Adsorption performance of polydopamine-modified attapulgite granular adsorbent for methylene blue

Weisheng Zheng, Hailing Wang, Zhaolian Zhu and Peng Wei

ABSTRACT

Polydopamine-modified granule organo-attapulgite adsorbent (PDA-GOAT) was facilely prepared via a dip-coating approach. The samples were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Surface area and pore size were calculated from the Brunauer–Emmett–Teller method by N2 adsorption–desorption isotherm. The adsorption behaviour of methylene blue (MB) onto PDA-GOAT was systematically investigated. The experimental data revealed that the adsorption process fitted well with the pseudo-second-order kinetics equation and the adsorption isotherm fitted better with the Langmuir model. Thermodynamic analyses illustrated that MB adsorption onto PDA-GOAT was a physisorption endothermic process. Importantly, PDA-GOAT can be regenerated by NaBH4 aqueous solution. The obtained results prove that PDA-GOAT can be a superior reusable adsorbent for the removal of MB from effluent.

Key words | adsorption, granular adsorbent, methylene blue, polydopamine, regeneration

INTRODUCTION

Dyes from textile industries, paper mills and dyestuff manufacturing have caused serious environmental issues and received widespread attention because of their volume of discharge and effluent ingredients. Moreover, the presence of even very small amounts of dyes in water is highly visible and hazardous to ecosystems and human health (Yagub et al. 2014; Shu et al. 2015). Therefore, dyes must be treated before discharge, so as to minimize the damage to the environment. In recent decades, several chemical, biological and physical techniques have been adopted to remove organic pollutants from effluent, including adsorption (Gomes et al. 2015), flocculation (Zahrim & Hilal 2015), membrane separation (Chen et al. 2015), photocatalytic degradation (Liu et al. 2015a), electrochemical (Liu et al. 2014a) and aerobic and anaerobic microbial degradation (Khan et al. 2014). The dye colored effluents are difficult to be degraded by biological and chemical techniques since dyes are stable to light, oxidizing agents and aerobic digestion; in addition, chemical and biological techniques require specialized equipment and are usually quite energy intensive (Aldegs et al. 2008; Fernandes et al. 2010; Zhang et al. 2010; Madrakian et al. 2011). By contrast, adsorption is known to be a promising technique because of its high efficiency and easy operation as well as there being an abundant raw material source (Ai et al. 2011a; Liu et al. 2015b).

Attapulgite, a hydrated magnesium aluminum silicate clay mineral, is low-cost and rich in nature (Liu et al. 2014b; Mu & Wang 2016). The functional modification of attapulgite with different methods can provide good adsorbents, and has been widely used for the removal of various dyes, organic compounds and heavy metal ions from industrial effluents (Zhang et al. 2015). In a previous work, the natural attapulgite was firstly surface-modified to develop a granular adsorbent (Yu et al. 2015): based on the sol-gel transition property of sodium alginate and calcium chloride (Rocher et al. 2008; Liu et al. 2012), the granule organo-attapulgite adsorbent (GOAT) was then prepared by an embedding method with powder organo-attapulgite (POAT), which solved the problem that powder adsorbent cannot be easily separated and recovered from treated water (Wei et al. 2015). Nevertheless, GOAT lacks high adsorption capacity compared with other absorbents which possess special porous structure or modified surface. Hence, surface modification of GOAT via a facile approach is extremely necessary to enhance its adsorption ability.
It is well-known that polydopamine (PDA) can be obtained from self-polymerization of dopamine under mild aqueous conditions and form an adhesive coating layer on a wide range of substrates, as inspired by the special underwater adhesion property of marine mussel foot proteins (Lee et al. 2007; Bandara et al. 2013; Liu et al. 2014c). PDA, one kind of (synthetic) melanins, possesses surface functional groups (–OH, –NH₂), exhibiting a remarkable multifunctional active nature (Ju et al. 2011; Yan et al. 2013). Accordingly, PDA serves as a functional surface coating layer (Sileika et al. 2011). For example, Gao et al. (2013) prepared a PDA-modified graphene hydrogel which exhibits outstanding adsorption capacities toward a wide scope of contaminants. Huang et al. (2013) presented a montmorillonite coated with a thin layer of PDA via in situ polymerization of dopamine under basic solution conditions. On the basis of these properties of dopamine, including self-polymerization, abundant functional groups and strong adhesion, PDA-modified GOAT (PDA-GOAT) was successfully prepared via a one-step procedure, in which GOAT plays the role as a template. Methylene blue (MB) (Wang et al. 2014) was chosen to be studied by a batch adsorption system. The results of PDA-GOAT as adsorbent to remove MB from aqueous solution demonstrated that PDA-GOAT has improved performance for the removal of MB compared to GOAT. Moreover, PDA-GOAT exhibits excellent cyclic performance via solid–liquid separation and can be regenerated by NaBH₄ to desorb the contaminants, revealing the good potential in practical applications.

**EXPERIMENTAL**

**Materials**

Attapulgite was purchased from Jiangsu Xuyi Qi Rui Mining Co., Ltd, and Dopamine hydrochloride from Aladdin. MB, sodium alginate, hydrochloric acid, sodium hydroxide, calcium chloride, sodium chloride, cetyl trimethyl ammonium bromide and tris(hydroxymethyl)aminomethane (Tris) were of analytical reagent grade and purchased from Nanjing Wanqing Instrument Co., Ltd.

**Preparation of adsorbent**

Attapulgite (50 g) was mixed with 5 g cetyl trimethyl ammonium bromide and 300 mL deionized water by magnetic stirring for 2 h at ambient temperature, and washed with deionized water and dried after centrifugation, resulting in the POAT. Next, 6 g sodium alginate was added to deionized water and heated at a certain temperature to fully dissolve with stirring. Then POAT was mixed with a solution of sodium alginate by magnetic stirring for 2 h to ensure thorough mixing. The mixed solution was dropped into CaCl₂ solution with a concentration of 3%, to form gel beads, by a peristaltic pump at a certain speed, left to stand for 12 h to ensure its full cross-linking, and dried in a vacuum drying oven to obtain GOAT. Finally 5 g dopamine hydrochloride and 3 g GOAT were dissolved in 1 L Tris-buffer solution (10 mM, pH = 8.5) and stirred gently for 24 h at ambient temperature. After the reaction, the beads were separated and washed with deionized water and dried to yield PDA-GOAT.

**Adsorption experiments**

Batch adsorption experiments were performed using 100 mL Erlenmeyer flasks with addition of 100 mg PDA-GOAT and 50 mL of MB solution of desired initial concentrations at pristine solution pH in a constant shaking incubator at a shaking speed of 150 rpm. Kinetic experiments were performed by keeping 100 mg/L of MB solution at 298 K. To study the adsorption isotherms and thermodynamics, MB solutions of different initial concentrations (25–500 mg/L) were incubated with adsorbents at natural pH in flasks, and the temperature was held at 298, 313 and 328 K, respectively. The concentrations of MB in supernatant solutions were assessed using a UV-vis spectrophotometer, before and after the adsorption process. The adsorption amount (qₑ, mg/g) was calculated according to Equation (1):

\[
qₑ = \frac{(c₀ - cₑ)V}{m}
\]

where \(c₀\) and \(cₑ\) (mg/L) are the initial and final concentration of MB solution, respectively. \(V\) (L) is the volume of MB solution and \(m\) (g) represents the dry weight of PDA-GOAT.

The effects of pH and ionic strength on the adsorption process were investigated. The initial solution pH was adjusted to values in the range of 2 to 11 by adding diluted NaOH or HCl solutions (0.1 mol/L). The effect of salt addition on the amount of MB adsorbed was studied by gradually increasing NaCl concentration in MB solution from 0 to 0.5 mol/L.

**Desorption and reusability**

An amount of 0.1 g of PDA-GOAT after MB adsorption was immersed in fresh NaBH₄ aqueous solution (50 mL,
1.5 mmol/L) and was shaken for 12 h at 298 K and then washed three times with deionized water and dried. Subsequently, PDA-GOAT was in touch with MB solution for another cycle of adsorption. The adsorption–desorption procedures were repeated five times. The desorption percentage of MB is defined by Equation (2):

\[
\%\text{DP} = \frac{M_d}{M_a} \times 100
\]  

(2)

where DP is the percentage of MB desorbed into NaBH₄, \(M_a\) is the amount of MB adsorbed on PDA-GOAT, and \(M_d\) is the amount of MB desorbed from PDA-GOAT by NaBH₄.

**Characterization**

The morphology of samples were observed on a scanning electron microscope (SEM) (S-3400N II, Japan). The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an X-ray photoelectron spectrometer (PHI 5000 VersaProbe, Japan). The Fourier transform infrared (FTIR) spectra of samples were acquired on a spectrometer (NEXUS870, USA) using KBr method. The surface area, pore volume and pore diameter of samples were determined by the Brunauer–Emmett–Teller (BET) method by means of the \(N_2\) adsorption–desorption isotherm on an automatic surface area and pore size analyzer (NOVA3000e, USA). The value of the pH\textsubscript{PZC} (PZC: point of zero charge) of adsorbent was determined using the modified pH drift method (Jiménez-Cedillo et al. 2015).

**RESULTS AND DISCUSSION**

**Characterizations**

SEM micrographs of samples are shown in Figure 1. As can be seen, PDA-GOAT is an absolutely regular sphere, and its diameter is about 2.5 mm. The surfaces of PDA-GOAT possess more microscopic spherical aggregates than GOAT in high-magnification SEM images. The change is due to the formation of the PDA layer.

Figure 2 shows the XPS survey spectra of GOAT and PDA-GOAT. Compared with GOAT, the peaks of C 1s are significantly enhanced and the peaks of O 1s are weakened after surface modification by dopamine. This is due to the high carbon content and the low oxygen content of PDA. At the same time, a new peak of N 1s emerges in PDA-GOAT.

For PDA-GOAT, the C 1s spectrum can be curve into three peak components of the aromatic C–H at 284.5 eV, C–OH/C–N at 286.1 eV, and C = O at 288.1 eV (Xu et al. 2010; Gao et al. 2013). Also, three N 1s spectra peaks are
assigned to $-N^+R_3$ (402.5 eV), $-NH_2$ (400.5 eV) and $-NH$ (399.6 eV), respectively. The appearance of the C–N peak and N 1s peak in the spectrum of PDA-GOAT illustrates the formation of the PDA layer on GOAT (Xu et al. 2010).

The FTIR spectra of dopamine and PDA-GOAT are presented in Figure 3. A few intense adsorption features could be observed in the FTIR spectra of PDA-GOAT. The absorption band at 3,382 cm$^{-1}$ is ascribed to the phenolic O-H and N-H stretching vibration, 1,625 cm$^{-1}$ is associated with the stretching vibration of the aromatic ring and bending vibration of N-H, 1,500 cm$^{-1}$ is assigned to N-H shearing vibration, and the peak at 1,392 cm$^{-1}$ is attributed to the stretching vibration of phenolic C-O-H, owing to the successful polymerization of dopamine and the presence of PDA on the surface of GOAT (Liu et al. 2013; Fu et al. 2015).

The surface area, pore volume and pore diameter of POAT, GOAT and PDA-GOAT are summarized in Table 1. The results show that surface area and pore volume of GOAT and PDA-GOAT are lower than that of POAT, revealing the micropores of POAT were partially blocked by calcium alginate after embedding.
Adsorption kinetics studies

Adsorption kinetic studies of POAT, GOAT and PDA-GOAT were studied at the condition of 298 K, and Figure 4(a) shows two kinetic curves for the MB removal onto three adsorbents, respectively. The linear forms of these two kinetic models are given as follows (Dabrowski 2001):

\[
\ln \left( \frac{q_e}{C_0} \right) = \ln \left( \frac{q_e}{C_0} \right) - \frac{k_1 t}{2.303}
\]

\[
\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e}
\]

where \( q_e \) and \( q_t \) (mg/g) represent the amounts of MB adsorbed at equilibrium and any time (min), respectively; \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/(mg min)) are the rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively. The kinetic parameters including correlation coefficients (\( R^2 \), \( k_1 \), \( k_2 \) and calculated \( q_{\text{calc}} \) values are determined by linear regression, and are displayed in Table 2.

As shown in Figure 4(a), the adsorption processes of MB on GOAT and PDA-GOAT reach equilibrium within 720 min, which is longer than for POAT (60 min) because internal pores are blocked by calcium alginate resulting in a decrease of surface area and pore volume (Table 1), whereas the adsorption capacity of MB onto PDA-GOAT is obviously higher than that of POAT and GOAT. This result may be due to the electrostatic attraction interactions between the catechol groups of PDA and functional groups of MB as well as \( \pi-\pi \) stacking interactions between aromatic moieties of PDA and MB (Xie et al. 2014). It is seen from Table 2 that all the values of \( R^2 \) for the pseudo-first-order model are relatively lower than those of the second-order model, implying that the pseudo-second-order model is suitable to describe the adsorption kinetics.

The intraparticle diffusion model is given by Weber & Morris (2005). The equation can be described as:

\[
q_t = k_i t^{0.5} + c
\]

where \( k_i \) (mg/(g min\(^{0.5}\))) is the intraparticle diffusion rate constant. From the Figure 4(b), it can be seen that the plots present a multi-linearity throughout the whole range, which signifies that two steps affected the adsorption process (Zhou et al. 2005). The first rapid removal of MB is the external surface adsorption correlated to the boundary layer diffusion and the second stage is due to the intraparticle diffusion mechanism. The values of \( k_i \) and the corresponding correlation coefficients at three different adsorbents are listed in Table 2.

Effects of initial solution pH

Figure 5(a) shows the effects of initial solution pH on the adsorption capacity of PDA-GOAT for MB at ambient temperature. The adsorption capacities of MB indicate a distinct increasing trend with the increase of pH value from 2 to 11. The pHPZC is an important indicator of the net surface charge of the adsorbent (Aldegs et al. 2008). The surface charge of adsorbent will remain neutral when solution pH equals pHPZC, positively charged at pH < pHPZC or negatively charged at pH > pHPZC (Mandal & Ray 2014). It can be seen from Figure 5(b) that the pHPZC of PDA-GOAT is about 3. When pH is lower than 3, the excess H\(^+\) ions

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET} (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POAT</td>
<td>180.1</td>
<td>0.3422</td>
<td>7.63</td>
</tr>
<tr>
<td>GOAT</td>
<td>81.2</td>
<td>0.1325</td>
<td>3.26</td>
</tr>
<tr>
<td>PDA-GOAT</td>
<td>61.7</td>
<td>0.1852</td>
<td>6.00</td>
</tr>
</tbody>
</table>
compete with the cationic groups of MB for the adsorption sites due to the protonation of the amino groups. When pH is higher than 3, the surface of the adsorbent gathers negative charges, which can enhance the electrostatic attraction between adsorbent and MB molecules.

**Effect of ionic strength**

The effects of NaCl concentration (0, 0.01, 0.05, 0.1, 0.15, 0.2, 0.3 mol/L) on MB adsorption are shown in Figure 6. It shows that the adsorption capacities of MB increase with the increase of NaCl concentration when the NaCl concentration is lower than 0.1 mol/L. Moreover, higher NaCl concentrations higher than 1 mol/L attenuate the adsorption significantly. The reason may be the salt-out effect and competitive adsorption between dyes and sodium ions, successively (El-Nahhal & Safi 2013; Witek-Krowiak 2014). In low salt concentrations, the salt-out effect on the adsorption process can increase the hydrophobic attraction of MB, resulting in more organic molecules adsorbed on the surface of PDA-GOAT. Conversely, high salt concentrations make adsorption sites be occupied by sodium ions because inorganic cation may compete with cations of MB for the negatively charged active sites on the adsorbent surface.

**Adsorption isotherm**

The experimental equilibrium data of MB adsorption onto PDA-GOAT are fitted to Langmuir and Freundlich models. The equations are respectively shown as follows (El et al. 2013):

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
<th>Intraparticle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_{e,cal}$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>POAT</td>
<td>0.4787</td>
<td>19.97</td>
<td>0.9551</td>
</tr>
<tr>
<td>GOAT</td>
<td>0.0131</td>
<td>17.13</td>
<td>0.9627</td>
</tr>
<tr>
<td>PDA-GOAT</td>
<td>0.0131</td>
<td>36.04</td>
<td>0.9527</td>
</tr>
</tbody>
</table>

**Table 2 | Adsorption kinetic parameters of MB adsorption on POAT, GOAT and PDA-GOAT**
where $q_e$ (mg/g) is the adsorption capacity at equilibrium and $q_m$ (mg/g) is the maximum adsorption capacity; $k_l$ (L/mg) is the Langmuir constant, and $k_f$ (L/g) and $n$ are Freundlich constants.

Figure 7 shows the adsorption isotherms of MB onto PDA-GOAT at 298, 313, and 328 K. Table 3 lists the model parameters mentioned above. It can be seen that the MB equilibrium adsorption capacity significantly increases with the rise of temperature, and all $R^2$ values of the Langmuir model are much larger than those of the Freundlich model, indicating that the Langmuir model is more eligible to describe this adsorption. Meanwhile, Table 4 compares the $q_m$ value of MB onto PDA-GOAT with other adsorbents. It can be clearly observed that PDA-GOAT shows a relatively higher adsorption capacity for MB than did the other adsorbents.

### Thermodynamic analyses

The thermodynamic parameters of free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$), and entropy change ($\Delta S^0$) can be calculated by the following equations (Gobi et al. 2011):

$$\Delta G^0 = -RT \ln(K_L)$$

$$\ln(K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where $K_L$ is the Langmuir constant (L/mol), $R$ is the gas constant (8.314 J/(mol K)) and $T$ is the temperature (K). $\Delta H^0$ and $\Delta S^0$ were determined using the slope and intercept of the plots of $\ln(K_L)$ versus $1/T$. The thermodynamic parameters are given in Table 5. The negative values of $\Delta G^0$ confirm the spontaneous nature of adsorption. The value of $\Delta H^0$ is 7.86 kJ/mol, which is smaller than 40 kJ/mol, indicating MB adsorption onto PDA-GOAT follows a physisorption process (Kara et al. 2003) and the adsorption reaction is endothermic.

### Regeneration and reuse

PDA-GOAT is easy to separate from water because of its granular form. The recyclability of the adsorbent was also
evaluated. Figure 8 shows that the adsorption capacity of PDA-GOAT still can reach up to 32.11 mg/g even after five adsorption–desorption cycles. Hence, the potentiality of PDA-GOAT as a reusable adsorbent for dye removal is of great prominence.

### Adsorption mechanism

Figure 9(a) shows the XPS survey spectra of PDA-GOAT and PDA-GOAT/MB (PDA-GOAT loaded with MB). The appearance of a new S 2p peak in the spectrum of PDA-GOAT/MB compared to that of PDA-GOAT indicates the existence of MB on the surface of PDA-GOAT. In Figure 9(b), the FTIR spectra of PDA-GOAT, MB, and PDA-GOAT/MB are shown. After the adsorption of MB onto PDA-GOAT, the new adsorption bands at about 1,397 cm\(^{-1}\) and 1,355 cm\(^{-1}\) can be clearly observed, which belong to the C-N bond of MB (Zhang et al. 2015). It should be noted that the band slightly shifts from 3,382 to 3,367 cm\(^{-1}\), which reveals that phenolic O-H is important in the adsorption process (Fu et al. 2016). The modified attapulgite using polymer with functional groups can effectively increase the active adsorption sites for the adsorption of pollutants (Mu et al. 2015). In addition, MB removal is strongly dependent on the pH of solution (Figure 5). The hydrophilic PDA coating with negatively charged functional groups can attract the positively charged dyes at pH values higher than 3. Thus, MB as a cationic dye can be adsorbed easily by electrostatic forces on the negatively charged surface of PDA-GOAT on which exist numerous phenolic groups (Chen et al. 2014). Furthermore, the peak at 1,625 cm\(^{-1}\) assigned to aromatic rings shifts to 1,604 cm\(^{-1}\) after MB adsorption. The change can be attributed to the π–π stacking interactions between the aromatic backbone of the dye and aromatic rings of the PDA layer (Ai et al. 2014b). Despite the fact that surface area and pore volume of PDA-GOAT show a significant decrease after embedding, the electrostatic attraction and π–π stacking interactions between PDA and MB could play a major role in the adsorption ability of the PDA-GOAT.

### Table 5

| Correlated adsorption coefficients of MB adsorption onto PDA-GOAT | ΔG° (kJ/mol) |
|---|---|---|---|
| ΔH° (kJ/mol) | ΔS° (J/(mol k)) | 298 K | 313 K | 328 K |
| 7.86 | 32.63 | −1.87 | −2.34 | −2.85 |
CONCLUSIONS

PDA-GOAT adsorbent used for the MB removal from aqueous solutions has been fabricated via a facile method.

Kinetics data obey the pseudo-second-order model. The adsorption process is controlled by both film diffusion and intraparticle diffusion. Equilibrium data are well described by the Langmuir isotherm model, and the maximum adsorption capacity for MB is 93.06 mg/g at 298 K.

Negative value of $\Delta G^0$ and positive value of $\Delta H^0$ confirmed that the adsorption process is spontaneous and endothermic. The adsorption capacity of MB is highly influenced by initial solution pH and NaCl concentration.

The desorption and regeneration experiment demonstrates that NaBH$_4$ could effectively regenerate PDA-GOAT. After five times of successive adsorption–desorption cycles, it still maintains a relatively high adsorption capacity.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 51308284).

REFERENCES


Jiménez-Cedillo, M. J., Olguín, M. T., Fall, C. & Colin-Cruz, A. 2013 As(III) and As(V) sorption on iron-modified non-pyrolyzed and pyrolyzed biomass from Petrosilinium crispum (parsley). J. Environ. Manage. 117, 242–252.


First received 6 December 2016; accepted in revised form 18 August 2017. Available online 17 October 2017.