Insights into properties of activated carbons prepared from different raw precursors by pyrophosphoric acid activation

Yuan Gao, Qinyan Yue⁎, Baoyu Gao

Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

ARTICLE INFO

Article history:
Received 12 March 2015
Revised 14 May 2015
Accepted 20 May 2015
Available online 21 July 2015

Keywords:
Solid waste
Pyrophosphoric acid
Low-cost adsorbent
Dye
Adsorption

ABSTRACT

Low-cost activated carbons (ACs) were prepared from four kinds of solid wastes: petroleum coke, Enteromorpha prolifera, lignin from papermaking black liquid and hair, by pyrophosphoric acid (H₄P₂O₇) activation. Thermo-gravimetric analysis of the pyrolysis of H₄P₂O₇-precursor mixtures implied that H₄P₂O₇ had different influences on the pyrolysis behavior of the four raw materials. N₂ adsorption/desorption isotherms, scanning electron microscopy, Fourier transform infrared spectroscopy and adsorption capacities for dyes were used to characterize the prepared activated carbons. AC derived from E. prolifera exhibited the highest surface area (1094 m²/g) and maximum monolayer adsorption capacity for malachite green (1250 mg/g). Kinetic studies showed that the experimental data were in agreement with the pseudo-second-order model. The adsorption isotherms were well described by the Langmuir isotherm model, indicating the adsorption of dye onto the ACs proceeded by monolayers.

© 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Keywords:
Solid waste
Pyrophosphoric acid
Low-cost adsorbent
Dye
Adsorption

Introduction

Activated carbons (ACs) have been extensively developed as effective adsorbents for the removal of inorganic/organic pollutants. The adsorption characteristics of ACs rely on their surface area, porous structure and surface chemical groups. The starting materials, activating agents and activation methods have significant influence on these properties. Generally, KOH, NaOH, ZnCl₂ and H₃PO₄ have been widely used as chemical activating agents for the preparation of ACs (Miao et al., 2013; Njoku et al., 2014; Rambabu et al., 2013; Wang et al., 2014). Pyrophosphoric acid, H₄P₂O₇, can be obtained by the dehydration of phosphoric acid at 213°C. In recent years, some researchers have applied H₄P₂O₇ as a novel activating agent to prepare ACs (Cheng et al., 2014; Kong et al., 2013; Liu et al., 2012). They found that H₄P₂O₇ has stronger dehydrating ability than H₃PO₄, which could create pores at low temperatures. In addition, the ACs produced by H₄P₂O₇ activation exhibited several excellent properties, such as high surface area, high mesopore content, and abundant acidic functional groups, which endowed them with good sorption affinities and capacities. However, previous works only focused on the preparation of ACs from lignin or leather by pyrophosphoric acid activation. There are no reports comparing the characteristics and adsorption properties of activated carbons prepared from different raw materials using pyrophosphoric acid as activating agent. Hence, it was necessary to carry out this research.

In fact, a large variety of precursors have been used for producing ACs including Bois carré seeds (Largitte and Lodewyckx, 2014), African biomass residues (Gueye et al., 2014), olive fruit stones (Obregón-Valencia and Sun-Kou, 2014), lotus stalk (Liu et al., 2012), seaweeds (Wang et al., 2014), and mushroom root (Cheng et al., 2014). Petroleum coke (PK), a by-product of the petroleum industry, is a common raw
material for AC preparation due to its high carbon content and low ash content (Jiang et al., 2008; Rambabu et al., 2013; Wu et al., 2005). Lignin from papermaking black liquid (LG) is widely utilized to prepare high value-added products, for example activated carbon. Enteromorpha prolifera (EP) is a marine biomass waste and is widely available, especially in the Asia-Pacific region (Özer et al., 2005; Wang et al., 2014). Hair (HR) has also been proved to be a good candidate for the synthesis of porous carbon (Guo et al., 2013). These materials possess typical coke-based, lignocellulosic, algal and fibrous properties. Thus, this study investigated the different roles of pyrophosphoric acid in reacting with these starting materials.

Synthetic dyes are extensively applied in many industries, e.g., paper, textile, leather tanning, printing, rubber and cosmetics (Bensalah et al., 2009; Yagub et al., 2014). Based on up-to-date data, the worldwide production of dyes is over 7 × 10^5 ton annually, and approximately 15% of dye-containing wastewater is discharged into the environment (Foo and Hameed, 2010b; Sen et al., 2010). Furthermore, dye wastewater has currently become one of the world’s serious environmental problems due to the dyes’ highly carcinogenic nature, mutagenic toxicity and physicochemical stability (Mahmoodi et al., 2011). Therefore, various methods, such as coagulation, photodegradation, membrane separation, microbial degradation, chemical oxidation and adsorption have been developed for the removal of dye from wastewater (de Luna et al., 2013; Toor and Jin, 2012; Vučurović et al., 2014; Xue et al., 2014). Among these technologies, adsorption is considered to be one of the most effective methods due to its simple design and ease of operation. Currently, ACs are widely used as adsorbents for dye removal from wastewater in commercial systems because of their large surface area, good thermo-stability, high mechanical strength, polymodal porous structure, variable surface chemical composition, high adsorption capacity and low cost.

In this study, pyrophosphoric acid was employed as activating agent for the preparation of ACs. The resultant carbons were characterized by scanning electron microscopy (SEM), pore structure analysis and Fourier transform infrared spectroscopy (FTIR). The adsorption capacity of the ACs was evaluated using Acid Brilliant Scarlet (anionic dye) and Malachite Green (basic dye) as the model adsorbates. The effects of adsorbent type and contact time were investigated to provide information on the adsorption characteristics of dyes on the four ACs. In addition, adsorption kinetics and isotherm tests were also performed to determine the adsorption rates and maximum adsorption capacities of the four ACs, as well as to analyze the adsorption mechanisms.

1. Experimental

1.1. Chemicals and materials

Pyrophosphoric acid (45 wt%), analytical grade Acid Brilliant Scarlet (GR) and Malachite Green (MG) were purchased from a chemical company (Sinopharm Chemical Reagent Co., Ltd, Beijing, China). All stock solutions were prepared by dissolving accurate amount of the dyes in distilled water. Various concentrations of dye solutions were diluted with distilled water. The molecular formulas of GR and MG are C_{22}H_{14}N_{4}Na_{2}O_{7}S_{2} and C_{23}H_{25}ClN_{2}, and the molecular weights are 556.49 and 364.92, respectively. All waste materials were collected and cut into pieces with diameter of 0.425 mm for further use.

1.2. Preparation of the absorbents

The four raw materials (PK, EP, LG and HR) were impregnated with H_{4}P_{2}O_{7} at a ratio of 1.5:1 (W/W) for 12 hr. Activation was achieved by heating the mixture in an electric resistance furnace (KSY-4D-16, Longkou Furnace Factory, Longkou, China) to the temperature of 450°C. The heating rate was 10°C/min and the preservation time was 60 min. The obtained samples were washed with distilled water until the pH of 6–7 was achieved. Then the samples were dried, ground, and sieved to the particle size range of 0.150–0.075 mm. The activated carbons (ACs) prepared by PK, EP, LG and HR were denoted as PCAC, EPAC, LGAC and HRAC, respectively.

1.3. Characterization

To measure how pyrophosphoric acid affected the thermal stability of the different raw materials, the thermal decompositions of the mixtures was analyzed using thermo-gravimetric analysis (SDT Q600, TA Instruments Co., Ltd, New Castle DE, USA). The surface morphologies of ACs were evaluated by employing a scanning electron microscope (S-520, Hitachi Ltd., Tokyo, Japan). The porous structure parameters of ACs were determined through N\textsubscript{2} sorption/desorption isotherms by using a surface area analyzer (JWBK122W, Beijing JWGB Sci. & Tech. Co., Ltd, Beijing, China). The surface functional groups of ACs were qualitatively characterized by using a Fourier transform infrared spectroscopy (Avatar 370, Thermo Nicolet Corporation, New York, USA).

1.4. Batch adsorption experiments

The adsorption experiments were conducted to assess the adsorption capacities of the four carbons. Each carbon (0.025 g) was mixed with 50 mL of dye solution in 250 mL Erlenmeyer flasks. The flasks were agitated at 170 r/min using a thermostatic water bath oscillator at room temperature. In kinetic tests, the initial concentrations of the dyes were 100 mg/L. The samples were withdrawn at predetermined intervals to investigate the effect of contact time. The samples were separated from the carbon particles by filtration. The residual concentrations of GR and MG were determined by using a UV–vis spectrophotometer (722E, Shanghai Spectrum Instruments Co., Ltd, Shanghai, China) at the maximum absorption wavelengths of 511 and 618 nm, respectively. In the adsorption isotherm tests, the initial concentrations of GR ranged from 50 to 600 mg/L and the initial concentrations of MG ranged from 100 to 600 mg/L. Blank control experiments were designed and conducted as described above. The amount of dye adsorbed, \( q_e \) (mg/g), was calculated as follows:

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

where \( C_0 \) (mg/L) and \( C_e \) (mg/L) are the initial and equilibrium concentration of dye, V (L) is the volume of dye solution and W (g) is the mass of adsorbent.
2. Results and discussion

2.1. Thermal analysis

Fig. 1 shows the thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of the H₄P₂O₇-raw material mixtures. A similar trend was observed for the decomposition of the four samples (Fig. 1a). However, the four samples had significant differences in their DTG curves (Fig. 1b). The weight losses of H₄P₂O₇-EP, H₄P₂O₇-LG and H₄P₂O₇-HR were 36.54%, 31.41% and 43.43%, respectively. But in the case of H₄P₂O₇-PC, the weight lost was not as great, at about 26.61%. This may be due to the highly stable micrographitic structure of petroleum coke, which is hard to decompose compared with cellulose or keratin. During heating, H₄P₂O₇ can transform into (HPO₃)₂, which can decompose or polymerize reactions. These acid derivatives can accelerate the bond cleavage reactions, promote the evolution of volatiles, occupy volume in the starting materials and further lead to the formation of new polymeric structures (Cheng et al., 2014; Liu et al., 2012).

2.2. Morphology analysis

The SEM images of the four raw materials and their corresponding carbons are presented in Fig. 2. E. prolifera exhibited a furrow-like surface morphology (Fig. 2b). The surface of petroleum coke and lignin resembled that of a stone without any obvious initial holes (Fig. 2a and c). The surface of hair displayed a filamentous structure with squamaceous walls (Fig. 2d). It is clearly seen that the surfaces of the raw materials were degraded to varying degrees by H₄P₂O₇ activation. The external surface of PCAC had shallower pores compared to other carbons (Fig. 2e). Due to the highly stable micrographitic structure and the absence of initial pores, it was difficult for the activating agent to penetrate into petroleum coke, further preventing the formation of internal pores. EPAC showed a regular and homogeneous surface morphology (Fig. 2f). A considerably different external surface was exhibited by LGAC, with some crack-like pores of various dimensions (Fig. 2g). In the case of HRAC, the pores are small and deep (Fig. 2h).

Significant differences in surface texture were observed for the carbons, which was associated with the varying natures of the raw materials.

2.3. Textural structure analysis

The pore size distribution and N₂ adsorption–desorption isotherms at 77 K of the resultant carbons are shown in Fig. 3. The type of starting material seemed to have a remarkable influence on the classification of the N₂ adsorption–desorption isotherms. EPAC possessed a typical Type IV adsorption isotherm with a significant hysteresis loop, indicating a mesoporous structure for EPAC. The adsorption–desorption isotherms of HRAC presented a Type I curve, which had dramatic adsorption at low relative pressure and then reached equilibrium. This shape suggested that HRAC possessed a narrow pore size distribution in the micropore range. These results are confirmed by the pore size distribution analysis in Table 1. EPAC gave the lowest micropore ratio of 6.78% and HRAC had the highest micropore ratio of 54.85%. The detail micropore size distributions of the carbons are illustrated in Fig. 4. The pore size distributions of the four carbons are quite distinct in the microporous range. EPAC and HRAC exhibited a much higher distribution of peaks between 0.2 and 1.8 nm than LGAC and PCAC.

The pore properties of the carbons, including BET specific surface area (S_BET), micropore internal surface area (S_mic), BJH internal surface area (S_BJH), total pore volume (V_tot), micropore volume (V_mic) and mean pore size (D_m), are summarized in Table 1. The BET surface area followed the order of EPAC (1094 m²/g) > HRAC (723 m²/g) > PCAC (117 m²/g) > LGAC (104 m²/g). This suggested that EP was a better precursor for the preparation of high-surface-area ACs by pyrophosphoric acid activation, compared with PC, LG and HR under the same preparation conditions. This result could be explained by two aspects. On the one hand, the heterogeneous compositions of the raw materials played a crucial role in the formation of the polyhexagonal carbon structure. PC is a carbonaceous solid with stable micrographitic structure, resulting in difficulty in thermal breakdown of the component by pyrophosphoric acid. The dominant constituents of EP are polysaccharides, proteins and hemicellulose (Özer et al., 2009; Zhao et al., 2013), which could be decomposed easily. Similarly, HR is primarily
composed of protein, for example keratin (Si et al., 2013). Hence, HR was also prone to react with the activation agent. On the other hand, the pyrophosphoric acid and its derivatives preferred to react with the organic matters in the biomasses to form phosphate linkages, which may facilitate the creation of pores. What’s more, these polyphosphate compounds have greater size than KOH and ZnCl₂ molecules, thus leading to the generation of large sized mesopores (Heidari et al., 2014).

2.4. FTIR analysis

The adsorption performance of an adsorbent material not only depends on the textural structure but also its surface chemical properties. Therefore, FTIR analysis was conducted to better understand the surface chemistry differences of the four carbons. The spectra of all carbons show some similar characteristic absorption peaks (Fig. 5). The bands at about 3425 cm⁻¹ can be assigned to O–H vibrations in hydroxyl groups of alcohols, phenols or carboxylic acids. The bands observed at 1560 cm⁻¹ correspond to C=O stretching in carboxylic acids or esters (Heidari et al., 2014; Lü et al., 2012). The bands located around 1156, 1215 and 1294 cm⁻¹ for EPAC, HRAC and LGAC are due to C–O stretching in acids, alcohols, and phenols (Ceyhan et al., 2013), respectively. The differences in position and intensity of the bands were related to the diverse starting materials. The bands in the spectrum of LGAC around 2925 cm⁻¹ indicated the presence of C–H bond stretching in carboxylic acids. The relatively intense bands appearing at 1041 cm⁻¹ found only in LGAC are also characteristic of C–O vibrations (Huang et al., 2011). The sharp bands appearing around 736 cm⁻¹ only for LGAC may be attributed to the vibrations of the aromatic substituents (Ceyhan et al., 2013; Liu et al., 2012).

Fig. 2 – SEM (scanning electron microscopy) images of (a) petroleum coke, (b) Enteromorpha prolifera, (c) lignin, (d) hair, (e) PCAC, (f) EPAC, (g) LGAC and (h) HRAC. PCAC, EPAC, LGAC and HRAC refer to active carbons (ACs) prepared by PK, EP, LG and HR precursors.

Fig. 3 – Pore size distribution and (inset) N₂ adsorption/desorption isotherms for the carbons.

Table 1 – Textural characterization of the prepared carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} )</th>
<th>( S_{\text{mic}} )</th>
<th>( S_{\text{BJH}} )</th>
<th>( V_{\text{tot}} )</th>
<th>( V_{\text{mic}} )</th>
<th>( V_{\text{mic}}/V_{\text{tot}} )</th>
<th>( D_{\text{AC}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCAC</td>
<td>117</td>
<td>84</td>
<td>228</td>
<td>0.117</td>
<td>0.035</td>
<td>29.91</td>
<td>3.986</td>
</tr>
<tr>
<td>EPAC</td>
<td>1094</td>
<td>250</td>
<td>983</td>
<td>1.695</td>
<td>0.115</td>
<td>6.78</td>
<td>6.200</td>
</tr>
<tr>
<td>LGAC</td>
<td>104</td>
<td>62</td>
<td>56</td>
<td>0.150</td>
<td>0.028</td>
<td>18.67</td>
<td>5.786</td>
</tr>
<tr>
<td>HRAC</td>
<td>723</td>
<td>566</td>
<td>228</td>
<td>0.454</td>
<td>0.249</td>
<td>54.85</td>
<td>2.513</td>
</tr>
</tbody>
</table>

PCAC, EPAC, LGAC and HRAC refer to active carbons (ACs) prepared by petroleum coke, Enteromorpha prolifera, lignin, and hair precursors. \( S_{\text{BET}} \): BET specific surface area; \( S_{\text{mic}} \): micropore internal surface area; \( S_{\text{BJH}} \): BJH internal surface area; \( V_{\text{tot}} \): total pore volume; \( V_{\text{mic}} \): micropore volume; \( D_{\text{AC}} \): mean pore size.
2.5. Dye adsorption

2.5.1. Effect of adsorbent type and contact time

The effects of adsorbent type and contact time on the removal of dye by the four carbons are shown in Fig. 6. The adsorption kinetics of both dyes were evaluated at an initial concentration of 100 mg/L for the four samples. In the case of GR, the adsorption amount increased dramatically in the first 60 min, then tended to become slow, and adsorption equilibrium was gradually obtained within 700 min. By contrast, the adsorption of MG increased sharply within the first 10 min, and adsorption equilibrium was achieved in 30 min. This may be attributed to the larger mass transfer driving force from the high initial dye concentration at the beginning stage. Moreover, large numbers of available adsorptive sites also facilitated the formation of a high concentration gradient between the adsorbent surface and the adsorbate in solution, further leading to high sorption rate at the initial stage (Peng et al., 2014). The higher adsorption rates for MG were due to the stronger attraction between the basic dye and negatively charged AC particles. Fig. 6 also shows that the adsorption curves were smooth and continuous, indicating that the surface of the adsorbents was possibly covered by monolayers of dye molecules (Alkan et al., 2008).

2.5.2. Adsorption kinetic study

The pseudo-first-order model (Eq. (2)), pseudo-second-order model (Eq. (3)) and intra-particle diffusion model (Eq. (4)) were applied to study the kinetic adsorption behavior.

\[
\ln (q_e - q_t) = \ln q_e - k_1 t \tag{2}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}
\]

\[
q_t = k_{pi} t^{1/2} + C \tag{4}
\]

where \(q_e\) (mg/g) and \(q_t\) (mg/g) are the amount of dye adsorbed at equilibrium and time \(t\) (min), \(k_1\) (min\(^{-1}\)), \(k_2\) (g/(mg·min)) and \(k_{pi}\) (mg·min\(^{1/2}\)/g) are the pseudo-first-order rate constant, the pseudo-second-order rate constant and the intra-particle rate diffusion constant, and \(C\) is a dimensionless constant.

Fig. 4 – Micropore size distribution for (a) PCAC, (b) EPAC, (c) LGAC and (d) HRAC.

Fig. 5 – FTIR (Fourier transform infrared spectroscopy) spectra of the prepared carbons.
The calculated parameters based on the three equations are listed in Table 2. The calculated $q_e$ values from the pseudo-second-order kinetic model were in good agreement with the experimental data. In addition, high correlation coefficients were obtained for the pseudo-second-order kinetics, compared with the other models. Thus, the kinetic data were well represented by the pseudo-second-order model, suggesting that the predominant rate limiting step for the adsorption of dye was chemisorption. The lower predicted $q_e$ values for the pseudo-first-order model may be attributed to a time lag produced by a boundary layer or external resistance at the initial sorption stage (Febrianto et al., 2009). It can be observed that the values of the intercept $C$ were not zero, implying that the rate-limiting step was boundary layer diffusion. Furthermore, the values of the intercept $C$ in the case of EPAC and HRAC were higher than those in PCAC and LGAC. This result suggested that boundary layer diffusion was more dominant for EPAC and HRAC.

### 2.5.3. Adsorption isotherm study

To effectively evaluate the adsorption capacity of the four carbons, Langmuir isotherm (Eqs. (5)-(6)) and Freundlich isotherm (Eq. (7)) models were used to fit the isotherm data.

$$
C_e = \frac{1}{Q_m b} + \frac{C_e}{Q_m}
$$

### Table 2 – Comparison of pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models constants calculated for Acid Brilliant Scarlet (GR) and Malachite Green (MG) adsorption.

<table>
<thead>
<tr>
<th>Type of the adsorbents</th>
<th>GR adsorption</th>
<th>MG adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PCAC</td>
<td>EPAC</td>
</tr>
<tr>
<td>$q_e$ (exp) (mg/g)</td>
<td>18.71</td>
<td>185.93</td>
</tr>
<tr>
<td>First-order kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1$ (min$^{-1}$)</td>
<td>$5.4 \times 10^{-3}$</td>
<td>$6.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$q_e$ (cal) (mg/g)</td>
<td>10.08</td>
<td>126.01</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9268</td>
<td>0.9639</td>
</tr>
<tr>
<td>Second-order kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_2$ (g/(mg·min))</td>
<td>$1.991 \times 10^{-3}$</td>
<td>$1.71 \times 10^{-4}$</td>
</tr>
<tr>
<td>$q_e$ (cal) (mg/g)</td>
<td>19.12</td>
<td>188.68</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9934</td>
<td>0.9958</td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_p1$ (mg·min$^{1/2}$/g)</td>
<td>0.9361</td>
<td>12.25</td>
</tr>
<tr>
<td>$C_1$</td>
<td>6.9467</td>
<td>29.719</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9227</td>
<td>0.9791</td>
</tr>
<tr>
<td>$k_p2$ (mg·min$^{1/2}$/g)</td>
<td>0.4375</td>
<td>5.8748</td>
</tr>
<tr>
<td>$C_2$</td>
<td>8.7004</td>
<td>68.681</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9768</td>
<td>0.9893</td>
</tr>
<tr>
<td>$k_p3$ (mg·min$^{1/2}$/g)</td>
<td>0.3821</td>
<td>2.6897</td>
</tr>
<tr>
<td>$C_3$</td>
<td>10.022</td>
<td>117.61</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9043</td>
<td>0.9838</td>
</tr>
</tbody>
</table>

$q_e$ is the amount of dye adsorbed at equilibrium, $k_1$, $k_2$ and $k_p1$ are the pseudo-first-order rate constant, the pseudo-second-order rate constant and the intra-particle rate diffusion constant, $C$ is a dimensionless constant, and exp and cal refer to the experimental and calculated data.
\[
R_L = \frac{1}{1 + bC_0}
\]

(6)

\[
\log q_e = \log K_F + \frac{1}{n}\log C_e
\]

(7)

where \(C_0\) (mg/L) and \(C_e\) (mg/L) are the concentration of dye at beginning and equilibrium, \(Q_m\) (mg/g) is the theoretical saturation capacity, \(b\) (L/mg) is the parameter of the Langmuir equation, \(R_L\) is a dimensionless constant, and \(K_F\) ((mg/L)^{1-n}) and \(n\) are parameters of the Freundlich equation. The Langmuir adsorption isotherm has been widely applied for homogeneous surfaces along with monolayer sorption processes, and does not fit data very well in high concentration systems. The Freundlich adsorption isotherm assumes multi-layer adsorption processes in heterogeneous systems. However, the Freundlich isotherm is limited in its applicability for low concentration systems due to lacking a fundamental thermodynamic basis and not reaching the Henry’s law value at low concentrations (Febrianto et al., 2009; Foo and Hameed, 2010a).

The isotherm parameters were calculated and summarized in Table 3. By comparison of the correlation coefficients, it can be concluded that the Langmuir equation represented a better fit to the experimental data, demonstrating that the adsorption of the two dyes onto the four carbons was homogeneous monolayer adsorption. This result can also be confirmed through the L-type isotherms in Fig. 7. The values of \(R_L\) were between 0 and 1 and the values of Freundlich constant \(1/n\) were below 1, indicating that the adsorption of each dye onto the four carbons was favorable. The maximum monolayer adsorption capacities of GR onto EPAC, HRAC, LGAC and PCAC were 558.24, 357.14, 68.49, and 26.88 mg/g, respectively, and the maximum monolayer adsorption capacities of MG onto EPAC, HRAC, LGAC and PCAC were 1250.0, 714.28, 147.06 and 66.22 mg/g, respectively. These sequences generally agreed with the order of the BET specific surface areas. The BET specific surface area of PCAC was slightly larger than that of LGAC, but the maximum monolayer adsorption capacities of the two dyes onto PCAC were slightly smaller than those of LGAC. This may be ascribed to the abundant chemical groups on the surface of LGAC (Fig. 5). The maximum monolayer adsorption capacities of MG onto other adsorbents are listed in Table S1. By comparing the maximum monolayer adsorption capacities of MG with those in previous works (Ahmad and Alrozi, 2011; Akar et al., 2013; Hameed and El-Khaiary, 2008a, 2008b; Önal et al., 2007; Santhi et al., 2010), the results indicate that EPAC is a high-efficiency adsorbent.

### 3. Conclusions

The current study demonstrated that \(\text{H}_3\text{PO}_4\) can be used as an effective activator for producing high-quality activated carbon. Activated carbons prepared from different starting
materials presented different physicochemical characteristics and adsorptive properties. The highest surface area activated carbon was derived from Enteromorpha prolifera. The adsorption capacities were significantly affected by adsorbent type, contact time and adsorbate type. The adsorption kinetic data were best fitted to the pseudo-second-order model and the isotherm data were well described by the Langmuir isotherm model.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2015.05.016.

REFERENCES


