td>0.86</td>
<td>0.67</td>
<td>0.67</td>
<td>2.6</td>
<td>13.6</td>
</tr>
<tr>
<td>Fir woods</td>
<td>KOH</td>
<td>780</td>
<td>1</td>
<td>1064</td>
<td>0.93</td>
<td>0.61</td>
<td>0.84</td>
<td>2.3</td>
<td>14.9</td>
</tr>
<tr>
<td>Pistachio</td>
<td>KOH</td>
<td>780</td>
<td>1</td>
<td>1096</td>
<td>0.94</td>
<td>0.61</td>
<td>0.91</td>
<td>2.2</td>
<td>22.7</td>
</tr>
</tbody>
</table>

\(^a\) Activation temperature.
\(^b\) Activation time.
grape seeds, and cherry stones had an \( S_p \) value of 1175, 487, and 836 m\(^2\)/g, respectively [18]. The fractions of micropore area, \( S_{micro}/S_p \), for the carbons derived from fir woods and pistachio shells by KOH activation are 0.93 and 0.94, respectively, which are larger than those obtained by steam activation (0.70 and 0.86). This indicates that KOH activation produces more micropores, as clearly shown in Fig. 2. The fractions of micropore volume, \( V_{micro}/V_{pore} \), also support the conclusion that KOH activation produces more micropore volume. For example, the carbons derived from fir woods and pistachio shells have the fractions of 0.84 and 0.91 (KOH activation), and 0.51 and 0.67 (steam activation), respectively.

On the other hand, steam activation produces larger pore size \( D_p \). They are 2.2–2.3 nm by KOH activation and 2.6–2.9 nm by steam activation. The present \( D_p \) values for KOH-activated carbons are comparable to commercially available activated carbons such as 0.91 (Spectracorp M-10), 1.5 (Spectracorp M-20), 2.2 (Calgon F400), 2.0 (Barney Cheney SK1301), 1.9 (Westvaco Nuchar MV-L), and 2.3 nm (Westvco WV-DC). The \( D_p \) values of 2.1, 2.4, 1.5, and 2.4 nm were reported for the carbons derived from coconut shells, palm seeds, bagasse, and plum kernel, respectively [5,10,19].

Finally, the yield of the carbons prepared by chemical activation is 1.4–1.7 times larger than that at carbons by physical activation method. An important advantage of chemical activation process is that it normally proceeds at lower temperature and takes shorter time than those required in physical activation [2]. The higher yield from chemical activation is because the chemical agents used are substances with dehydrogenation properties that inhibit formation of tar and reduce the production of other volatile products [2,20].

The main surface functional groups present in char surface are carbonyl groups (e.g., ketone and quinone) and aromatic rings [21–23]. For the carbon activated at high temperatures (900 °C) and long holding times (60 min), only aromatic rings are remained [23]. These surface functional groups are generally neutral (or slightly acidic), which should not have much effect on adsorption capacity of the carbon [23].

### 3.2. Adsorption equilibrium

The adsorption isotherms of TA, MB, 4-CP, and phenol on steam- and KOH-activated carbons at 30 °C are shown in Figs. 3–6. The correlation of isotherms by theoretical or empirical equations is essential to practical operation. The widely used two-parameter Langmuir equation is given as

\[
\frac{C_e}{q_e} = \left( \frac{1}{K_L q_{mon}} \right) + \left( \frac{1}{q_{mon}} \right) C_e,
\]

where \( q_{mon} \) is the amount of adsorption corresponding to monolayer coverage (mol/kg) and \( K_L \) is the Langmuir constant (m\(^3\)/mol). Linear plots of \( (C_e/q_e) \) vs \( C_e \) give \( K_L \) and
The value of $\Delta q_e$ for the Langmuir equation is large (2.7–23.0%). Basically, Eq. (3) is intended for a homogeneous surface although it obeys Henry’s law at very low concentrations. The poor fit of the isotherm data is likely due to the highly heterogeneous surface of steam- and KOH-activated carbons. On the other hand, the Freundlich fit is better ($\Delta q_e = 0.5$–5.9%). This equation is suitable for a highly heterogeneous surface, which often gives a good representation of adsorption data over a restricted range of concentrations [24].

It should be noted that the physically meaningful quantity $q_{mon}$ in the Langmuir equation is still treated as the adsorption capacity for comparison in this work, although the Langmuir fit is worse. For higher MW solutes such as TA, it is observed from Table 2 that the adsorption capacity with steam-activated carbon is higher than that with KOH-activated carbon. This is consistent with the result that steam-activated carbons have more external surface area. For lower MW solutes such as 4-CP and phenol, the adsorption capacity with both steam- and KOH-activated carbons is comparable.

### 3.3. Adsorption kinetics

The large number and array of different functional groups on carbon surface (e.g., carboxylic, carbonyl, hydroxyl, ether, quinone, lactone, anhydride, etc.) imply that there are many types of solute–adsorbent interaction [25]. Any kinetic or mass transfer representation is likely to be global. From a system design viewpoint, a lumped analysis of adsorption rates is sufficient for practical operation. Three simplified kinetic models are adopted to examine the mechanism of adsorption processes such as mass transfer and chemical reaction.

### Table 2

<table>
<thead>
<tr>
<th>Solute</th>
<th>Adsorbent</th>
<th>Langmuir equation</th>
<th>Freundlich equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$q_{mon}$ (mol/kg)</td>
<td>$\Delta q_e$ (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1/n$</td>
<td>$K_F$ (g/kg)(g/m^3)$^n$</td>
</tr>
<tr>
<td>TA</td>
<td>Fir woods (steam)</td>
<td>0.43</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>Fir woods (KOH)</td>
<td>0.28</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>Pistachio (steam)</td>
<td>0.39</td>
<td>17.1</td>
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<tr>
<td></td>
<td>Pistachio (KOH)</td>
<td>0.24</td>
<td>8.4</td>
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<td>MB</td>
<td>Fir woods (steam)</td>
<td>1.59</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>Fir woods (KOH)</td>
<td>1.61</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>Pistachio (steam)</td>
<td>1.71</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>Pistachio (KOH)</td>
<td>1.63</td>
<td>23.0</td>
</tr>
<tr>
<td>4-CP</td>
<td>Fir woods (steam)</td>
<td>3.21</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>Fir woods (KOH)</td>
<td>3.35</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>Pistachio (steam)</td>
<td>2.97</td>
<td>15.6</td>
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<tr>
<td></td>
<td>Pistachio (KOH)</td>
<td>3.17</td>
<td>17.8</td>
</tr>
<tr>
<td>Phenol</td>
<td>Fir woods (steam)</td>
<td>2.72</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>Fir woods (KOH)</td>
<td>2.74</td>
<td>8.3</td>
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<tr>
<td></td>
<td>Pistachio (steam)</td>
<td>2.58</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>Pistachio (KOH)</td>
<td>3.03</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Fig. 6. Adsorption isotherms of phenol at 30 °C on the carbons activated by steam and KOH (the curves are calculated by the Freundlich equation).

$q_{mon}$. On the other hand, the widely used empirical Freundlich equation is given by

$$\log q_e = \log K_F + (1/n) \log C_e,$$

where $n$ and $K_F$ are the constants for a given solute–adsorbent system, which are obtained from a linear plot of $\log q_e$ vs $\log C_e$.

In order to compare the validity of two isotherm equations definitely, a normalized standard deviation $\Delta q_e$ (%) is calculated,

$$\Delta q_e(\%) = 100 \sqrt{\frac{\sum [(q_{e,exp} - q_{e,cal})/q_{e,exp}]^2}{(N - 1)}},$$

where $N$ is the number of data points.

The parameters obtained in two isotherm equations, together with $\Delta q_e$, are listed in Table 2. It is found that

In order to compare the validity of two isotherm equations definitely, a normalized standard deviation $\Delta q_e$ (%) is calculated,
First, the kinetics of adsorption is analyzed by the pseudofirst-order equation [26,27]

\[ \frac{dq_t}{dt} = k_1(q_e - q_t), \]

where \( k_1 \) is the pseudo-first-order rate constant (1/min) and \( q_e \) denotes the amount of adsorption at equilibrium. After integration by applying the initial conditions \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_t \) at \( t = t \), Eq. (6) becomes

\[ \log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right)t. \]

where the values of \( q_e \) must be obtained independently from equilibrium experiments.

The pseudo-second-order equation based on adsorption capacity has the form [28]

\[ \frac{dq_t}{dt} = k_2(q_e - q_t)^2, \]

where \( k_2 \) is the pseudo-second-order rate constant (mol/(g min)). Integrating Eq. (8) and applying the initial conditions, we have

\[ \frac{t}{q_e} = \frac{1}{k_2q_e^2} + \left( \frac{1}{q_e} \right)t. \]

(9)

It is noticed that \( k_2 \) and \( q_e \) in Eq. (9) can be obtained beforehand from the intercept.

Because the above two models cannot identify a diffusion mechanism, the intraparticle diffusion model is also tested. This model refers to the theory proposed by Weber and Morris [29]. The fractional approach to equilibrium will change according to a function of \((Dt/r^2)^{1/2}\), where \( r \) is the particle radius and \( D \) is the diffusivity of solutes within the particle. The initial rate of intraparticle diffusion can be obtained by linearization of the curve \( q_t = f(t^{1/2}) \) [29–31].

Evidently, the validity of these models can be checked by each linear plot of \( \log(q_e - q_t) \) vs \( t \), \( (t/q_t) \) vs \( t \), and \( q_t \) vs \( t^{1/2} \), respectively. The applicability of each model is quantitatively determined from the normalized standard deviation \( \Delta q_t \) calculated similarly to Eq. (5). Table 3 lists the results. It is seen that the adsorption of MB and phenol is best described by the intraparticle diffusion model; the values of \( \Delta q_t \) are less than 2.8 and 4.7%, respectively.

### Table 3

<table>
<thead>
<tr>
<th>Solute</th>
<th>Adsorbent</th>
<th>1st order ( \Delta q_t ) (%)</th>
<th>2nd order ( \Delta q_t ) (%)</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( k_{p1} ) (mol/(kg min(^{1/2})))</td>
<td>( k_{p2} ) (mol/(kg min(^{1/2})))</td>
<td>( \Delta q_t ) (%)</td>
</tr>
<tr>
<td>MB</td>
<td>Fir woods (steam)</td>
<td>3.2</td>
<td>7.8</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Fir woods (KOH)</td>
<td>5.6</td>
<td>18.9</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Pistachio (steam)</td>
<td>3.9</td>
<td>14.3</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>Pistachio (KOH)</td>
<td>8.2</td>
<td>17.9</td>
<td>0.18</td>
</tr>
<tr>
<td>Phenol</td>
<td>Fir woods (steam)</td>
<td>2.8</td>
<td>5.7</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>Fir woods (KOH)</td>
<td>5.6</td>
<td>9.8</td>
<td>0.37</td>
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<td></td>
<td>Pistachio (steam)</td>
<td>3.4</td>
<td>6.9</td>
<td>0.59</td>
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<td></td>
<td>Pistachio (KOH)</td>
<td>7.6</td>
<td>10.5</td>
<td>0.41</td>
</tr>
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</table>

### 3.4. Comments on adsorption mechanism

Figs. 7 and 8 show a linear fit of the intraparticle diffusion model. Such types of plots present multilinearity, indicating that two or more steps take place [32]. The first, sharper
portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. In some cases, the third portion exists, which is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution. It is evident that the rate of external surface adsorption (stage 1) with steam-activated carbons is higher than that with KOH-activated carbons for the adsorption of MB and phenol. Stage 1 is completed within about 5 min and the stage of intraparticle diffusion control (stage 2) is then attained. However, stage 3 (final equilibrium stage) is absent here over the whole range studied.

In general, the slope of the line in each stage is called the rate parameter \( k_{pi} (i \text{ stage number}) \). As discussed above, MB and phenol are slowly transported via intraparticle diffusion into the particles and are finally retained in micropores. The rate parameters for MB and phenol (Table 3) show that the \( k_{p1} \) value with steam-activated carbons is larger than that with KOH-activated carbons. This is because steam-activated carbons have a larger external surface area for solute adsorption instantaneously. In contrast the \( k_{p2} \) value with KOH-activated carbons is larger than that with steam-activated carbons, indicating that KOH-activated carbons possess more micropores for intraparticle diffusion.

Under comparable conditions, phenol has smaller \( k_{p1} \) and \( k_{p2} \) values than MB. Phenol exists mostly as undissociated forms in water before and after adsorption (pH < 8.19) since it has a pK\(_a\) of 9.92 [10]. The hydrogen binding between the hydroxyl group of phenol and the functional groups such as carboxylic acid on carbon surface can explain such results. One possible reason is the oxidative coupling of phenol on carbon surface [33], especially under conditions of relatively high pH or high availability of oxygen. In fact, desorption of phenol from the loaded carbons with deionized water at 30 °C was found to be inefficient (<40%).

4. Conclusions

The physical properties of the fir-wood- and pistachio-shell-based porous carbons activated by steam and KOH, as well as their characteristics for liquid-phase adsorption, were investigated. The following results are obtained:

(1) For N\(_2\) adsorption/desorption isotherms, hysteresis was present only with steam-activated carbons even at high relative pressures. On the other hand, KOH-activated carbons showed the Langmuir type, indicating a relatively small external surface area for the carbons.

(2) Irrespective of the source materials, KOH activation produced more micropores than steam activation. In other words, steam activation produced a larger mean pore diameter (2.6–2.9 nm) than KOH activation (2.2–2.3 nm).

(3) All the isotherms were better described by the Freundlich equation. The adsorption capacity of high MW solute such as tannic acid with steam-activated carbon was higher, but the adsorption capacity of low MW solute such as 4-chlorophenol or phenol with steam- and KOH-activated carbons was comparable.

(4) The adsorption of methylene blue and phenol on steam- and KOH-activated carbons obeyed the intraparticle diffusion model. Rate parameters showed that steam-activated carbons had much higher rate of external surface adsorption but KOH-activated carbons had higher rate of intraparticle diffusion.

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Appendix A. Nomenclature

- \( C_t \): solute concentration in the aqueous phase at time \( t \) (mol/m\(^3\))
- \( C_0 \): initial solute concentration in the aqueous phase (mol/m\(^3\))
- \( D_p \): mean pore diameter (nm)
- \( k_1 \): rate constant of pseudo-first-order equation defined in Eq. (6) (1/min)
- \( k_2 \): rate constant of pseudo-second-order equation defined in Eq. (8) (kg/(mol min))
- \( k_{pi} \): rate parameter of intraparticle diffusion model at stage \( i \) (mol/(kg min\(^{1/2}\)))
- \( q_e \): amount of adsorption at equilibrium (mol/kg)
- \( q_t \): amount of adsorption at time \( t \) (mol/kg)
- \( \Delta q_e \): normalized standard deviation defined in Eq. (5) (%)
- \( S_{micro} \): micropore surface area (m\(^2\)/g)
- \( S_p \): total BET surface area (m\(^2\)/g)
- \( t \): adsorption time (min)
- \( V \): volume of the solution (m\(^3\))
- \( V_{micro} \): micropore volume (cm\(^3\)/g)
- \( V_{pore} \): total pore volume (cm\(^3\)/g)
- \( W \): amount of dry adsorbents used (kg)

References