Adsorption behavior of activated carbon derived from pyrolusite-modified sewage sludge: equilibrium modeling, kinetic and thermodynamic studies
Yao Chen, Wenju Jiang, Li Jiang and Xiujuan Ji

ABSTRACT
Activated carbon was developed from sewage sludge using pyrolusite as an additive. It was demonstrated that the removal efficiency of two synthetic dyes (Tracid orange GS and Direct fast turquoise blue GL) by the produced adsorbent was up to 97.6%. The activated carbon with pyrolusite addition had 38.2% higher surface area, 43.8% larger micropore and 54.4% larger mesopore production than ordinary sludge-based activated carbons. Equilibrium adsorption isotherms and kinetics were also investigated based on dyes adsorption tests. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption, and the results fitted well to the Langmuir isotherm. The kinetic data have been analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion equation. The experimental data fitted very well with pseudo-second-order kinetic model. Activation energies for the adsorption processes ranged between 8.7 and 19.1 kJ mol\(^{-1}\). Thermodynamic parameters such as standard free energy (\(\Delta G^0\)), standard enthalpy (\(\Delta H^0\)) and standard entropy (\(\Delta S^0\)) were evaluated. The adsorption of these two dyes on the activated carbon was found to be a spontaneous and endothermic process in nature.

Key words | activated carbon, isotherm, kinetics, pyrolusite, sewage sludge, thermodynamics

INTRODUCTION
Synthetic dyes, one group of organic pollutants, are used extensively in dyeing and printing processes, paper, plastics, food, cosmetics, etc. These compounds are considered particularly dangerous to the environment due to their complex structure and synthetic origin (Demirbas 2009). Most of them are completely resistant to biodegradation processes. Therefore, various techniques have been employed for the removal of dyes from wastewaters in recent years (Dong et al. 2007; Tan et al. 2008; Al-Dece et al. 2009; Faria et al. 2009; Khataee et al. 2009). Among them, adsorption is one of the most effective methods. The advantages of the adsorption process are simplicity in operation, inexpensive compared to other separation methods and insensitivity to toxic substances. Activated carbon is the most common used adsorbent in dye removal (Gupta & Suhas 2009). However, the usage of activated carbon is expensive due to the tedious procedures of regeneration and reactivation. Therefore, low cost and effective adsorbents from different precursors, including agricultural residues (Demirbas et al. 2008; Hameed et al. 2008; Gad & El-Sayed 2009), sewage sludge (Calvo et al. 2001; Martin et al. 2003; Rio et al. 2005; Fan & Zhang 2008), industrial solid wastes (Kadirvelu et al. 2005; Fahim et al. 2006; Sanchez-Arias et al. 2008) are most desirable.

Sewage sludge has been produced in an ever-increasing amount at wastewater treatment plants in recent decades. The sludge that consists of a complex heterogeneous mixture of organic and inorganic materials is difficult and costly to handle and dispose of (Fytili & Zabaniotou 2008). For abundant in volatile matter, the conversion of the sludge into adsorbents, especially activated carbon, has been proved to be a cost effective and environmentally benign alternative (Smith et al. 2009). A wealth of research has been conducted into the production of sewage sludge-based adsorbents (Rozada et al. 2005; Zhang et al. 2005; Pietrzak & Bandosz 2007). Further interest is focused on the mixture of sewage sludge and mineral matter during carbonization/activation process to strengthen produced...
activated carbon adsorption capacity (Zubkova et al. 2005). Previous researches showed that mineral matter can exert a catalytic effect on the activation and carbonation process due to their complex compositions of various transition metals (Oya et al. 1995; Lorenc-Grabowska et al. 2004; Bandoz & Block 2006; Sanchez-Arias et al. 2008). Pyrolusite, an ordinary and economical mineral resource distributed in many areas, is proved to improve the dye adsorption by enhancing mesoporous production for the pyrolysis of sewage sludge (Liu et al. 2010). However, limited information is obtained on the characteristics of dye adsorption behavior of pyrolusite-modified sewage sludge adsorbent.

The emphasis of this study was to characterize a custom-made adsorbent from sewage sludge using pyrolusite as an additive. The adsorption equilibrium isotherms, adsorption kinetics and thermodynamics were extensively examined by removal of two synthetic dyes (Tracid orange GS and Direct fast turquoise blue GL) from aqueous solution.

## MATERIALS AND METHODS

### Materials and characterizations

Dewatered surplus sludge from a local municipal wastewater treatment plant was used for the preparation of activated carbons. The ultimate analysis of the raw sludge is in a weight ratio of: 24.7% C, 3.8% H, 3.8% N, 2.4% S and 65.3% O. The pyrolusite used in this study is a mineral powder (technical grade) sieved with 75 μm filter from an electrolytic manganese factory in Qingchuan County, Sichuan Province and mainly consists of (%): MnO$_2$: 44.05, SiO$_2$: 33.20, Fe$_2$O$_3$: 13.80, CaO: 3.62, Al$_2$O$_3$: 3.37.

The preparation of sewage sludge-based activated carbons was followed by the previous reports (Liu et al. 2010; Tang et al. 2010). The sludge was dried at 105 °C for 48 h, crushed and mixed with 0.2% (wt.) pyrolusite fine powder (designated as ACP). The activating agent used consists of ZnCl$_2$ (6 mol L$^{-1}$) and H$_2$SO$_4$ (wt. 35%) in a volume ratio of 4:1. The precursor was then impregnated with activating agent in a ratio of 2.5 (g ml) and placed on a ceramic boat, inserted in a tubular furnace (KXG-2-13A, Shanghai, China) with a constant heating rate of 10 °C min$^{-1}$ and the final carbonization temperature was 550 °C. After 40 min of pyrolysis under purified N$_2$ (99.999%) flow of 200 ml min$^{-1}$, the carbonization sample was cooled down to room temperature and taken out. The product was washed several times sequentially with 3 mol L$^{-1}$ HCl and hot distilled water to remove any residual chemicals. Activated carbon product was then dehydrated at 105 °C, ground and sieved to the mean particle size of 75 μm for further tests. All the chemical and reagents used were analytical grade. The compared activated carbon from the sewage sludge without pyrolusite addition (designated as ACS) was also prepared following the same procedures.

Methylene blue (MB), due to its relatively large size, is commonly used in assessing the dye uptake. The equilibrium MB adsorption capacity of ACP and ACS was obtained after 4 h adsorption (25 °C) with an initial concentration of 1,000 mg L$^{-1}$.

The surface area of prepared activated carbon was measured by BET (Brunauer-Emmett-Teller nitrogen adsorption technique) in a ZXF-06 sorptometer (Tianjin, China). From the isotherm data, BET surface area, micro- and mesopore volumes and mean pore radius were calculated. The surface of adsorbent was characterized by scanning electron microscopy (SEM, JSM-5900LV, Tokyo, Japan).

### Adsorption studies

Two types of dyes were used in this experiment to investigate the isotherm, kinetic and thermodynamic studies of the produced activated carbon. Those two dyes were commonly used in dyeing and printing of cotton, woolen, silk and viscose fiber. One is Tracid orange GS, chemical formula = C$_{34}$H$_{28}$K$_2$N$_2$O$_5$S$_2$, MW = 795 g mol$^{-1}$, λ$_{max}$ = 489.5 nm, the other is Direct fast turquoise blue GL, chemical formula = C$_{32}$H$_{14}$CuN$_6$O$_6$S$_2$2Na, MW = 780 g mol$^{-1}$, λ$_{max}$ = 620.0 nm.

Adsorption experiments with ACS and ACP were performed by batch technique to learn the isotherm models. The batch experiments were carried out in 150 ml Erlenmeyer flasks and an adsorbent dose of 2 g L$^{-1}$ was employed at different reaction temperature. Adsorption of Tracid orange GS and Direct fast turquoise blue GL from aqueous solutions onto ACS and ACP was measured at seven different initial dye concentrations (150–550 mg L$^{-1}$) after equilibrium. The Erlenmeyer flasks were capped and agitated in an isothermal shaker at 180 rpm and 25 °C for 6 h to achieve equilibrium. Similar procedures were followed for another two sets of Erlenmeyer flask containing the same initial dye concentrations and same ACS and ACP dosage, but were kept under 35 °C and 45 °C for thermodynamic studies. The pH of the solutions was kept original without any pH adjustment, i.e., pH (acid dye) = 5.3, pH (direct dye) = 5.4, respectively. Once the equilibrium was reached, activated carbons were sieved out using 60 μm filter and the concentration of the dye in solution was then...
determined by measuring the absorbance in a double beam UV-vis spectrophotometer (UV-1100, Shanghai, China) at the respective \( \lambda_{\text{max}} \) value.

The amount of adsorption at equilibrium, \( q_e \) (mg g\(^{-1}\)), was calculated by Equation (1)

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

where \( C_0 \) and \( C_e \) (mg L\(^{-1}\)) are the liquid-phase concentrations of dyes at initial and equilibrium, respectively. \( V \) is the volume of the solution (L) and \( m \) is the mass of dry adsorbent used (g).

The kinetic experiments were performed at the initial pH and dye concentration of 200 mg L\(^{-1}\) for Tracid orange GS, 250 mg L\(^{-1}\) for Direct fast turquoise blue GL, respectively. The adsorbent dose was 2 g L\(^{-1}\) at different temperatures. Samples were taken at preset time intervals and the concentrations of dyes were measured. The amount of adsorption at time \( t \), \( q_t \) (mg g\(^{-1}\)), was calculated by Equation (2)

\[
q_t = \frac{(C_0 - C_t) V}{m}
\]

Each experiment was duplicated twice under identical conditions and the mean values were presented.

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**RESULTS AND DISCUSSION**

**Characterization of adsorbents**

Figure 1 shows the SEM micrograph of ACS and ACP. As shown in Figure 1, the surface morphology of ACS and ACP was alike. The adsorbents’ surface exhibits an uneven and rough surface morphology. Considerable numbers of pores, cavities and crevices are present in the adsorbents’ surface, which enhance trapping and adsorbing dyes from aqueous solution to the solid layer. In this study, the mean pore size of ACS and ACP is 3.55 nm and 3.61 nm, respectively from BET data calculation. It can be concluded that the activation process mainly developed mesopores (2 nm < \( D < 50 \) nm) in the sewage sludge-based activated carbons.

Dye adsorption capacity and textural characteristics of adsorbents with and without pyrolusite addition (designated as ACP and ACS, respectively) are shown in Table 1. It is observed that with mineral addition, the MB adsorption capacity of ACP was 11.4% increased when compared to ACS. The surface physical properties of ACS and ACP were analyzed by nitrogen adsorption method. Table 1 shows an obvious increase of the specific surface area on ACP, approximately 38.2% larger than that of ACS. As shown in Table 1, the production of micro- and mesopores volume is significantly increased on ACP, which was 43.0% and 54.4%, respectively, higher than those in ACS. The total pore volume of ACP was then 52.6% higher than that of ACS. It is indicated that the larger total pore volume for ACP was due to the relative higher production of micro- and mesopores than ACS. Therefore, the properties of the adsorbent with pyrolusite addition are improved during the pyrolusite-catalyzed pyrolysis via enhancement.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>MB adsorption capacity (mg g(^{-1}))</th>
<th>( S_{\text{BET}} ) (m(^2) g(^{-1}))</th>
<th>Total volume (cm(^3) g(^{-1}))</th>
<th>( V_{\text{N2\text{micro}}} ) (cm(^3) g(^{-1}))</th>
<th>( V_{\text{N2\text{meso}}} ) (cm(^3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACS</td>
<td>170.4</td>
<td>224.0</td>
<td>0.19</td>
<td>0.032</td>
<td>0.158</td>
</tr>
<tr>
<td>ACP</td>
<td>189.8</td>
<td>309.5</td>
<td>0.29</td>
<td>0.046</td>
<td>0.244</td>
</tr>
</tbody>
</table>

ACS: without pyrolusite addition; ACP: with pyrolusite addition.

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*Figure 1* | SEM micrograph of the sewage sludge-based activated carbons (a) ACS (without pyrolusite addition) and (b) ACP (with pyrolusite addition).
of micro- and mesopore production, and the mesopore channels can provide fast mass transfer for large molecules such as dyes. Similar results were obtained in our previous study (Liu et al. 2010) in that the development of porosity by pyrolusite addition improved the performance of the laboratory produced adsorbents for dye removal.

In further dye adsorption tests, the dye removal rate of Tracid orange GS and Direct fast turquoise blue GL by ACP was high at up to 97.6%, while ACS had a dye removal rate of around 90%. It demonstrated that ACP was an efficient adsorbent in such dyeing wastewaters treatment.

**Adsorption isotherms**

The amount of adsorbed dyes onto ACP at equilibrium was calculated and plotted as a function of the equilibrium concentration of dye in Figure 2. As shown in Figure 2, the amount of adsorbed dye on ACP slightly increased by increasing the temperature of the dye solution from 25 to 45 °C.

The adsorption isotherm indicates the distribution of adsorption molecules between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Two isotherm models were used to fit the experimental data: Langmuir and Freundlich models. The applicability of the isotherm equation to describe the adsorption process was judged by the correlation coefficient, $R^2$ values.

Langmuir isotherm assumes monolayer adsorption onto a completely homogenous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules. The linear form of Langmuir isotherm equation is given as:

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

where $Q_m$ is the theoretical maximum adsorption capacity (mg g$^{-1}$) and $b$ is the Langmuir adsorption constant (L mg$^{-1}$). $C_e$ is the equilibrium concentration of the adsorbate (mg L$^{-1}$), $q_e$ is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g$^{-1}$).

Freundlich isotherm on the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage. The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

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

where $K_F$ and $n$ are Freundlich constants characteristic of the system, also being indicators of adsorption capacity and adsorption intensity, respectively.

The isotherm parameters of ACS and ACP are presented in Table 2. From Table 2, Langmuir isotherm model is found to best fit the experimental data with high values of correlation coefficients ($R^2 > 0.99$). That the values of $1/n$ are less than one in Freundlich model also indicate the adsorption process is a normal Langmuir isotherm (Fytianos et al. 2000). The values of Langmuir ($Q_m$) and Freundlich ($K_F$) were slightly increased with increasing temperature for both dyes from 25 to 45 °C (Table 2). But the increase of the adsorption was not drastic. The results showed that temperature did not demonstrate significant effect on the dyes removal. The increase in adsorption capacities of the adsorbents at high temperature may be attributed to the enlargement of pore size (Namasivayam & Yamuna 1999). With respect to the Langmuir model, the large $b$ value also implies a strong bonding of the dyes to the adsorbent.

![Image](https://iwaponline.com/wst/article-pdf/64/3/661/444403/661.pdf)  
*Figure 2 | Equilibrium adsorption isotherm of Tracid orange GS and Direct fast turquoise blue GL dyes onto pyrolusite modified adsorbent under different temperature. (a) Tracid orange GS and (b) Direct fast turquoise blue GL.*
Adsorption kinetics

Dye adsorption data was plotted as a function of time in Figure 3 for each dye. As shown in Figure 3, the amount of adsorbed dye relatively unchanged after 3 h adsorption, and the removal rate varied significantly in the first 1 h.

In order to investigate the adsorption processes of Tracid orange GS and Direct fast turquoise blue GL onto ACS and ACP, pseudo-first-order, pseudo-second-order, intra-particle diffusion kinetic models were studied.

The pseudo-first-order kinetic model was described by as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

(5)

where \( q_e \) and \( q_t \) are the amounts of dyes adsorbed (mg g\(^{-1}\)) at equilibrium and time \( t \) (min), respectively and \( k_1 \) is the adsorption rate constant (min\(^{-1}\)).

Adsorption isotherms equations and correlation coefficient of two dyes onto adsorbents with and without mineral addition

<table>
<thead>
<tr>
<th>Carbon product</th>
<th>Dye</th>
<th>Temperature (°C)</th>
<th>( q_e )</th>
<th>( b )</th>
<th>( R^2 )</th>
<th>( q_e )</th>
<th>( K_F )</th>
<th>( 1/n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACS Tracid orange GS</td>
<td>25</td>
<td>208.33</td>
<td>0.0936</td>
<td>0.9956</td>
<td>71.58</td>
<td>0.22</td>
<td>0.9132</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>35</td>
<td>212.77</td>
<td>0.1042</td>
<td>0.9957</td>
<td>69.33</td>
<td>0.23</td>
<td>0.9756</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>217.39</td>
<td>0.0231</td>
<td>0.9964</td>
<td>68.17</td>
<td>0.28</td>
<td>0.9487</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direct fast turquoise blue GL</td>
<td>25</td>
<td>185.19</td>
<td>0.1593</td>
<td>0.9962</td>
<td>64.65</td>
<td>0.22</td>
<td>0.9759</td>
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<tr>
<td></td>
<td>35</td>
<td>200.00</td>
<td>0.2008</td>
<td>0.9974</td>
<td>74.94</td>
<td>0.22</td>
<td>0.9580</td>
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</tr>
<tr>
<td></td>
<td>45</td>
<td>217.39</td>
<td>0.2000</td>
<td>0.9976</td>
<td>105.08</td>
<td>0.15</td>
<td>0.9967</td>
<td></td>
<td></td>
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<tr>
<td>ACP Tracid orange GS</td>
<td>25</td>
<td>227.27</td>
<td>0.0815</td>
<td>0.9962</td>
<td>45.53</td>
<td>0.35</td>
<td>0.8992</td>
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<tr>
<td></td>
<td>35</td>
<td>232.56</td>
<td>0.1012</td>
<td>0.9948</td>
<td>62.95</td>
<td>0.28</td>
<td>0.9308</td>
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<tr>
<td></td>
<td>45</td>
<td>238.10</td>
<td>0.0981</td>
<td>0.9926</td>
<td>60.59</td>
<td>0.29</td>
<td>0.8809</td>
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<tr>
<td>Direct fast turquoise blue GL</td>
<td>25</td>
<td>208.33</td>
<td>0.1684</td>
<td>0.9863</td>
<td>72.21</td>
<td>0.24</td>
<td>0.9796</td>
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<tr>
<td></td>
<td>35</td>
<td>217.39</td>
<td>0.1723</td>
<td>0.9966</td>
<td>73.52</td>
<td>0.25</td>
<td>0.9584</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>45</td>
<td>227.27</td>
<td>0.1947</td>
<td>0.9964</td>
<td>107.50</td>
<td>0.15</td>
<td>0.9916</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ACS: without pyrolusite addition; ACP: with pyrolusite addition.

The pseudo-second-order model equation based on equilibrium adsorption is expressed as:

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

(6)

where \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the rate constant of second-order adsorption.

Intra-particle diffusion model based on the theory proposed by Weber and Morris was tested to identify the diffusion mechanism. According to this theory:

$$q_t = k_d t^{1/2} + C$$

(7)

where \( k_d \) (mg g\(^{-1}\) min\(^{-0.5}\)) is the intra-particle diffusion rate constant.

Kinetic data were fitted with these three models and the results were given in Table 3. The dyes adsorption by ACS and ACP is not an ideal pseudo-first-order model due to...
the big difference between the experimental and the calculated $q_e$ values. In many cases, the first-order equation does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (Amin 2009). For the relatively low correlation coefficients ($0.71 < R^2 < 0.88$), the data indicate that intra-particle diffusion resistance may possibly affect the adsorption rate, whilst some other mechanism along with intra-particle diffusion is also involved (Chern & Chien 2002).

As listed in Table 3, the calculated $q_e$ values agree very well with the experimental data of the pseudo-second-order model and the correlation coefficients are higher than 0.99 in all cases. It indicates that the adsorption of these two dyes onto prepared ACS and ACP obey the pseudo-second-order kinetic model. The similar findings were reported for adsorption of acid and direct dyes with different types of adsorbent in many literatures (Malik 2004; Hoda et al. 2006; Gómez et al. 2007; Amin 2009). The pseudo-second-order kinetic behavior suggested that the adsorption mechanism was the rate-controlling step when using sewage sludge-based activated carbons for removing acid and direct dyes from aqueous solution.

**Adsorption thermodynamics**

Table 3 shows that the adsorption rate increases with increasing temperature. The increase in adsorption rate is described by the Arrhenius equation:

$$\ln(k) = \ln(k_0) - \frac{E_a}{RT}$$

where $k_0$ is the pre-exponential factor or the frequency factor, $k$ is a specific rate constant, i.e., $k_2$, the rate constant of second-order adsorption in this study. $E_a$ (kJ mol$^{-1}$) is called the activation energy, representing the minimum energy that reactants must have for the reaction to proceed.

The activation energy values during Tracid orange GS and Direct fast turquoise blue GL adsorption processes were calculated as: 16.00 and 8.76 kJ mol$^{-1}$ for ACS, 11.13 and 19.10 kJ mol$^{-1}$ for ACP, respectively. Those low activation energies (5–40 kJ mol$^{-1}$) are characteristic for physisorption, while higher activation energies (40–800 kJ mol$^{-1}$) suggest chemisorption (Nollet et al. 2005).

Thermodynamic parameters were evaluated to confirm the adsorption nature of ACS and ACP. The thermodynamic constants, free energy change ($\Delta G$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$) were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. The thermodynamics equations were as following:

$$\Delta G^0 = -RT \ln K_d$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$
ln \( K_d \) = \( \frac{\Delta S^0 - \Delta H^0}{R} \) \( \frac{T}{RT} \) (11)

where \( \Delta G^0 \) is change of Gibbs free energy (kJ mol\(^{-1}\)), \( \Delta S^0 \) (J K\(^{-1}\) mol\(^{-1}\)) and \( \Delta H^0 \) (kJ mol\(^{-1}\)) are change of entropy and enthalpy of reaction, \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the absolute temperature (K). \( K_d \) is the thermodynamic equilibrium constant of the adsorption process, i.e., the constants of adsorbate distribution between the solid and liquid phases at equilibrium, and were calculated with respect to temperature using method described by Lyubchik et al. (2004) by plotting ln \( (q_e/C_e) \) versus \( q_e \) and extrapolating to zero \( q_e \).

The thermodynamics parameters are listed in Table 4. The \( \Delta G^0 \) values for both dyes were decreased with an increase in temperature. This indicates that the adsorption process was spontaneous and the spontaneity increased with the temperature increasing. The positive value of \( \Delta H^0 \) indicates that the reaction between dyes and adsorbent was endothermic. It is consistent with the results obtained earlier in this study where the dyes adsorption increased with increasing temperature. The adsorption reaction for the endothermic processes may be due to the increasing temperature which increased the rate of the adsorbate molecules across the external boundary layer and the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution or an increase in the mobility of the adsorbate molecules (Chern & Chien 2002).

The positive values \( \Delta S^0 \) obtained shows the affinity of the prepared ACS and ACP for both dyes and the increasing randomness at the solid-solution interface during the adsorption process. It may be the appearance of ion-exchange and replacement reactions resulted in the creation of steric hindrance (Lyubchik et al. 2004). Thus the adsorption of dyes onto the prepared activated carbon was rather a complex process.

**CONCLUSIONS**

In this study, experimental results showed that sewage sludge-based activated carbon with pyrolusite addition (ACP) was effective for the removal of both synthetic dyes from aqueous solution. The quality of the activated carbon with the addition of pyrolusite was improved owing to the significant increase of specific surface area and micro- and mesopore production. Results obtained were modeled using two isotherm models: Langmuir and Freundlich. Equilibrium isotherms were well described by the Langmuir equation. The results fitted very well with the pseudo-second-order kinetic model. Activation energies for the adsorption processes were relatively low and characteristic for physisorption. The thermodynamic parameters (\( \Delta G^0 \), \( \Delta H^0 \), \( \Delta S^0 \)) obtained in this study indicated the spontaneous and endothermic nature of the dye adsorption on ACS and ACP.

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