Original Article

Methylene Blue Adsorption by Novel Magnetic Chitosan Nanoadsorbent

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ABSTRACT

A novel magnetic nanoadsorbent (magnetic chitosan modified by *N,N*-bis (carboxymethyl) glutamic acid, G-MCTS for short) was prepared by covalent binding of tetrasodium of *N,N*-bis (carboxymethyl) glutamic acid onto the surface of chitosan-coated Fe_3O_4 nanoparticles. The adsorbent was characterized by scanning electron microscopy, infrared spectrum, vibrating sample magnetometer and X-ray powder diffractometer. It was found that G-MCTS had a spherical structure with a particle size ranging from 100 – 150 nm and a saturation magnetization value of 21 emu/g. Meanwhile, the adsorption performances of G-MCTS were tested with adsorption of methylene blue. Correspondingly, the adsorption effect factors (initial concentration, solution pH, contact time and temperature), adsorption kinetics, isotherms and adsorption thermodynamics were investigated in detail. Results showed that the adsorption could reach equilibrium within 30 min, besides, the adsorption kinetics accepted the pseudo-second-order kinetic model, and the adsorption isotherm data fit with Freundlich model as well as Langmuir model. More importantly, the maximum adsorption capacity was 3.3 g/g obtained by Langmuir model and the adsorption capacity was more than 90% of the initial saturation adsorption capacity after being used for four times. All of these results indicated that, G-MCTS can serve as an effective adsorbent for the adsorption of methylene blue.

Keywords: adsorption, magnetic adsorbent, methylene blue

INTRODUCTION

Water pollution that arisen during the industrialization process has become a critical environmental and economic issue worldwide. Dyes from the industries such as dye synthesis, paper, printing, electroplating, food, and cosmetic are major sources of water pollution [1], and undergo chemical as well as biological changes after being released into water resulting in further increase of the chemical oxygen demand and reduction of light penetration as well as visibility [2,3]. Furthermore, certain dyes and their degradation counterparts are potentially carcinogenic and toxic, and hence, their presence in water is a serious threat to aquatic life and human populations [4–8]. The removal of dye pollutants from wastewater effluents becomes very important, because even a small quantity of dye in water is toxic and highly visible.

Methylene blue is one of the dyes widely used in textile industry. However, methylene blue in contact with skin may

cause discoloration, coldness, redness or dryness (due to chronic exposure), and the ingestion of this dye may result in gastrointestinal irritation, discoloration of oral mucosa, irritation of lips, mouth and throat, paleness of complexion, insufficient coordination or drowsiness [9]. Thus, the water contaminated with methylene blue needs to be tackled without resulting to secondary pollution.

Considered the pervasive methylene blue contamination, a wide range of methods have been developed for the removal of methylene blue from contaminated water and wastewater to decrease their impact on environment. These methods include electrochemical technique to destroy the color groups [10], biodegradation process to mineralize colorless organic intermediates [11]; and chemical heterogeneous photocatalytic oxidation [12] among others. However, most of these techniques have associated drawbacks, such as high operational cost, generation of toxic residues causing secondary pollution, or incomplete removal of pollutants.

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Fig. 1 Synthesis route of G-MCTS and its application for the removal of methylene blue with the help of an external magnetic field.

Comparatively speaking, adsorption is frequently used, considering its cheapness and efficiency, as advanced treatment employed in industries [13–15]. Therefore, exploring some novel adsorption materials with high adsorption capacity, which are environmentally friendly, and have even high selectivity towards specific dyes, has drawn great attention.

In recent years, magnetic nanoparticles, especially Fe_3O_4 , have already attracted many scientists to remove pollutants from aqueous solution. On the one hand, nano-sized particles with high surface-to-volume ratio and high loading capacity, has made it as ideal adsorbents to remove pollutants [4]. On the other hand, magnetic Fe_3O_4 possessed superior properties, such as low toxicity, good dispersability and biocompatibility. Moreover, adsorptive materials incorporating magnetic nanoparticles were able to control the binding process and simplified the separation and purification processes. Adsorption was achieved by dispersing nanoparticles in solution and separating them from matrix with an external magnetic field [16–18]. In comparison with conventional separation techniques, such as filtration, centrifugation and precipitation, magnetic separation technology is a promising technique with its easy operation and fast separation. The main advantage of this technology was that a large amount of wastewater can be purified in a very short period of time by using less energy without producing contaminants [19].

Inspired by these capabilities, a novel magnetic nano-adsorbent has been designed and synthesized as follows: Fe_3O_4 was coated with chitosan (CTS). As a suitable biopolymer, CTS had effective adsorbability for almost all classes of dyes [20–22] because of its high content of amino and hydroxyl

functional group [23]. And then, surface modification was done for magnetic CTS composite through *N,N*-bis (carboxymethyl) glutamic acid (GLDA) by taking 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide/ *N*-hydroxysuccinimide (EDC/NHS) as cross-linker (**Fig. 1**). In this process, EDC just acts as a carboxyl and amino crosslinker, which could react with a carboxyl group first and formed an amine-reactive *O*-acylisourea intermediate that quickly reacted with an amino group to form an amide bond and release of an isourea by-product. The intermediate was unstable in aqueous solutions, and therefore, two-step conjugation procedures required NHS for stabilization [24,25]. As one of the novel chelating agents, tetrasodium of GLDA was produced based on a green chemistry process involving the fermentation of readily available corn sugars. More than 60% of GLDA can be degraded within 28 days due to its excellent biodegradability. Another notable feature is that, the ecological footprint of GLDA was far smaller than those from traditional counterparts because of its efficient manufacturing process [26]. In order to investigate the adsorbability, reusability and pH condition were studied as the key factor for the adsorption of methylene blue from aqueous solution by magnetic chitosan modified by GLDA (G-MCTS for short). Adsorption kinetics, isotherms and adsorption thermodynamic models were used to fit the experimental data.

MATERIALS AND METHODS

Chemicals and materials

Chemicals were obtained as follows: GLDA tetrasodium

(40%) from Tokyo Chemical Industry (Tokyo, Japan), NHS (98%) and EDC (99%) hydrochloride from Baomanbio Company (Shanghai, China), CTS (purity > 99.8%) from Aladdin Company (Shanghai, China), and methylene blue from Beijing Chemical Works (Beijing, China). Glutaraldehyde, hydrochloric acid, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NH}_3 \cdot \text{H}_2\text{O}$, CH_3COOH , NaOH, Span-80 and liquid paraffin from Kermel Chemical Reagent Company (Tianjing, China), were of analytical grade.

Preparation of Fe_3O_4 , MCTS and G-MCTS nanoparticles

Magnetic Fe_3O_4 nanoparticles were prepared by co-precipitation method [27–29]. First, 5.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.8 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved into 100 mL of deoxygenated distilled water. After stirring for 30 min, chemical precipitation was achieved under vigorous stirring by adding 20 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution (28%, v/v) through a syringe needle (1 mm in diameter). Then, the above reaction system was kept at 60°C for 40 min before the mixture was cooled down to room temperature. The precipitate was then washed with ethanol until neutrality and dried at 50°C in the vacuum oven for 12 h.

Magnetic chitosan nanoparticles (MCTS) were synthesized through water/oil (W/O) emulsion cross-linking method as follows: Firstly, 0.5 g of CTS was dissolved into 20 mL aqueous acetic acid (2.0%), then 0.15 g of the previously prepared Fe_3O_4 nanoparticles were fully dispersed in the CTS solution under ultrasonic vibration for 5 min, followed by the addition of 80 mL liquid paraffin solution and 4 mL Span-80. After stirring for 30 min, 10 mL of glutaraldehyde solution (7%, v/v) was added and stirred at 40°C for 1 h. The pH value of the mixed solution was adjusted to 9.0 and the solution was stirred at 60°C for 2 h. Finally, the products were washed with petroleum ether and double-distilled water until neutrality, and dried at 50°C in the vacuum oven for 12 h.

The surface modification of MCTS with GLDA was performed as follows: the previously prepared MCTS (0.1 g) was dispersed in 6.0 mL of phosphate solution (0.005 M, pH = 5.0) under ultrasonic vibration for 5 min, followed by the addition of 2.0 mL GLDA. Then, 4.0 mL of EDC/NHS solution was added. After stirring for 5 h, the resultant products were washed with disodium hydrogen phosphate (0.1 M) until the supernatant was alkaline, then rinsed with water for three times and dried in the vacuum oven at 50°C for 12 h.

Characterization of samples

The surface morphologies of samples were obtained

through JSM-7500F scanning electron microscopy (SEM, JEOL Ltd, Tokyo, Japan), and the wide-angle (20° – 80°, 40 kV/30 mA) X-ray powder diffraction (XRD) measurements were carried out by a Advance D8 X-ray diffractometer (Bruker, Karlsruhe, Germany) at room temperature. In addition, IMPACI-410 model infrared spectroscopy (IR, Nicolet, Madison, USA) was used to analyze the functional groups of samples and 7404 model vibrating sample magnetometer (VSM, Lake Shore, Columbus, USA) was adopted to obtain the magnetization curves of samples under room temperature.

Adsorption experiments

Adsorption experiments were performed in a 50 mL conical flask. First, 0.01 g of G-MCTS was equilibrated with 20 mL of solution containing various amounts of methylene blue and then the solution was oscillated at constant temperature for 12 h. In pH studies, the initial pH of methylene blue solution with G-MCTS was adjusted to 3.0 – 12.0 by adding 0.1 M HCl or NaOH solution. Moreover, the temperature of solutions was controlled by a thermostatic bath and the concentration of methylene blue after adsorption was measured with 750 model UV-Vis spectrophotometer at 665 nm.

The adsorbed amount of methylene blue per unit weight of G-MCTS, Q [mg/g], was calculated from the mass balance equation as Eq. (1):

$$Q = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where Q [mg/g] is the adsorption capacity, C_0 [mg/L] is the initial concentration of methylene blue; C_e [mg/L] refers to the methylene blue concentration at equilibrium; while V [L] and M [g] are the volume of methylene blue solution and the mass of G-MCTS, respectively.

Adsorption models

In order to understand the behavior of adsorbent, both the pseudo-first-order and the pseudo-second-order were applied to the experimental data. The pseudo-first-order rate expression is given below:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (2)$$

where Q_e [mg/g] and Q_t [mg/g] are the adsorption capacity at equilibrium and at any time respectively, and K_1 is the rate constant of pseudo-first-order adsorption. The slopes and intercepts of the plots of $\ln(Q_e - Q_t)$ vs. t were applied to determine the first-order rate constant K_1 .

The pseudo-second-order equation is often successfully used to describe the kinetics of pollutant adsorption as Eq. (3):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \quad (3)$$

where K_2 is the rate constant of second-order adsorption. The slopes and intercepts of plots of t/Q_t vs. t were separately used to calculate the second-order rate constant K_2 and Q_e .

Analysis of equilibrium data is important for evaluating the adsorption properties of G-MCTS. Two adsorption isotherms, Langmuir model and Freundlich model, were utilized to describe the equilibrium adsorption according to Eq. (4) and Eq. (5).

Langmuir adsorption isotherm:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (4)$$

Freundlich adsorption isotherm:

$$\ln Q_e = \ln K_F + b_F \ln C_e \quad (5)$$

where Q_e [mg/g] is the adsorption capacity and C_e [mg/L] is the methylene blue concentration at equilibrium. K_L [L/mg] is the Langmuir constant related to the energy of adsorption, $Q_{\max}$ [mg/g] refers to the maximum adsorption capacity, while K_F and b_F are constants of Freundlich isotherm.

To examine the effect of temperature, adsorption experiments were also conducted at 298 K, 308 K and 318 K. The experimental data obtained at different temperatures were used for calculating the thermodynamic parameters, such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) according to the following equations [30]:

$$\ln \left(\frac{Q_e}{C_e} \right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

Where T is the absolute temperature in Kelvin; R [8.314 J/(mol·K)] is the universal gas constant; ΔH and ΔS were obtained from the slope and intercept of the plot $\ln (Q_e/C_e)$ vs. $1/T$.

Regeneration experiments

Reuse of adsorbents was important due to economic and

resource reasons. In this study, desorption experiments were carried out in a 50 mL conical flask. The G-MCTS nanoparticles loaded with methylene blue (0.01 g) were added into 20 mL of each of the desorbents (ethanol, double-distilled water and acetone) under ultrasonic vibration until the methylene blue concentration remained unchanged. The concentration of methylene blue after desorption was measured with 750 model UV-Vis spectrophotometer at 665 nm. The adsorption / desorption of the methylene blue onto / from the G-MCTS nanoparticles were assessed in five cycles.

The desorption ratio, E [%], was calculated as Eq. (8):

$$E = \frac{C_E}{C_0 - C_e} \times 100\% \quad (8)$$

where E [%] is the desorption ratio and C_E [mg/L] refers to the methylene blue concentration after desorption.

RESULTS AND DISCUSSION

Characterization of samples

The SEM analysis of products provides information on their size and morphology. As shown in **Fig. 2 (a)**, Fe_3O_4 nanoparticles are nearly spherical with an average diameter around 20 – 30 nm. After coated by CTS, a well-defined core-shell structure was clearly presented and the average diameter reached 60 – 90 nm (**Fig. 2 (b)**), or even reached to 100 – 150 nm (**Fig. 2 (c)**) after further modification by GLDA, which indicates that Fe_3O_4 surface was coated and modified successfully by CTS and GLDA.

The XRD patterns of the Fe_3O_4 , MCTS and G-MCTS are presented in **Fig. 2 (d)**. The characteristic diffraction peaks appeared in Fe_3O_4 at 30.1°, 35.5°, 43.1°, 53.4°, 57.0° and 62.6° which could be assigned to (220), (311), (400), (422), (511) and (440) planes of magnetite, respectively, and matched very well with pure magnetite reflections. It is evident that these characteristic diffraction peaks are observable for the samples of MCTS and G-MCTS, which reflected that Fe_3O_4 was existent in MCTS and G-MCTS, and the whole preparation processes did not result in the phase change of Fe_3O_4 .

In addition, Fe_3O_4 , CTS, MCTS and G-MCTS could be also approved by IR as shown in **Fig. 2 (e)**. In the IR spectra of Fe_3O_4 , the strong absorption band at 587 cm^{-1} was assigned to the Fe-O vibration frequency of magnetite. On the IR spectra of CTS, the strong peak around 3,430 cm^{-1} is associated to the combination of contributions from stretching vibration of -OH groups, extension vibration of N-H groups, and inter- hydrogen bonds of polysaccharides. Adsorption

Fig. 2 Characterization of samples. (a) SEM image of Fe₃O₄ nanoparticles. (b) SEM image of MCTS. (c) SEM image of G-MCTS. (d) XRD patterns of Fe₃O₄, MCTS and G-MCTS. (e) IR spectra of Fe₃O₄, CTS, MCTS and G-MCTS. (f) Magnetization curves of Fe₃O₄, MCTS and G-MCTS.

peaks around 1,645, 1,600 and 1,384 cm⁻¹ can be assigned to amide I band, amide II band and CH₃ symmetrical angular deformation respectively. Compared with that of CTS, the peaks of amide I and II band are weakened in the spectrum of MCTS, instead, the strong absorption appeared at 1,641 cm⁻¹ and can be assigned to the C=N bond generated from the cross-linking of CTS with glutaraldehyde. After MCTS were modified by GLDA, the evidently enhanced absorption peaks at 1,636 cm⁻¹ and 1,575 cm⁻¹ were assigned to the C=O stretching vibrations of -COO⁻ and N-H bending vibration of amide groups respectively, which further indicated the successful combination of amino group on MCTS with GLDA through amide bond. Moreover, the strong characteristic absorption band that appears at 1396 cm⁻¹ can be assigned to C-O stretching vibration of the -COO⁻ group, which suggested the existence of carboxyl group of G-MCTS.

The magnetization curves of Fe₃O₄, MCTS and G-MCTS

at room temperature are showed in **Fig. 2 (f)**. The saturation magnetization value of Fe₃O₄ was 49 emu/g, while the saturation magnetization values of MCTS and G-MCTS were reduced to 35 emu/g and 21 emu/g, respectively. In spite of these low magnetization values with respect to saturation magnetization of pure Fe₃O₄ nanoparticles, owing to the decrease of surface moments of the magnetic nanoparticles by non-magnetic CTS and GLDA coating, it is still sufficient for magnetic separation by a conventional magnet.

Effect of pH

The pH value is a vital factor for the adsorption process, because pH affects not only the surface charge of adsorbent, but also the dissociation of functional groups [31]. It can be seen from **Fig. 3** that, G-MCTS displays an increase of adsorption capacity with the increment of pH value. At low pH, most of the functional groups are protonated and pre-

Fig. 3 Effect of pH on adsorption capacity for methylene blue by G-MCTS (initial concentration 100 mg/L; RT).

sented in positively charged form. In addition, the presence of large number of H^+ in the aqueous solution may compete with methylene blue for adsorption sites available, thus, a lower adsorption capacity can be observed consequently. The adsorption capacity was rapidly increased when the pH was higher than 7.0. Because the carboxyl groups on G-MCTS surface was deprotonated to be $-COO^-$ groups, the electrostatic interaction between adsorbent and methylene blue was significantly enhanced. Thus, pH 11.0 was selected as the optimum pH value of methylene blue solution for the following adsorption experiments.

Adsorption kinetics

Different kinetic parameters of methylene blue adsorption onto G-MCTS are obtained from the results (**Fig. 4**) and listed in **Table 1**. The R^2 values complied with the experimental results showing that the pseudo-second-order kinetic model was more valid to describe the adsorption behavior of methylene blue onto G-MCTS. This indicates that the rate-limiting step in the adsorption of methylene blue is dominated by chemical adsorption, high specific surface area and the absence of internal diffusion resistance. It was likely that

Fig. 4 Adsorption kinetics of methylene blue. (a) Pseudo-first order kinetic ; (b) Pseudo-second order kinetic.

the adsorption behavior may involve valence forces by sharing of electrons between cations and adsorbents.

Adsorption isotherms

Different isotherm constants of methylene blue adsorption onto G-MCTS after calculation are listed in **Table 2**. After Langmuir and Freundlich adsorption constants were obtained from the results (**Fig. 5**), it is clear that the adsorption isotherm of methylene blue fits the Freundlich model very well. This means that the adsorption of methylene blue on G-MCTS was not a simple monolayer adsorption, and the Fe_3O_4 nanoparticles, which were coated, may affect the adsorption process.

Table 1 Parameters for the adsorption of methylene blue on the G-MCTS according to kinetic models.

Concentration [mg/L]	Pseudo-first order			Pseudo-second order		
	K_1	Q_e [mg/g]	R	K_2	Q_e [mg/g]	R
100	0.0644	11.7001	0.9798	0.0165	129.8701	0.9999

Table 2 Parameters for the adsorption of methylene blue on the G-MCTS according to isotherms models.

Temperature [°C]	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	K_L	Q_{max} [g/g]	R	K_F	b_F	R
65	0.0016	3.33	0.9923	7.33	0.8737	0.9989

Fig. 5 Adsorption isotherms of methylene blue. (a) Langmuir adsorption isotherm; (b) Freundlich adsorption isotherm.

The Freundlich model predicted that the adsorption capacity for methylene blue would be increased as long as there is an increase of initial concentration. Moreover, calculated according to the Langmuir adsorption isotherm, the maximum adsorption capacity for methylene blue on G-MCTS was 3.33 g/g, which was comparable and even higher than that of other CTS based adsorbents: N-benzyl-O-carboxymethyl-chitosan magnetic nanoparticles (223 mg/g) [32]; Graphene oxide / chitosan composite (468 mg/g) [33]; glutamic acid modified chitosan and silica coated Fe_3O_4 nanoparticles (182 mg/g) [34]; magnetic β -cyclodextrin-chitosan/graphene oxide (84.3 mg/g) [35]; chitosan hydrogel beads generated by anionic surfactant gelation (226 mg/g) [36].

Fig. 6 Thermodynamic plots of the adsorption.

Adsorption thermodynamics

The values of ΔG , ΔH and ΔS for methylene blue adsorption of G-MCTS were obtained from the results (Fig. 6) and shown in Table 3. The positive ΔS value suggested the increasing randomness at adsorbent / adsorbate interface during the process of adsorption. While the negative values of ΔG obtained from Eq. (7) reflected a spontaneous adsorption process of methylene blue within the studied temperature, and the positive value of ΔH indicated that the adsorption reaction was endothermic.

Regeneration and reuse

The results (Fig. 7 (a)) indicated that ethanol could desorb more than 90% of methylene blue from G-MCTS surface. Thus, ethanol was selected as the desorption agent. Besides, the effect of recycling times for adsorption was repeated 5 times (Fig. 7 (b)), and the adsorption capacity of methylene blue on G-MCTS was decreased with increasing cycle number, or even hardly decreased after the 4th recycling. All of these results showed that the adsorbents can be recycled for methylene blue adsorption with ethanol.

CONCLUSIONS

An environmentally friendly magnetic GLDA modified adsorbent (G-MCTS) was synthesized by surface modification of chitosan/ Fe_3O_4 with GLDA which was used as adsorbent

Table 3 Parameters for the adsorption of methylene blue on the G-MCTS according to thermodynamic model.

Temperature [K]	ΔG [kJ/mol]	ΔH [kJ/mol]	ΔS [J/(mol·K)]	R^2
298	-23.0090	19.4523	77.2379	0.9898
308	-23.7814	—	—	—
318	-24.5538	—	—	—

Fig. 7 Characteristics of regeneration and reuse. (a) Desorption ratio of different desorbents. (b) Effect of recycling adsorbents on methylene blue adsorption.

for adsorption of methylene blue from aqueous solution. The results showed that, the optimal pH for adsorption of methylene blue was 11.0. In addition, the adsorption models indicated that the adsorption was dominated by chemical adsorption and the adsorption process was spontaneous endothermic. Moreover, G-MCTS showed a high maximum adsorption capacity of 3.3 g/g for methylene blue than other CTS-based adsorbents because of size minimization. Besides, the adsorption capacity was more than 90% of the initial saturation adsorption capacity after being used for four times by ethanol. Thus the G-MCTS could serve as a promising adsorbent for the purification of water contaminated by methylene blue.

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