Performance and characteristics of methylene blue adsorption using nanomagnetite graphite adsorbent

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Abstract. In this paper, a nanomagnetite graphite adsorbent (MGNP) was developed for removal of methylene blue from aqueous solutions. MGNP was synthesized through the nanographite powder (GNP) functionalized with magnetic γ-Fe₂O₃ nanoparticles under alkaline conditions and calcining for 3 h at 300 °C. The MGNP featured a quick separation process from solutions with an external magnet. The surface charge of the adsorbent was pH-dependent, the pH pzc of MGNP was approximately 7.2. The methylene blue adsorption isotherm of the MGNP can be well fitted by the Langmuir model, the maximum adsorption capacity was about 114.94 mg/g at 25 °C when pH = 7 ± 0.1. In conclusion, the MGNP could be a potential adsorbent for the uptake of methylene blue from wastewater.

1. Introduction
Methylene blue (C₁₆H₁₈ClN₃S) is a kind of important chemical materials in many industrial fields such as plastics, textiles, paper, food and rubber[1-2], at the same time it is also one of the most typical dye pollutants in aqueous systems. It causes human health hazards and environmental pollution if the wastewater containing methylene blue not treated before drawn into the natural water. It is known to have several harmful effects to man including eye irritation, increased heart rate, vomiting, shock, rapid pulse, haziness, hemolytic anemia, and methemoglobinemia[3].

Various technologies, such as precipitation, flotation, flocculation, coagulation, ion exchange, membrane filtration and adsorption, have been employed to uptake of methylene blue from wastewater[4-5]. Adsorption is regarded as an environmentally friendly and economical techniques because of its low operating cost and high selectivity. Corn cob, rice husk, cornhusk, coconut shell fibers and industrial residues like furnace slags, sludges and fly ash[6-7] are reportedly used as adsorbents for dye removal. However, these adsorbents have certain shortcomings, including narrow available pH range, low adsorption capacity, poor mechanical strength and separation difficulty. Therefore, developing an adsorbent that features easy separation and high methylene blue removal efficiency is necessary.

In recent years, nanomagnetite adsorbents have become a research hotspot due to its easy separation and large adsorption capacity[8]. Compared with the traditional adsorbents, magnetic adsorbents have a quick and easy separation process that does not require additional filtration or centrifugation procedures[9-10].

The main purpose of the present work is to synthesis a nanographite-loaded magnetic γ-Fe₂O₃ adsorbent (MGNP) for uptake of methylene blue from wastewater. The MGNP were characterized
using vibrating sample magnetometer (VSM), zeta potential analysis and field emission scanning electron microscopy (SEM). Batch experiments that considered the adsorption equilibrium and kinetics of methylene blue uptake were conducted to estimate the adsorption performance of the MGNP adsorbent.

2. Materials and methods

2.1. Materials
Nanographite powder (content ≥ 99.9%; average granularity, 85 nm) was purchased from Beijing Nachen Co., Ltd. All the used chemicals were analytical grades including C₁₆H₁₈ClN₃S were purchased from Sinopharm in Beijing.

2.2. Preparation of the MGNP adsorbent
Nanographite powder was purified for 6 h with 3 mol/L HNO₃, then activated via sonication for 3 h in the mixture of concentrated nitric acid and sulfuric acid (1:3) at 70 °C. The activated nanographite was washed with distilled water (DW) and dried. 2 g of activated nanographite was added to 100 mL mixed solution (FeCl₂ꞏ4H₂O 1.7296 g; FeCl₃ꞏ6H₂O, 4.7030 g), and then 15 mL ammonia was introduced by dripping slowly at 80 °C. Keep reaction for 90 min, the nanomagnetite graphite was magnetically separated, and then washed with DW until the pH was approximately 7. The nanomagnetite graphite was calcined in a muffle furnace for 3 h at 300 °C. After cooling, the product was washed with DW and dried at 60 °C over night.

2.3. Methylene blue adsorption experiments
All adsorption experiments were performed in 150 mL polypropylene (PP) bottles. The MGNP concentration was fixed at 0.2 g/L, pH of the methylene blue solution was adjusted with 0.05 mol/L NaOH and HCl. The MGNP adsorbent was magnetically separated after adsorption. Adsorption kinetic experiments were carried out under different temperatures (25, 35 and 45 °C) by using methylene blue solutions with an initial concentration of 25 mg/L (pH = 7.0 ± 0.1). For tests on the isotherm experiments, the methylene blue concentrations varied from 0 mg/L to 50.00 mg/L under different temperatures (25, 35 and 45 °C), the mixed reaction solutions were shaken for 12 h. To quantify the uptake mechanism of methylene blue molecules in MGNP, equilibrium adsorption capacity of the MGNP were fitted with Freundlich and Langmuir models.

The Langmuir equation:

\[ Q_e = \frac{Q_mK_L C_e}{1 + K_L C_e} \]  

(1)

where \( Q_m \) is the maximum adsorption capacity (mg/g), \( Q_e \) is the amount adsorbed under equilibrium (mg/g), \( C_e \) is the equilibrium concentration (mg/L), and \( K_L \) (L/mg) is the Langmuir equilibrium constant.

The Freundlich equation:

\[ Q_e = K_f C_e^{1/n} \]  

(2)

where \( 1/n \) and \( K_f \) are the Freundlich equilibrium constants related to adsorption intensity and adsorption capacity, respectively.

2.4. Characterization of the MGNP
Morphological property of the MGNP were analyzed by a scanning electron microscope (SEM, Carl Zeiss-Merlin). Analyses of the magnetism characteristics of the MGNP were conducted by a vibrating sample magnetometer (VSM, LakeShore-7407). The zeta potentials of the MGNP was analyzed by a zeta potential meter (Zetasizer 2000, Malvern, UK).
3. Results and discussion

3.1. Characterization of adsorbent

In Fig. 1, the SEM images showed the layered structure of the nanographite (Fig. 1a). The MGNP nanoparticles became an amorphous structure of small aggregated particles (Fig. 1b) after the magnetic γ-Fe₂O₃ nanoparticles were loaded on the nanographite.

![Figure 1. SEM micrographs of the GNP and MGNP](image)

The magnetization curves (Fig. 2a) and zeta potential (Fig. 2b) of the MGNP adsorbent were shown in Fig. 2. The saturation magnetization value of the MGNP reached 36.18 emu/g (Fig. 2a). The picture in the Fig. 2a showed that the MGNP adsorbent was attracted to the wall of the vial with an external magnet.

![Figure 2. Magnetization curves (a) and zeta potential (b) of MGNP](image)

The pHₚzc of the MGNP adsorbent was about 7.2 (Fig. 2b), which expressed that the surface charge of MGNP was highly related to the pH of solution. When the pH > 7.2, the zeta potentials of MGNP were negative, in this condition there is a strong electrostatic repulsion between the methylene blue anions and the MGNP adsorbent. When the pH of solution was below pHₚzc, the surface charge of the adsorbent became positive, which is conducive to the uptake of methylene blue by MGNP.

3.2. Adsorption kinetics

According to Fig. 3, the amount of methylene blue adsorbed by the MGNP increased rapidly and almost reached adsorption equilibrium within 25 min under 25, 35 and 45 °C, in addition, the methylene blue adsorption capacity of MGNP increased with the increase of temperature.
3.3. Adsorption isotherm

The methylene blue adsorption isotherms of the MGNP under 25, 35 and 45 °C are shown in Fig. 4. According to Fig. 4, the adsorption capacity increased rapidly when the concentration of methylene blue was less than 15 mg/L. When the concentration of methylene blue was higher than 15 mg/L, the adsorption capacity increased gradually and reached adsorption equilibrium. Furthermore, the adsorption capacity increased with the increase of temperature.

In this study, the Freundlich and Langmuir models were used to fit the experimental adsorption results. The corresponding isotherms parameters were given in Tab. 1. According to Table 1, the value of determination coefficients ($R^2$) for Langmuir model was higher than that of Freundlich model, it is proved that the Langmuir equation was better fitted to describe the adsorption behavior of methylene blue onto MGNP. Indicated that the adsorption of methylene blue by MGNP is monolayer adsorption. In addition, the maximal adsorption capacities ($Q_m$) of methylene blue calculated with the Langmuir equation were 114.94, 117.65, and 123.46 mg/g under 25, 35 and 45 °C, respectively.
Table 1. Methylene blue adsorption isotherm Parameters of MGNP

| Temperature (°C) | \( Q_{\text{exp}} \) (mg/g) | \( Q_m \) (mg/g) | \( K_L \) (L/mg) | \( R^2 \) | \( 1/n \) | \( K_f \) (L/mg) | \( R^2 \) |
|-----------------|--------------------------|----------------|-----------------|--------|--------|-----------------|--------|
| 25              | 108.52                   | 114.94         | 0.43            | 0.99   | 0.44   | 29.66           | 0.96   |
| 35              | 115.54                   | 117.65         | 0.88            | 0.99   | 0.36   | 41.24           | 0.98   |
| 45              | 121.05                   | 123.46         | 0.99            | 0.99   | 0.35   | 45.38           | 0.97   |

4. Conclusion
In this work, a two-element adsorbent (MGNP) was synthesised for methylene blue uptake. These nanoparticles have several advantages compared to other adsorbents: their synthesis is environmentally friendly; they possess large adsorption capacities; and they can be easily magnetically separated from water. The adsorption equilibrium data fitted well with the Langmuir model. Consequently, the prepared MGNP can be applied as an eco-friendly and high-performance adsorbent for the removal of methylene blue.

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