Kinetics and equilibrium studies of methylene blue adsorption on 2D nanolamellar Fe₃O₄

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ABSTRACT
Nanolamellar Fe₃O₄ as magnetic adsorbents was prepared using sodium dodecyl sulfonate as a template. Thermogravimetric measurements characterisation showed that the as-synthesised product contained about 6 wt% sodium dodecyl sulfonate. The adsorption performance of nanolamellar Fe₃O₄ for the removal of organic dye from aqueous solution was evaluated using methylene blue as a model dye. The product exhibited an excellent ability to adsorb methylene blue from aqueous solutions with a maximum methylene blue removal rate of 96.8%. The adsorption kinetics can be described by a pseudo-second-order equation, and the adsorption isotherm agreed well with Langmuir adsorption equation. Furthermore, the dye saturated nanolamellar Fe₃O₄ could be regenerated using acidic ethanol solution, and the nanolamellar Fe₃O₄ showed excellent reusability. The results indicate the potential use of the adsorbent for the removal of methylene blue from aqueous solution.

1. Introduction
Magnetite as a kind of environmental–functional adsorbent has attracted increasing attention because of their excellent superparamagnetism and low toxicity [1–5]. In addition, the easy separation of used magnetic adsorbent from solution can be achieved using an external magnetic field [6–11]. Magnetic properties and applications of magnetic nanomaterials are tightly related to the shape, which has a great influence on the magnetic anisotropy and orientations of the easy magnetisation direction. Furthermore, the magnetic nanomaterials with different shapes may serve as nanoscale building blocks for the construction of superlattices. For these reasons, increasing attention has been focused on the design and exploration of novel methodologies for the fabrication of magnetic nanostructures with controlled morphologies. Up to now, Fe₃O₄ with two-dimensional lamellar structure has been scarcely reported.

Methylene blue (MB) is widely used for colouring paper, temporary hair colorant, dyeing cottons and wools, and its release in the environment can generate health disease to
human and animals such as eye burns or permanent injuries to eyes. MB is difficult to remove completely because of its stable aromatic structure consisting of a chromophore and polar groups. Various techniques have been developed to improve the efficiency of MB removal, including adsorption, chemical oxidation and electrocoagulation [12]. Among these, adsorption has proven particularly effective, mainly because of its simplicity and efficiency [13–15].

In our previous study, nanolamellar Fe$_3$O$_4$ (magnetite) (NLM) was synthesised by a template method [16]. The characterisations showed NLM-possessed properties of novel microwave absorption in the frequency range 1–18 GHz. An obvious multiple-reflection loss phenomenon was observed with the increase of matching thickness. In the present work, the NML materials were further characterised using X-ray photoelectron, Fourier transform infrared and differential scanning calorimetry. The adsorption ability of NML for organic dye from aqueous solution was examined using MB as a model. The adsorption performance of MB was analysed by using the adsorption kinetics and isotherm models. The impact of pH on adsorption and the reuse ability of NML were also investigated. Owing to its ordered nanolamellar structure, the resultant NML can realise perfect absorption separation of MB.

2. Experimental

The typical experiment procedure was similar to that described in literature, and sodium dodecyl sulfonate (SDS, C$_{12}$H$_{25}$SO$_3$Na) was used as the template. The solution of FeCl$_3$.6H$_2$O–FeCl$_2$.4H$_2$O–H$_2$O (0.02 mol–0.01 mol–30 mL) was mixed with the solution of SDS–ethanol (0.004 mol–30 mL). Then the solution of NaOH–ethanol–H$_2$O (0.09 mol–30 mL–30 mL) was added using a magnetic stirrer and a nitrogen stream all along to prevent the oxidation of Fe$^{2+}$ in the system. Before being mixed together, the above solutions were preheated to 70 °C to get each solution species fully dissolved. The mixture was refluxed at 85 °C for 14 h and deposited at room temperature for 5 days. And then, the black precipitate was centrifuged and immersed in water for 4 days. Finally, the precipitate was centrifuged and dried at 60 °C, and the black powder of NLM was obtained. For comparison, solid Fe$_3$O$_4$ was prepared under the same conditions except that no template was added (designated as solid Fe$_3$O$_4$).

The structure of product was characterised with X-ray diffraction (XRD, Rigaku D/Max 2500, Cu Kα, λ = 0.15406 nm). Field emission scanning electron microscope (FE-SEM, FEI NANOSEM 430) was employed to characterise the morphologies. Magnetic and microwave electromagnetic properties were measured by vibrating sample magnetometer (VSM, PPMS-9 from Quantum Design) and vector network analyser (HP-8722ES), respectively. Fourier transform infrared (FT-IR) spectra were obtained in KBr pellets using a Thermo Nicolet Nexus 470 spectrometer. Thermogravimetric measurements and differential scanning calorimetry (TG-DSC) of the as-synthesised sample were performed on a NETZSCH STA 409 thermal analysis system from ambient to 700 °C at a heating rate of 10 K/min under air atmosphere. X-ray photoelectron spectroscopy (XPS) was performed on a PHI5000 Versa Probe system with monochromatic Al Kα X-rays.

For the desorption study, 100 mg of the NML was added to 100 mL of MB solution (the initial concentrations of MB of 10, 20 and 30 mg/L) and the mixture was shaken for 2 h. Then, the MB-adsorbed sample was dispersed into 20 mL of acidic ethanol
(HCl/ethanol) with a pH of 2.0 and shaken for 2 h. The sample was collected by magnetic field and reused for adsorption again. The concentration of MB was analysed by using a UV–Vis spectrometer (Shimadzu UV1700) at 664 nm.

The adsorption capacity $Q_e$ (mg/g) and the removal rate were calculated using the following equation:

\[
\text{Removal rate} = \left(1 - \frac{C_0 - C_e}{C_0}\right) \times 100\%
\]

\[
Q_e = \frac{C_0 - C_e}{m} V
\]

where $C_0$ (mg/L) and $C_e$ (mg/L) are the initial and equilibrium concentrations of MB solutions; $m$ is the weight of sorbent (g) and $V$ is the volume of the MB solution (L).

3. Results and discussion

3.1. Characterisation of NML

Figure 1(a) shows the XRD patterns of NML. Magnetite is believed to be the major crystalline phase for the synthesised NML as identified by the wide-angle diffraction peaks [17]. Figure 1(b) shows that the positions and the relative intensity ratios of the NML diffraction peaks match the solid Fe$_3$O$_4$. For small-angle XRD pattern as shown in the inset of Figure 1(a), the d$_{100}$ reflection for NML was found at $2\theta = 2.37^\circ$, corresponding to a periodical spacing of 3.72 nm.

The corresponding FESEM image of the NML in Figure 2 demonstrates that the NML consisted of stacked nanosheets is several micrometres. The ordered nanolamellar structure of Fe$_3$O$_4$ can be clearly identified from the parallel sheet-like and step-like structure, which is corresponding to the XRD analysis results.

Figure 1. (a) X-ray diffraction patterns of NML, small-angle X-ray diffraction of NML (inset); (b) X-ray diffraction patterns of NML and solid Fe$_3$O$_4$. 

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As shown in Figure 3, according to the XPS spectrum, the photoelectron peaks at approximately 710.5 and 724.7 eV could correspond to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, respectively [6]. The binding energies of 711.2 and 713.4 eV demonstrated the presence of Fe$^{2+}$ and Fe$^{3+}$, a finding which correlates with the literature data of Fe$_3$O$_4$. Moreover, there is no obvious shake-up satellite line at approximately 719.0 eV, indicating that the NML prepared by a template method exist mainly in the form of Fe$_3$O$_4$.

A typical TG-DSC curve of the NML sample under air atmosphere is shown in Figure 4. The TG curve shows three weight loss regions in 25–200, 200–350 and 350–700 °C. The
sample has a total weight loss of ~8.5%. The first is an endothermic loss which can be easily attributed to the water desorption present on external or internal surfaces constituting about 2% weight loss. The long endothermic process (DSC) from 200 to 350 °C is corresponding to the decomposition of SDS composed with ~6% of the weight loss. The residues after decomposition of the sample in air at 700 °C were α-Fe₂O₃, which was identified by XRD.

The FTIR spectra for NML, solid Fe₃O₄ and SDS are shown in Figure 5, respectively. As can be seen from Figure 5, the corresponding absorption of SDS (1179 and 1063 cm⁻¹) is easily to be found in NML [18]. This means the SDS was entrapped in the lamellar structures during the NML was synthesised. A strong peak appearing at around 580 cm⁻¹ and a weak one at approximately 436 cm⁻¹ were related to the vibration of Fe–O functional group. According to the related works, the characteristic peak of bulk Fe₃O₄ was 570 and 375 cm⁻¹ [19,20].

Figure 4. TG-DSC curve of NLM.

Figure 5. FT-IR spectra curve of NLM.
The FTIR spectrum of NML exhibited a blue shift, and the characteristic peak of Fe–O in NML had a higher wavenumber than that of solid Fe$_3$O$_4$. A broad peak appearing at around 3421 cm$^{-1}$ was likely owing to the stretching vibration of O–H bond, which is owing to the adsorbed water in Fe$_3$O$_4$. In comparison with the solid Fe$_3$O$_4$, the main bands of NML are well accordant with the standard spectrum of Fe$_3$O$_4$, except for the special absorption band at 1179 cm$^{-1}$, which is assigned to SDS.

Figure 6 shows the magnetic hysteresis loop of NML at room temperature. The saturation magnetisation value ($M_s$) was measured to be 34.8 emu/g, but possesses no residual magnetisation and coercivity. It should be noted that almost no hysteresis loops were found in the magnetisation curve, suggesting the superparamagnetism of NML. Owing to the high magnetisation values and superparamagnetic characteristics, the NML can be magnetically separated from aqueous solution within a few seconds and redispersed well once the magnet is removed, rendering them economic and reusable for various applications [20,21].

### 3.2. Adsorption and recycling studies

The adsorption ability of NML for organic dye from aqueous solution was examined using MB as a model. Figure 7 shows the removal rate of MB with different initial concentrations on NML. It is clear that the removal rate of MB on NML increased gradually within the first 20 min for all the concentrations and then reached a plateau, indicating that the MB amount being adsorbed onto the NML and desorbing from the NML reached equilibrium. The removal rate of MB within 200 min can be up to 96.8%, 95.2% and 93.4% for the initial concentrations of MB of 10, 20 and 30 mg/g, respectively.

The pseudo-second-order kinetic models were applied to analyse the kinetic data. The pseudo-second-order kinetic model is expressed by the following equation [22]:

$$\frac{t}{q_t} = \frac{1}{K q_e^2} + \frac{t}{q_e}$$
where \( q_e \) (mg/g) and \( q_t \) (mg/g) are the amount of dye adsorbed onto adsorbent at time \( t \) (min) and at equilibrium, respectively; \( K \) (g/mg/min) is the rate constant of second-order adsorption. Figure 8 shows the plots of \( t/q_t \) versus \( t \), and the calculated \( q_e \), \( K \) and the corresponding linear regression correlation coefficient (\( R^2 \)) values are summarised in Table 1.

The results show that there is a good agreement between the calculated and experimental \( q_e \) values. \( R^2 \) for the second-order kinetics model under four different concentrations are all greater than 0.964, which is close to 1, suggesting that the pseudo-second-order model is applicable for the description of dye adsorption.

The adsorption isotherm of dye on NML was studied at room temperature. Figure 9 shows the results of the experimental data and the fitted isotherms. The adsorption amounts of dye on NML increased with dye concentration increasing. The equilibrium
isotherm equation is usually used to describe the experimental adsorption data. Thus, the obtained experimental adsorption data were analysed by the Langmuir model [23]:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}}K_L}
\]

where \( C_e \) and \( q_e \) are the equilibrium concentration of adsorbate in liquid phase (mg/L) and on the solid phase (mg/g), respectively, \( q_{\text{max}} \) and \( K_L \) are Langmuir constants related to the maximum dye sorption capacity (77.39 mg/g) and affinity parameter (0.367 L/mg). The calculated \( R^2 \) is 0.999, which shows that the Langmuir model fits the result well.

The pH value of the dye solution is one of the important factors that affect the whole adsorption process, particularly on the removal rate [15,24,25]. To study the effect of pH on MB adsorption on NML, the experiments were carried out at 30 mg/L initial MB concentration at 20 °C for 120 min, and the pH of the MB solutions was adjusted using 0.1 mmol/L diluted HCl or NaOH solution before the addition of the as-prepared NML. As shown in Figure 10, the adsorption performance of MB of NML is better at high pH than at low pH. Hence it is clear that the adsorption process is dependent on the pH of the solution. The adsorbed amount of MB increased with increasing the pH of the solution and being at a maximum at pH 11. Reduced adsorption of MB at acidic pH reflects the presence of excess H+ ions that compete with dye cations for the adsorption sites.

The regeneration and recycling abilities of the adsorbent are crucial for its practical application. The recycling ability of the NML was investigated. The adsorbed MB can be efficiently desorbed from NML using acidic ethanol (pH = 2) and simultaneity the

| Conc of MB (mg/L) | \( q_e \) (mg/g) | \( K_s \) (g/mg min) | \( R^2 \) |
|------------------|-----------------|---------------------|---------|
| 10               | 9.84            | 0.0512              | 0.0998  |
| 20               | 19.33           | 0.0283              | 0.0992  |
| 30               | 28.71           | 0.0118              | 0.0964  |

Figure 9. Adsorption isotherm of dye on NML.
adsorbent was regenerated. As shown in Figure 11, there is only a very slight decrease of the removal after five recycles, indicating the excellent recycling abilities of NML for recovery of MB from aqueous media.

4. Conclusions

In this study, the as-prepared NML exhibited high magnetisation characteristics. Given these properties, the sample displayed excellent adsorption ability of MB with rapid adsorption rate, high adsorption efficiency, and quick magnetic separation from treated water. The adsorption kinetics can be described by pseudo-second-order equation, and adsorption isotherm of NML agreed well with Langmuir sorption equation. Moreover,
the product could be regenerated via combustion and reused several times. Owing to its nanolamellar structures and magnetic properties, the resultant NML can realise perfect absorption and magnetic separation of MB.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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