Adsorption of methyl orange from aqueous solution using chitosan/diatomite composite

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ABSTRACT

A novel chitosan/diatomite composite was prepared by a simple mixture in the mass ratio to remove methyl orange (MO) from aqueous media in this study. The composite adsorbent was characterized by Fourier transform infrared spectroscopy and scanning electron microscopy analysis. The parameters to influence the adsorption of MO were studied under such conditions as kinetics, adsorption isotherm, pH effect, and thermodynamics. The results revealed that adsorption of MO was initially rapid and the equilibrium time was reached after 40 min. The optimal value of the pH was 5.0 for better adsorption. The equilibrium data were well fitted to the Langmuir isotherm compared to the Freundlich isotherm, and exhibited the highest capacity and a removal rate of 88.37% under an initial dye concentration of 50 mg/L. The kinetic data were well described by the pseudo-second order model. The thermodynamic calculations revealed that the sorption was viable, spontaneous, and exothermic under the conditions studied. In addition, the chitosan/diatomite composite had good adsorption and desorption performance with respect to reusability after six cycles. These results showed that the chitosan/diatomite could be considered as a potential adsorbent for the removal of MO in aqueous solution.

Key words | adsorption, chitosan/diatomite, kinetics, methyl orange, thermodynamics

INTRODUCTION

Industrial wastewaters resulting from the indiscriminate discharge of toxic dyes have aroused environmental concerns for the past few decades. Nevertheless, it is extremely difficult to treat tremendous amounts of modern dyes with resistance to sunlight, water and other atrocious conditions for the long-term (Fan et al. 2009). Actually numerous dyes have been developed for their chemical stability and do not suffer biochemical degradation easily. Methyl orange (MO) is extensively applied in the fields of printing, food, textiles, scientific research and the pharmaceutical industries (Gong et al. 2005). The dyes, especially MO with toxic, mutagenic and carcinogenic features, play an important role in industrial waste-water, and exhibit poor biodegradability (Parshetti et al. 2010; Mathur et al. 2012). Consequently, there is a tremendous need to remove MO from aqueous solution. Up to the present time, various methods such as ion exchange, adsorption, reverse osmosis, ultrafiltration, electrochemical degradation, coagulation/ flocculation, extraction, oxidation and ozonation have been studied for the treatment of wastewater contaminated with dyes (Nataraj et al. 2009; Kiran et al. 2013; Sheng et al. 2013, 2014; Ferreira et al. 2014; Mishra & Kumar 2014; Sun et al. 2014; Ge et al. 2016). However, these techniques are costly, and especially ineffective for removing trace amounts of MO. The ability of a large variety of adsorbent materials to remove dyes has been proposed and investigated (Auta & Hameed 2009). Chitosan is a natural polysaccharide with appealing intrinsic properties, such as non-toxicity, biocompatibility and biodegradability (Kumar 2000). In particular, Chitosan displays a powerful adsorption performance toward dyes from aqueous solutions (Ngah et al. 2011; Dotto et al. 2013). It is massively applied in the removal of organic dyes and metal ions (Lazaridis et al. 2007; Crini & Badot 2008; Wu et al. 2010). However, pure chitosan as an adsorbent has several disadvantages, including high cost and low chemical stability, which limits its application in adsorption processes (Jing et al. 2013; Correa-Murrieta et al. 2014). Immobilizing chitosan on a low-cost material such as bentonite, clay, coal ash, or sand could reduce the required amount of
chitosan without affecting the overall adsorption capacity. Diatomite is a kind of lightweight sedimentary rock that consists primarily of the fossilized skeletal remains of the diatom. Diatomite is highly porous, with its structure containing up to 80–90% voids (Khraisheh et al. 2004). It is abundant in many areas of the world, and it is less expensive than chitosan. Therefore, diatomite is an attractive immobilization material for chitosan owing to its low cost as well as its chemical and mechanical stability. On the basis of the above background, we prepared in this study a novel chitosan/diatomite composite to enhance the strength and chemical stability of chitosan.

To the authors’ knowledge, the use of chitosan/diatomite composite for removing MO has not been well investigated. The aim of the present study was to investigate and explore the feasibility of using chitosan/diatomite composite for removing MO from aqueous solutions. The influence of several operating parameters for adsorption of MO, such as contact time, temperature and pH, were investigated in batch mode. In addition, the equilibrium isotherms and kinetic parameters involved were also determined and discussed. The reusability performance of chitosan/diatomite was investigated in the course of consecutive sorption and desorption cycles.

**MATERIALS AND METHODS**

**Materials and analytical method**

All the chemical reagents were analytical grade and were thus used without further purification. Deionized water was used for preparing all of the solutions and reagents. A stock solution of 2,000 mg/L of MO dye (molecular formula: C14H14N3NaO3S, molecular weight: 327.34, Shanghai Sanai Chemical Reagent Co. Ltd, China) was prepared by dissolving the appropriate amount of dye with deionized water. Other working solutions with different concentrations were obtained by successive dilution. The concentration of the MO solution was analyzed by a UV-Visible spectro-photometer (Shimadzu UV-160A) at maximum wave lengths of 465 nm (Ma et al. 2015).

The adsorbed amount of MO at equilibrium, \( q_e \) (mg/g) was calculated by using the mass balance:

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

(1)

where \( V \) is the solution volume (L), \( W \) is the amount of adsorbent (g), and \( C_0 \) and \( C_e \) are the initial and equilibrium MO concentrations (mg/L), respectively.

**Preparation of adsorbents**

Chitosan powder (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 g) was dissolved in 100 mL of 4% (w/v) acetic acid solution, and then diatomite (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 g) was added and stirred until the mixture was homogeneous and gel-like. The chitosan/diatomite composite was dried in an oven at 100 °C for 3 h. After drying, the final product was ground and sieved using a 200 mesh sieve and then sealed as chitosan/diatomite sorbent.

**Characterization of the adsorbent**

The Fourier transform infrared (FTIR) spectra of chitosan/diatomite composite were recorded on a FTIR spectrometer (Nexus 470, Thermo Nicolet, USA) using KBr pellets over the range 4,000–400 cm\(^{-1}\). The scanning electron microscopy (SEM) images of chitosan/diatomite composite were carried out using an SEM (Hitachi S-5500N, Hitachi Company, Japan).

**Adsorption studies**

Batch experiments were carried out to evaluate the effect of contact time, solution pH, adsorbent dosage and temperature for the removal of MO dye on chitosan/diatomite adsorbent from aqueous solutions. The effect of contact time on the sorption process was determined as follows: to each 0.2 g the chitosan/diatomite sample, 100 mL of solution containing 50 mg/L of MO was added subsequently. The samples were shaken at room temperature for periods ranging from 5 min to 1.0 h, and then centrifuged and 5 mL portions of liquid phases were measured. The effect of pH on the adsorption of MO was examined by mixing 0.20 g of chitosan/diatomite with 100 mL of an MO (50 mg/L) solution in a pH ranging from 1 to 9. The initial pH of the MO solutions was adjusted by adding 0.01 M HCl or NaOH solution. The mixture was shaken for 1 h at 20 °C. Under optimum conditions of shaking time and pH, the effect of adsorbent dosage on the removal of MO at \( C_0 = 50 \text{ mg/L} \) was also studied by shaking 100 mL of solution with 0.05–0.4 g of adsorbent.

The isotherm studies were conducted by varying the initial MO concentration (20, 30, 40, 50 mg/L) at 20 °C while the adsorbent was kept at 2 g/L. The kinetics studies were conducted with an initial MO concentration of
50 mg L\(^{-1}\) at 293 K. Samples were collected at various shaking intervals until the concentration of MO in the dilute phase became constant. Finally, the effect of temperature (20, 30, 40, and 50 °C) was studied by using a 50 ml dye solution (50 mg/L) and 0.2 g of adsorbent dosage at pH 5.0 for 1 h.

**RESULTS AND DISCUSSION**

**Sorbent characterization**

The SEM microphotographs of the raw diatomite and chitosan/diatomite samples are presented in Figure 1. It is clear that the raw diatomite has a well-developed porous structure and looks like a circular sieve (Figure 1(a) and 1(b)). After loading with chitosan, the pore structure of the raw diatomite surface was still maintained, which provided a great possibility for dyes to be gathered and adsorbed (Figure 1(c)).

Figure 2 shows the FTIR spectra of the raw diatomite, the chitosan/diatomite sorbent, and the sorbent after adsorption. The bands at 2,880, 1,632, 1,095 cm\(^{-1}\) corresponding to \(-\text{NH}_2\) are present in chitosan. Accordingly, it confirms that the chitosan was well-integrated with the diatomite. The peak at 3,400 cm\(^{-1}\) is broadened and weakened, resulting from overlapping between the N – H and \(-\text{OH}\) stretching vibrations. Compared to the spectrum of the raw diatomite, there is significant difference, with two new peaks appearing in the spectrum of the chitosan/diatomite at 1,640 and 1,610 cm\(^{-1}\) attributed to \(-\text{N} = \text{N}\) of the MO. Furthermore, the band at 1,386 cm\(^{-1}\) is probably related to the blending vibration of C – N of MO corresponding to the spectra of (b). The band around 615 cm\(^{-1}\) is likely attributed to the presence of the symmetrical stretch vibration of Si-O. Within the spectrum of the chitosan/diatomite after adsorption, the band at 1,650 cm\(^{-1}\) shifted to 1,610 cm\(^{-1}\), indicating that the sulfonic acid group on MO was attached to the amino group in the chitosan/diatomite.

**Effect of the loading amount of chitosan in the chitosan/diatomite**

The effect of the loading amount of chitosan in the chitosan/diatomite on adsorption is shown in Figure 3. It was observed that initially the removal percentage increased rapidly with an increase in the loading amount of chitosan,
and after the critical loading amount of chitosan the removal percentage almost reached a constant value. When the content of the loading amount of chitosan reached 60%, the removal rate could reach 88.37%. A further increase in the loading amount of chitosan had almost no influence on the removal. Therefore, 60% of the loading amount of chitosan was adopted for the preparation of the chitosan/diatomite composite.

**Effect of contact time**

The effect of contact time on the removal percentage of MO is shown in Figure 4. The uptake of MO by chitosan/diatomite was rapid within the first 30 min, due to the larger surface area of adsorbent, and gradually decreased with time until it reached saturation. The adsorption reached equilibrium in about 40 min. The observed removal efficiency was 86.62% at 40 min. The differences in the adsorption values after 40 min were very small. Thus, this duration was selected as the optimum contact time.

**Effect of pH**

The pH of the solution plays a significant role in controlling the sorption process. The effect of pH on the removal of MO dye from aqueous solution at various solution pH is shown in Figure 5. It was found that the highest adsorption capacity of MO occurred at pH 5, with an MO removal of over 87%. A pH lower or higher than this pH value was adverse to the adsorption. According to the literature (Huang et al. 2015),
the optimum pH was frequently reported around pH 3–6 when chitosan was used as an adsorbent for adsorption of MO. At a lower pH, chitosan is soluble in water, which leads to active adsorption sites decreasing on the adsorbent surface. The low pH leads to an increase in H\(^+\) ions on the chitosan/diatomite surface, which results in a strong electrostatic attraction between the negatively charged dye molecules and the positively charged chitosan/diatomite (Al-Degs et al. 2008). As the pH of the system increases, the number of hydroxide ions increases and competes with the anionic ion MO for the adsorption. Therefore, the optimum pH for dye removal is 5.

**Effect of adsorbent dosage on adsorption**

Figure 6 shows the effect of the adsorbent dose on the adsorption of MO using the chitosan/diatomite. It was observed that the adsorption capacity of the chitosan/diatomite improved with increasing dose, indicating the greater availability of exchangeable sites. This also suggests that after a certain adsorbent dose (0.2 g), the adsorption reaches a maximum and then remains constant even with further adsorbent addition.

**The adsorption isotherm**

To investigate the sorption isotherms, the well-known Langmuir and Freundlich isotherm models were applied for describing the adsorption data (Freundlich 1906; Langmuir 1917).

The linearised isotherm equations are expressed as the following.

**Langmuir:**

\[
\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0b}
\]  

**Freundlich:**

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

where \(C_e\) is the equilibrium liquid phase concentration (mg/L), \(q_e\) is the amount of sorbent adsorbed per unit weight (mg g\(^{-1}\)), and \(Q_0\) and \(b\) are the Langmuir constants related to the sorption capacity and the rate of adsorption, respectively. \(K\) and \(1/n\) are Freundlich constants. The values of \(K\) and \(1/n\) roughly correspond to the adsorption capacity and the heterogeneity factor representing the deviation from the linearity of adsorption, respectively.

Moreover, the degree of suitability of the adsorbent towards MO was estimated from the values of the separation factor constant, \(R_L\) (Hall et al. 1966), given by Equation (4):

\[
R_L = \frac{1}{1 + bC_0}
\]

where \(b\) (L/mg) is the Langmuir constant and \(C_0\) (mg/L) is the initial highest concentration of MO. The value of \(R_L\) lies between 0 and 1 for a favorable adsorption, while \(R_L > 1\) represents an unfavorable adsorption, and \(R_L = 1\) represents a linear adsorption, while the adsorption operation is irreversible if \(R_L = 0\).

The linearized Langmuir and Freundlich isotherms are represented in in Figures 7 and 8. The correlation
Thermodynamic parameters

Thermodynamic parameters such as the free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$), and entropy ($\Delta S^\circ$) change of sorption of MO onto chitosan/diatomite can be evaluated from the following equations (Singh et al. 2006; Ho 2003):

$$K_c = \frac{C_{ae}}{C_e}$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where $K_c$ is the equilibrium constant, $C_{ae}$ is the amount of MO (mg) adsorbed on the adsorbent per liter of the solution at equilibrium, and $C_e$ is the equilibrium concentration (mg/L) of the MO in the solution. $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), and $T$ is the temperature in K.

The values of $\Delta H^\circ$ and $\Delta S^\circ$ are calculated from the slope and intercept of the van't Hoff plot ($\ln K_c$ vs. $1/T$) shown in Figure 9. The values obtained for $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ are given in Table 3. $\Delta G^\circ$ values were found to be $-5.42$, $-4.37$, $-3.31$, and $-2.26$ kJ/mol for 20, 30, 40 and 50 °C, respectively. The values of the Gibbs free energy change were negative, confirming the feasibility of the process and the spontaneous nature of the adsorption process. In addition, the more negative value with a decrease in temperature shows that the amount adsorbed at equilibrium must decrease with increasing temperature. The negative value of $\Delta H^\circ$ ($-36.30$ kJ/mol) confirmed the exothermic nature of the adsorption of MO.

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**Table 1** | Parameters of the Langmuir and Freundlich isotherm models

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$Q_0$ (mg g$^{-1}$)</th>
<th>$B$ (L mg$^{-1}$)</th>
<th>$R^2$</th>
<th>$K$ (mg g$^{-1}$)</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>35.12</td>
<td>0.218</td>
<td>0.9957</td>
<td>7.20</td>
<td>1.76</td>
<td>0.9930</td>
</tr>
</tbody>
</table>

**Table 2** | Different values of $R_L$ at different concentrations of MO

<table>
<thead>
<tr>
<th>MO concentrations (mg L$^{-1}$)</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.1866</td>
</tr>
<tr>
<td>30</td>
<td>0.1326</td>
</tr>
<tr>
<td>40</td>
<td>0.1029</td>
</tr>
<tr>
<td>50</td>
<td>0.0840</td>
</tr>
</tbody>
</table>
on the chitosan/diatomite sorbent. In other words, high temperature is unfavorable to the progress of adsorption. The negative value of $\Delta S^\circ (-105.39 \text{ J mol}^{-1} \text{ K}^{-1})$ reflected a decrease in the disorder of the system at the solid-solution interface, and no significant change occurred in the internal structure of the adsorbent during the adsorption process.

**Adsorption kinetics**

In order to analyze the sorption rate, the kinetic data were modeled using the Lagergren pseudo-first-order and Ho pseudo-second-order equations (Ho & McKay 2000; Rudzinski & Plazinski 2006).

Lagergren pseudo-first-order:

$$\log \left( \frac{q_e - q_t}{q_t} \right) = \log \left( \frac{q_e}{k_1 t} \right)$$

Ho pseudo-second-order:

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

where $q_t$ and $q_e$ are the amount of MO adsorbed (mg g$^{-1}$) at time $t$ and at equilibrium, respectively; $k_1$ (min$^{-1}$) and $k_2$ (mg g$^{-1}$ min$^{-1}$) are the pseudo-first-order and pseudo-second-order rate constants.

For the pseudo-first-order equation, a plot of $\log (q_e - q_t)$ vs. $t$ for sorption of MO is shown in Figure 10. The application of the pseudo-second-order equation by plotting $t/q_t$ vs. $t$ is shown in Figure 11. The kinetic parameters, together with correlation coefficients ($R^2$), have been postulated from the slopes and the intercepts of the respective plots and are listed in Table 4. By comparing the correlation coefficients ($R^2$) values obtained for the pseudo-first-order ($R^2 = 0.9459$) and pseudo-second-order ($R^2 = 1.0000$) kinetics, it can be concluded that the pseudo-second-order fitted better than the pseudo-first-order model with the kinetic data. The theoretical $q_e$ values obtained from the pseudo-second-order model are also closer to the experimental $q_e$ exp values. These results show that the rate of adsorption conforms to pseudo second-order kinetics. Similar results have been observed in the adsorption of MO onto chitosan/alumina composite (Zhang et al. 2012).

**Reusability performance of chitosan/diatomite**

An estimate of the extent of recovery of MO absorbed from aqueous solution can be made by means of the sorption-desorption cycle as illustrated in Figures 12 and 13. In this respect, the sorption-desorption cycles were analyzed to investigate the composite’s reusability for the removal of MO from aqueous solutions. The cycle was performed six times by repeating the use of sodium hydroxide solution.

**Table 3** | Thermodynamic parameters for adsorption of MO on CDS

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>-5.42</td>
<td>-36.30</td>
<td>-105.39</td>
</tr>
<tr>
<td>303</td>
<td>-4.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>-3.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>-2.26</td>
<td></td>
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</table>
After 10 min, desorption efficiency of chitosan/diatomite composite rapidly reached 97.7%. The results of regeneration are shown in Figure 12; after being reused six times, the adsorption decreased from 88.37% to 83.52, exhibiting extremely stable adsorption capacity. The chitosan/diatomite composite has a good sorption-desorption performance, and can be used confidently without an obvious reduction in its sorption capacity for the removal MO.

## CONCLUSIONS

Chitosan is a great potential adsorbent for wastewater treatment. In this study, a novel chitosan/diatomite sorbent was prepared, characterized and applied as a sorbent for the removal of MO from aqueous solution using the batch method. The optimized values of contact time, pH and adsorbent dose were found to be 40 min, 5 and 0.2 g, respectively. The Langmuir model fitted the equilibrium data well and the adsorption quantity from the Langmuir model was 35.12 mg/g at 293 K. The kinetic study of the sorption of MO shows that the pseudo-second-order model provides a better correlation of sorption data than the pseudo-first-order model. In addition, the values of $\Delta H^\circ$ and $\Delta G^\circ$ prove that the adsorption of MO on chitosan/diatomite is feasible, and is an exothermic and spontaneous process. Furthermore, the removal rate reached 88.37% and the desorption efficiency reached 98.1%. Most importantly, the data obtained in this study show that there is no significant decrease after six cycles, particularly in the sorption capacity of the chitosan/diatomite composite, with satisfactory adsorption performance. All evidence also once more confirms the fact that chitosan/diatomite composite also has a strong absorption capability and excellent stability. The study will be useful for using the novel materials as a low-cost adsorbent for the removal of MO from waste water.

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## REFERENCES


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