Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–9

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

# Enhanced removal performance for methylene blue by kaolin with graphene oxide modification

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ARTICLE INFO

*Article history:*
Received 18 January 2018
Revised 1 April 2018
Accepted 12 April 2018
Available online xxx

*Keywords:*
Kaolin
Graphene oxide modification
Methylene blue
Adsorption process

ABSTRACT

In this study, graphene oxide modified kaolin (GO-kaolin) composites (named 2% GK, 5% GK, and 10% GK) were synthesized by a facile method. Characterization results indicated the successful modification of GO on kaolin surface. To understand the dye removal performance of kaolin with GO modification, batch adsorption experiments were carried out using methylene blue (MB) as a model dye pollutant in various experimental conditions The adsorption results showed that the increase of GO content in modified kaolin composite could effectively enhance the removal of MB from aqueous solution in each experiment condition, which was attributed to the increase of special surface area and active adsorption sites. Kinetic analysis of MB adsorption by GO-kaolin samples was shown a better fitting to pseudo-second-order kinetic models. The adsorption isotherm data were better fitted to Langmuir isotherm models. The values of thermodynamics constants suggested that the adsorption reaction was endothermic in nature. Furthermore, adsorption process of MB on kaolin was changed after the introduction of GO. An excellent regeneration performance of 10% GK was observed via the regeneration experiment. The results show that kaolin modified with suitable GO content is a high-efficiency and reusable adsorbent in the removal of MB from wastewater.



## 1. Introduction

With the rapid economic development, various types of pollutants including heavy metals [1,2], organic compounds [3–6], and dyes [7–10] will be inevitably or unconscionably released into environment, which will lead to severe environmental problems. Water resource is vital for the development and survival of human, however, water pollution caused by these pollutants has become a critical issue worldwide [11]. Among these pollutants, dyes, a kind of colored chemical agents, have been attracted great attentions due to their wide productions and applications [12]. Unfortunately, the discharge of dyes into water bodies is the major source of water pollution. Because of their undesirable diverse colors in waters even at low concentration (less than 1 ppm) and toxicity, they have been considered as a major threat to environment. Commonly, they will cause the abnormal coloration of surface waters, hinder the infiltration of sunlight and pose severe damage to the aquatic organisms [13,14]. To date, dyes wastewater treatment is still a serious challenge to environmental scientists. Several commonly used treatment technologies including adsorption [15–19], membrane filtration [20], coagulation–flocculation [21], oxidation processes [22,23], and biodegradation [24,25] have been applied for dyes removal. However, each of these methods has their own benefits and limitations, which have been summarized in previous reviews [26–28].

Adsorption has been considered as an efficient and attractive method in pollutants removal due to its low-cost, high efficiency, and easy design [16]. Currently, various low-cost and eco-friendly adsorbents including natural inorganic and agricultural materials have been reported for the removal of dyes from aqueous solutions. Particularly, kaolin as one of the common clay mineral materials has been widely used in wastewaters treatment [29–31]. Due to its chemical composition and crystalline structure, the surfaces of kaolin are believed to carry a constant structural negative charge derived from the isomorphous substitution of Si(IV) by Al(III) in silica layer [32]. Therefore, it could be used as adsorbent for the treatment of cationic dyes wastewater [16,31–34]. However, the existing disadvantages such as severe agglomeration and low

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https://doi.org/10.1016/j.jtice.2018.04.013
1876-1070/

adsorption capacity in solution will impede its practical applications [7,29]. Methylene blue (MB), a kind of phenothiazine salt, was selected as a model cationic dye in this study. In a preliminary experiment, we have verified the low adsorption performance of kaolin on MB. Likewise, it has been reported that the maximum adsorption capacity of MB by raw kaolin was only 13.99 mg/g [33]. Consequently, it is necessary to seek a simple and effective method to activate the adsorption capacity of kaolin.

Graphene oxide (GO), one of the typical graphene materials, has a unique two-dimensional (2D) atomic crystal with a single layer of $sp^2$-bonded carbon atoms closely packed into honeycomb lattice [35,36]. It has become the research hotspot due to the intriguing structure and physicochemical properties [37,38]. In addition, GO has abundant oxygen containing functional groups and has been reported as good adsorbent for the removal of cationic dyes [39,40]. However, the separation of GO from aqueous solution is difficult due to its excellent hydrophilicity. Thus, the design of hybrid GO-based materials is important for pollutants removal. Previous studies have shown that GO enwrapped nanomaterial photocatalysts could enhance the adsorption, photocatalytic activity, and stability [41,42]. In a word, GO modification is an ideal route to improve the removal performance of other materials towards special pollutants. With this in mind, it is expected that hybridizing GO with kaolin may lead to considerable performance in dyes removal. To our knowledge, however, little research has been carried out to utilize the GO and kaolin composite for cationic dyes removal. Thus, the application of GO as an adsorption activator on kaolin for dyes wastewater treatment is worth exploring.

To take advantage of the recent developments in graphene and kaolin materials, a set of modified kaolin composites containing different contents of GO (GO-kaolin) using 3-aminopropyltrimethoxysilane (APTMS) as linkage were produced in laboratory through simple electrostatic interaction. In the present study, the main objectives were to investigate the adsorption processes and behaviors of MB on the as-prepared GO-kaolin composites from aqueous solution. Herein, we deem that this study can provide theoretical basis for further design and practical applications of graphene modified clay composites in future work.

## 2. Materials and methods

### 2.1. Materials

GO was prepared according to the modified Hummers method [43] and was confirmed before use in Supplementary Materials. APTMS, Kaolin ($Al_2Si_2O_9H_4$), MB, and all other chemicals used were purchased from Shanghai First Reagent Co., China. Solutions were prepared with distilled water in all experiments.

### 2.2. Synthesis of GO-kaolin nanocomposites

The synthesis of GO-kaolin was conducted by the electrostatic interaction using APTMS as linkage [44]. In this study, 1.0 g kaolin power was first dispersed in 200 mL distilled water by magnetic stirring and ultrasonication for 2 h. Then, adding 4 mL APTMS into the suspension while stirring for 10 min, followed by adding different amounts of GO suspension to change the weight ratio of GO to kaolin (2%, 5%, and 10%) under vigorous stirring. After stirring for another 2 h, the composites were separated by filtration and washed with distilled water for three times. The composites were dried at 50 °C overnight to obtain the GO-kaolin samples. According to the GO content, the resultant GO-kaolin samples were named as 2% GK, 5% GK, and 10% GK, respectively. The preparation illustration of Go-kaolin is shown in Scheme S1.

### 2.3. Characterizations

The element compositions and surface functional groups of raw kaolin and GO-kaolin samples were investigated by X-ray photoelectron spectroscopy (XPS), which was performed on ESCALAB 250Xi (Thermo Fisher Scientific, USA). Field Emission Scanning Electron Microscope (FE-SEM, JSM-6700F, Japan) was used to observe the surface morphology of composites. The specific surface area was measured based on Brunauer–Emmett–Teller (BET) method using nitrogen as absorbent.

### 2.4. Adsorption experiments

In this study, the cationic dye, MB was used as the model pollutant to investigate the adsorption performance of GO-kaolin samples. Batch adsorption experiments were carried out at room temperature (25 ± 1 °C) by adding a known amount of adsorbent (80 mg) into 100 mL MB solution (pH 7.0) in a shaking bath with a shaking speed of 180 rpm. Initial dye concentrations (5–40 mg/L) were chosen to investigate the concentration effect. Herein, a set initial dye concentration of 20 mg/L was used for the following adsorption experiments in other solution conditions. Effect of solution pH ranged from 4.0 to 11.5 on the dye removal was examined. Different mass of adsorbents were employed to explore the effect of adsorbent dosage in a range of 0.4–1.6 g/L. The temperatures of solutions at the desired values (15 °C, 25 °C, 35 °C, and 45 °C) were controlled for the adsorption thermodynamics analysis. To study the effect of ionic strength on the dye adsorption, different concentrations of NaCl solutions (5–50 mM) were adjusted in the mixture. The dye concentration was measured at 664 nm by using a UV–vis spectrophotometer (UV-2550) based on a standard curve. The removal efficiency ($R$) and adsorption capacity ($Q_e$ (mg/g)) of MB were determined with the following equations, respectively:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

where $C_0$ and $C_e$ (mg/L) are the initial and equilibrium dye concentrations, respectively. $V$ (L) represents the volume of dye solution, and $m$ (g) is the mass of adsorbent added into the dye solution.

## 3. Results and discussion

### 3.1. Characterization of raw kaolin and GO-kaolin

The successful synthesis of GO was confirmed by characterization analysis. As can be seen from the SEM image (Fig. S1), the typical ripples are presented on GO surface [45]. Moreover, Fig. S2a and b showed the obvious characteristic peaks of oxygen-containing groups, D band and G band, respectively. For example, the vibration bands of O–H at 3394 $cm^{-1}$, the stretching vibration of the C=O group at 1726 $cm^{-1}$, the stretching vibration bands of O–C=O, C–O at 1400 $cm^{-1}$, 1055 $cm^{-1}$, respectively, indicating the successful preparation of GO [46]. In our experiment, GO-kaolin composites were prepared by binding GO flakes to kaolin with help of APTMS. The surface of kaolin will be positively charged after grafting with APTMS, thereby combining with negatively charged GO sheets by instant electrostatic interactions [44,47]. The color change of raw kaolin powder from white to brown after GO modification verified the successful introduction of GO sheets. This phenomenon is agreement with the observation of Zhang's group [44]. The morphological characteristics of kaolin and GO-kaolin samples were obtained by SEM (Fig. 1). The particle size of kaolin was rather inhomogeneous, and the small particles could form larger