Adsorption kinetics and thermodynamics of acid Bordeaux B from aqueous solution by graphene oxide/PAMAMs

Fan Zhang, Shengfu He, Chen Zhang and Zhiyuan Peng

ABSTRACT

Graphene oxide/polyamidoamines dendrimers (GO/PAMAMs) composites were synthesized via modifying GO with 2.0 G PAMAM. The adsorption behavior of the GO/PAMAMs for acid Bordeaux B (ABB) was studied and the effects of media pH, adsorption time and initial ABB concentration on adsorption capacity of the adsorbent were investigated. The optimum pH value of the adsorption of ABB onto GO/PAMAMs was 2.5. The maximum adsorption capacity increased from 325.78 to 520.83 mg/g with the increase in temperature from 298 to 328 K. The equilibrium data followed the Langmuir isotherm model better than the Freundlich model. The kinetic study illustrated that the adsorption of ABB onto GO/PAMAMs fit the pseudo-second-order model. The thermodynamic parameters indicated that the adsorption process was physisorption, and also an endothermic and spontaneous process.

INTRODUCTION

Dyes are widely used in industries such as rubbers, pesticides, plastics, textiles, varnishes and dyestuffs. Textile wastewater has a serious environmental impact because of the high biotoxicity and potential mutagenic and carcinogenic effects. Therefore, the treatment of textile wastewater is of special interest and great importance. Various methods have been implemented to treat textile wastewater, including ion-exchange (Karcher et al. 2002), adsorption (He et al. 2013), coagulation/flocculation (Yang et al. 2013a, b), photocatalysis (Zhuang et al. 2014).

Among these methods, adsorption has been considered as one of the most widely used treatment approaches for the removal of textile wastewater because of its high efficiency, ease of operation, fewer harmful secondary products as well as comparable low cost of application (Yang et al. 2013a, b). Regarding the adsorption technique, the application of effective adsorbents is critical to guaranteeing the efficiency of water treatment. Various adsorbents, such as activated carbon (Gong et al. 2013), chitosan (Nikolina et al. 2013), silica gel (Soumitra et al. 2014), zeolite (Zhu et al. 2014), and carbon nanotube (Ladan et al. 2014) have been utilized to treat textile wastewater.

Some recent literature has focused on the use of graphene or graphene oxide (GO) materials as promising adsorbent materials for the removal of dye from water (Li et al. 2012; Xu et al. 2012; Yuan et al. 2013). Owing to the large theoretical surface area (2,620 m^2/g), potential environmental applications of graphene as a promising adsorbent have been suggested and examined for removal of organic contaminants from water (Wang et al. 2013). However, it is generally difficult to maintain the large surface area of graphene because of the strong van der Waals interaction (Allen et al. 2013). Bai et al. (2012) developed a one-pot solvothermal synthesis method to prepare reduced GO supported ferrite (MFe_2O_4, M = Mn, Zn, Co and Ni) hybrids and used the obtained hybrids as adsorbents for removal of dye pollutants. It was found that over 92% rhodamine B (RhB) and 100% methylene blue (MB) with a concentration of 5 mg/L could be removed by the hybrids within 2 min when the concentration of the hybrids was 0.6 g/L. In addition, the hybrids also showed enhanced photocatalytic activity in the degradation of RhB and MB.

In this article, graphene oxide/polyamidoamines dendrimers (GO/PAMAMs) composites were synthesized via a grafting-to method (Zhang et al. 2014) and it was then utilized to investigate its adsorption efficiency toward acid Bordeaux B (ABB) in aqueous solution at different parameters, including pH, temperature, time and ABB.
concentration. The aim of the study is to investigate the kinetics and isotherm of the ABB adsorption onto GO/PAMAMs and hope to find an efficient adsorbent for removing ABB from aqueous solutions.

METHODS

Materials

The suppliers and purities of the chemicals used in this work are listed in Table 1. Graphite, sodium nitrate, potassium permanganate were prepared using an electronic balance with uncertainty of 0.001 g, and N,N-dimethylformamide (DMF), concentrated sulfuric acid and hydrogen peroxide were prepared using a graduated container with uncertainty of 0.1 mL.

Preparation of GO/PAMAMs

The GO/PAMAMs were prepared according to the reported literature (Zhang et al. 2014). GO (2.0 g) was dissolved in DMF in a three-necked round-bottomed flask. Then, PAMAMs (20 mL) were added into the flask dropwise and the solution was refluxed under 80 °C for 24 h. The resultant product was filtered and washed with DMF. The colloidal sediment was dried under vacuum at 100 °C for 12 h and the GO/PAMAMs were prepared. The physico-chemical characteristics of the GO/PAMAMs can be found in the reported literature and its supporting information (Zhang et al. 2014).

Analysis method

A stock solution containing ABB 500 mg/L was prepared by dissolving 0.5000 g of ABB with distilled water in a 1,000 mL measuring flask and diluted to the desired concentration, the pH of ABB solution was adjusted to the desired value with 0.1 M of HNO₃ and NaOH solution under the pH meter (Jingke, Shanghai Co. Ltd, Shanghai, China). The concentration of ABB was determined using an ultraviolet-visible spectrophotometer (UV-2250, Shimadzu, Kyoto, Japan) at λ = 520 nm. The standard curve of ABB concentration (pH = 2.5) was obtained through determining the absorbance of the known concentration of ABB (0–150 mg/L). The linear equation of ABB concentration (C, mg/L) versus absorbance (A) was calculated as follows: A = −0.0637 + 0.0181C, the scope of C is 0–150 and the correlation coefficient of the standard curve is 0.9998 (Figure 1). Similarly, more standard curves and the correlation coefficient of ABB concentration at different pH were obtained and are listed in Table 2.

Adsorption experiments

Typically, a 100 mL solution of ABB concentrate and 0.1 g of GO/PAMAMs were added into glass flasks and then

Table 1  | Chemical suppliers and purities

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Supplier</th>
<th>Weight fraction purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N-Dimethylformamide</td>
<td>Shanghai Reagents Company, Shanghai, China</td>
<td>99.0</td>
</tr>
<tr>
<td>Graphite</td>
<td>Tianjin Kemiou Graphite Company, Tianjin, China</td>
<td>99.0</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>Shanghai Reagents Company, Shanghai, China</td>
<td>99.0</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>Shanghai Reagents Company, Shanghai, China</td>
<td>99.5%</td>
</tr>
<tr>
<td>Concentrated sulfuric acid</td>
<td>Shanghai Reagents Company, Shanghai, China</td>
<td>98.0%</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>Shanghai Reagents Company, Shanghai, China</td>
<td>30.0%</td>
</tr>
<tr>
<td>ABB</td>
<td>BASF SE, Ludwigshafen, Germany</td>
<td>100% (effective ingredients)</td>
</tr>
</tbody>
</table>

Figure 1  | Calibration curve of ABB solution at λ = 520 nm, pH = 2.5.
stirred under 25°C. At the completion of preset time intervals, 10 mL dispersion was drawn and filtered. Residual ABB concentration in the aqueous solution was determined by using a Shimadzu UV-2250 spectrophotometer (Shimadzu Corp., Kyoto, Japan). The adsorption amount was calculated according to the following equation:

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

(1)

where, \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of ABB (mg/L), respectively, \( V \) is the volume of ABB solution (L), and \( W \) is the weight of the GO/PAMAMs used (g).

### RESULTS AND DISCUSSION

**Effect of pH value on adsorption**

The effect of initial pH on the adsorption of ABB was studied in a pH range of 1.5–7.0 using 100 mL of solutions with ABB concentrations of 100 mg/L. Figure 2 shows the effect of the initial pH on the adsorption of ABB onto GO/PAMAMs. It can be seen that the adsorption capacity of ABB on GO/PAMAMs sharply increased when pH increased from 1.5 to 2.5, decreased from pH = 2.5 to 4, almost unchanged from pH = 4 to 7. What caused the changes of the adsorption capacity of ABB on GO/PAMAMs? The answers might be found from the structures of ABB and GO/PAMAMs. Figure 3 presents the structures of ABB and GO/PAMAMs. It was found that the ABB contained sulfonyl groups and the GO/PAMAMs contained multi-amide groups. When pH = 2.5, the GO/PAMAMs might have a stronger protonation degree of the amino groups. The ABB acted as anionic dye while the GO/PAMAMs acted as the cationic groups. The appropriate pH might help to strengthen the electrostatic attraction between GO/PAMAMs and ABB, which contribute to the increase of the adsorption capacity of GO/PAMAMs for ABB. As shown in Figure 2, the optimum pH value of ABB onto GO/PAMAMs was 2.5, and the optimum pH value was adopted for the following adsorption experiment.

**Effect of contact time**

The kinetic experiments were carried out using 50 mg/L, 150 mg/L or 200 mg/L of ABB solutions, respectively, at 298 K as shown in Figure 4. It is apparent that the adsorption capacities gradually increase with the increase of the contact time for the three concentrations. The adsorption reaction reached equilibrium after 300 min. The amount of ABB adsorbed at equilibrium slightly increases from 127.2 to 332.5 mg/g with the increase in dye concentration from 50 to 150 mg/L.

### Adsorption kinetics

To interpret the kinetic characteristics of ABB adsorption processes, the pseudo-first-order (Lagergren 1898) and pseudo-second-order (Ho & McKay 1998) kinetic models have been employed to analyze the experimental data at three different initial ABB concentrations (50, 100 and 150 mg/L) in this work. The pseudo-first-order kinetic model was generally expressed as the equation:

\[ -\ln\left(1 - \frac{Q_t}{Q_e}\right) = k_1 t + C, \quad F = \frac{Q_t}{Q_e} \]  

(2)
where $Q_e$ and $Q_t$ are the amounts of the ABB adsorbed (mg/g) at equilibrium and contact time $t$ (min), respectively, $k_1$ (1/min) is the rate constant. The plots of $-\ln(1-F)$ versus $t$ are shown in Figure 5(a).

The experimental data were also fitted by the pseudo-second-order kinetic model which is given with the equation below:

\[
\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \left(\frac{1}{Q_e}\right)t
\]

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

The plots of $t/Q_t$ versus $t$ are shown in Figure 5(b) and the rate constants ($k_2$) are presented in Table 3. It is observed that the corrected correlation coefficients ($R^2$) of the pseudo-second-order model were 0.9183, 0.8648 and 0.9662, respectively, while those of the pseudo-second-order kinetic model were 0.9861, 0.9973, 0.9964 at three different initial ABB concentrations (50, 100 and 150 mg/L). It was obvious that the pseudo-second-order kinetic model provided a better correlation in contrast to the pseudo-first-order model for adsorption of ABB on GO/PAMAMs, which implies that the adsorption of ABB onto GO/PAMAMs is described well by the pseudo-second-order model. It is possible to suggest that the adsorption of ABB onto GO/PAMAMs followed a second-order type
reaction kinetics which was based on the assumption that the rate-determining step was a chemical adsorption (Bai et al. 2014).

**Effect of temperature**

The effect of temperature on adsorption of ABB onto GO/PAMAMs was investigated by adding 0.02 g adsorbent into 100 mL solution with initial ABB concentration ranging from 50 mg/L to 250 mg/L at 298 K, 308 K, 318 K and 328 K, respectively, and the results are presented in Figure 6. It can be seen that the adsorption capacity increases as the temperature increases.

**Adsorption isotherms**

 Isotherm studies describe how adsorbates interact with adsorbents, affording the most important parameter for designing a desired adsorption system. The equilibrium adsorption data were analyzed by the Langmuir and Freundlich isotherm models (Freundlich 1907; Langmuir 1918). The Langmuir isotherm is often applicable to a homogeneous adsorption surface with all the adsorption sites having equal adsorbate affinity, while the Freundlich isotherm model assumes heterogeneity of adsorption surfaces, which can be expressed as:

**Langmuir isotherm**

\[ \frac{C_e}{Q_e} = \frac{1}{b Q_m} + \frac{C_e}{Q_m} \]  

**Freundlich isotherm**

\[ \ln Q_e = \ln k + \frac{1}{n} \ln C_e \]

where \( Q_m \) (mg/g) is the maximum adsorption capacity of ABB per unit weight of adsorbent; \( b \) represents the equilibrium constant of adsorption reaction (L/mg); and \( k \) and \( n \) are the Freundlich constants.

The plots of \( C_e/Q_e \) versus \( C_e \) are shown in Figure 7(a) and the values of \( Q_m \) and \( b \) are presented in Table 4. The \( k \) is roughly an indicator of the adsorption capacity (mg/g) and \( 1/n \) is an empirical parameter relating to the adsorption intensity. The plots of \( \ln Q_e \) versus \( \ln C_e \) are shown in Figure 7(b) and the values of \( k \) and \( n \) are also presented in Table 4.

As shown in Table 4, the linear correlation coefficients (\( R^2 \)) values of Langmuir isotherms were 0.9995, 0.9965, 0.9983 and 0.9979, respectively, at 298, 308, 318 and 328 K, respectively, and the results are presented in Figure 6. It can be seen that the adsorption capacity increases as the temperature increases.

**Table 3** | First-order, second-order rate constants

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_e ) (mg/g)</td>
<td>( k_1 ) (1/min)</td>
</tr>
<tr>
<td>100</td>
<td>127.2</td>
<td>0.0108</td>
</tr>
<tr>
<td>150</td>
<td>207.3</td>
<td>0.0159</td>
</tr>
<tr>
<td>200</td>
<td>332.5</td>
<td>0.0113</td>
</tr>
</tbody>
</table>
calculated from the fitting results that the adsorption capacity $Q_m$ of ABB onto GO/PAMAMs were 325.78, 386.10, 398.41 and 520.83, respectively, at 298, 308, 318 and 328 K. It was obvious that the maximum adsorption capacity of ABB onto GO/PAMAMs increased with the increase in temperature. The experimental results demonstrate that the process of adsorption of ABB onto GO/PAMAMs is endothermic.

As can be seen from Table 4, the $R^2$ values of Freundlich isotherms were in the range 0.5593–0.8857, which suggested that the adsorption processes did not fit well with the Freundlich model.

Another parameter $R_L$, a dimensionless equilibrium parameter, is defined as follows (Weber & Chakravorti 1974):

$$R_L = \frac{1}{1 + bC_0}$$

where $b$ is the Langmuir constant (L/mg) and $C_0$ is the highest initial dye concentration (mg/L). The $R_L$ values within the range $0 < R_L < 1$ indicate a favorable adsorption (Chen et al. 2013). Table 4 shows that $R_L$ values are between 0 and 1, indicating a favorable adsorption of ABB onto GO/PAMAMs. Also, the value of $1/n$ is lower than 1, indicating a normal Langmuir isotherm (Fan et al. 2015). The result is in agreement with the above research about the Langmuir and Freundlich isotherm models.

**Thermodynamic study**

To evaluate the effect of temperature on the adsorption process of ABB onto GO/PAMAMs, the thermodynamic parameters such as Gibbs free energy ($\Delta G^0$), enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) were calculated according to the following equations (Sari & Tuzen 2008):

$$\Delta G^0 = -RT \ln K_d = \Delta H^0 - T\Delta S^0$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where $R$ is the universal gas constant (8.314 J/mol K), $K_d$ is the distribution coefficient ($K_d = Q_e/C_e$) and $T$ is the absolute temperature (K). The $\Delta S^0$ and $\Delta H^0$ were calculated from the intercept and slope of the plot of $\ln(K_d)$ versus $1/T$. The values of $\Delta S^0$ and $\Delta H^0$ were calculated from the slope and intercept of van’t Hoff plot ($\ln K_d$ vs. $1/T$) shown in Figure 8, and the thermodynamic parameters are listed in Table 5. The valuation of thermodynamic

328 K, for ABB onto GO/PAMAMs. These results indicated that the adsorption of ABB on GO/PAMAMs was a typical monomolecular layer adsorption. In addition, it can be
parameters provides an insight into the interaction between the surface of GO/PAMAMs and ABB. The negative value of $\Delta G^0$, $-8.722$ kJ/mol, $-9.653$ kJ/mol, $-10.583$ kJ/mol and $-11.513$ kJ/mol at 298 K, 308 K, 318 K and 328 K, respectively, indicated the adsorption of ABB onto GO/PAMAMs was a spontaneous process. The values of $\Delta G^0$ were between 0 and $-20$ kJ/mol, which indicated that the adsorption process was physisorption (Weng et al. 2009).

The value of $\Delta G^0$ becomes more negative with the increase of temperature, indicating that the adsorption process is more favorable at higher temperature. The positive value of $\Delta H^0$ indicated that the adsorption reaction was endothermic, which is supported by the results that the adsorption of ABB on the GO/PAMAMs increases with the increase in temperature (Figure 6). Similar results have been previously published (Sheng et al. 2010; Zhao et al. 2011). The positive standard entropy change of $\Delta S^0$ demonstrates the increased randomness at the solid-solute interface and the affinity of the GO/PAMAMs for the ABB (Zhao et al. 2011). Before adsorption occurs, the ABB in solution is surrounded by a tightly bound hydration layer where water molecules are more highly ordered than in bulk water. Once the ABB comes into close interaction with the hydration surface of the GO/PAMAMs, the ordered water molecules in these two hydration layers are compelled and disturbed, resulting in the increased freedom of the system. Besides, the entropy of activation ($\Delta S^0$) is generally identified as a measure of the saddle point width of the potential energy surface over which GO/PAMAMs act as activated complexes (Sheng et al. 2010).

**CONCLUSIONS**

This study investigated the equilibrium and the dynamic adsorption of ABB onto GO/PAMAMs. Batch adsorption experiments showed that the adsorption of ABB onto GO/PAMAMs were dependent on pH, contact time and temperature. The optimum pH value of the adsorption of ABB onto GO/PAMAMs was 2.5. The maximum adsorption capacity increased from 325.78 to 520.83 mg/g with the increase in temperature from 298 to 328 K. The equilibrium data followed the Langmuir isotherm model better than the Freundlich model. The pseudo-first-order model and pseudo-second-order rate model were applied to study the kinetics of the adsorption. The results illustrated that the adsorption of ABB onto GO/PAMAMs fitted well with the pseudo-second-order model. The thermodynamic

<table>
<thead>
<tr>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta H^0$ (J/mol)</th>
<th>$\Delta S^0$ (J/mol·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$-8.722$</td>
<td>19.01</td>
</tr>
<tr>
<td>308</td>
<td>$-9.653$</td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>$-10.583$</td>
<td></td>
</tr>
<tr>
<td>328</td>
<td>$-11.513$</td>
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