



Facile fabrication of magnetic carboxymethyl starch/poly(vinyl alcohol) composite gel for methylene blue removal



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ABSTRACT

This study presents a simple method to fabricate magnetic carboxymethyl starch/poly(vinyl alcohol) (mCMS/PVA) composite gel. The obtained mCMS/PVA was characterized by Fourier transform infrared (FTIR) spectra, vibrating-sample magnetometer (VSM) and scanning electron microscopy (SEM) measurements. The application of mCMS/PVA as an adsorbent for removal of cationic methylene blue (MB) dye from water was investigated. Benefiting from the combined merits of carboxymethyl starch and magnetic gel, the mCMS/PVA simultaneously exhibited excellent adsorption property toward MB and convenient magnetic separation capability. The effects of initial dye concentration, contact time, pH and ionic strength on the adsorption performance of mCMS/PVA adsorbent were investigated systematically. The adsorption process of mCMS/PVA for MB fitted pseudo-second-order model and Freundlich isotherm. Moreover, desorption experiments revealed that the mCMS/PVA adsorbent could be well regenerated in ethanol solution without obvious compromise of removal efficiency even after eight cycles of desorption/adsorption. Considering the facile fabrication process and robust adsorption performance, the mCMS/PVA composite gel has great potential as a low cost adsorbent for environmental decontamination.

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1. Introduction

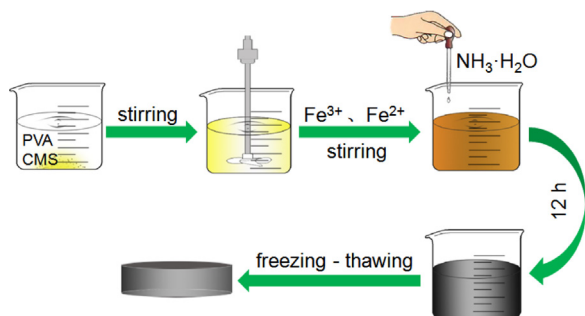
Dye effluents discharged from various industrial fields such as textile, plastic, leather, dyestuff and paper-making have mutagenic and carcinogenic effects on the aquatic biota and human being because they are generally toxic and hard to degrade [1–3]. Therefore, it is of great importance to deal with the dye effluents. Various techniques such as biological treatment [4], advanced oxidation process [5], photocatalytic degradation [6] and adsorption [7–10] have been developed to remove dyes from water. Among them, adsorption technique is particularly attractive because of its simplicity of design, high efficiency and ease of operation [11]. In recent year, numerous attempts have been made to develop low cost and effective adsorbent. In this regard, increasing attention was paid on agricultural residues (e.g., rice husk [12] and wheat shell [13]) and natural polymers (e.g., chitosan [14,15] and cellulose [16,17]) because they are easy-available, renewable, and biodegradable.

Starch, one of the most abundant renewable resources in the world has been investigated as an adsorbent to remove water pollutants [18–21]. For instance, Guo et al. [22] synthesized a crosslinked porous starch and found that its adsorption capacity of product for methylene blue (MB) can reach 9.46 mg g^{-1} , which was much higher than that of native starch. Mahmoud et al. [23] prepared a series of starch-based gels and used them to adsorb acid dye. Despite the progress on using starch as an adsorbent in recent years, the starch-based adsorbents generally suffer from several drawbacks such as low adsorption capacity [24], complex separation process and poor reusability [25]. Therefore, the practical applications of starch-based adsorbents for treatment of water pollutants are seriously restricted.

Recently, magnetic adsorbents are emerging as a new generation of adsorbent for environmental cleanup because they can be readily separated from dye solution by an external magnetic field after adsorption [26–33]. Compared with other traditional separation techniques such as filtration and centrifugation, the magnetic separation process is easy to operate with high separation efficiency and low cost. Therefore, numerous natural polymer-based magnetic biosorbents (e.g., xylan [27], cellulose [28], chitosan [29], alginate [30,31]) have been explored for environmental decontamination. For example, Luo et al. [28] prepared

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Scheme 1. Synthetic route to the mCMS/PVA composite gel.

magnetic cellulose/activated carbon beads for adsorption of organic dyes from water. Cao and coworkers [29] fabricated magnetic Fe_3O_4 /chitosan nanoparticles and investigated their adsorption behaviors toward reactive brilliant red X-3B.

In this contribution, we present a facile one-step approach to prepare magnetic carboxymethyl starch sodium (CMS)/poly(vinyl alcohol) (PVA) (mCMS/PVA) composite gels based on the simultaneous formation of magnetic iron oxide nanoparticles and crosslinking of CMS and PVA (Scheme 1). Compared with the previous reports on starch-based adsorbents, the merits of this approach are as follows. First, the mCMS/PVA composite gels can not only show strong magnetic property associated with facile magnetic separation process but also can be readily fabricated in a large quantity, which is highly desired for practical applications [34]. Second, the utilization of CMS instead of native starch for preparing magnetic adsorbent can enhance the adsorption capacity significantly because the CMS contains abundant carboxylic groups [35]. The employment of mCMS/PVA composite gels as magnetic adsorbents to adsorb MB dye, one of the most widely used cationic dyes, from water was systematically investigated.

2. Materials and methods

2.1. Materials

Carboxymethyl starch sodium (CMS, the degree of substitution is 0.35–0.5), poly(vinyl alcohol) (PVA, $M_w = 195$ kDa), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) powder, iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonia solution (25 wt%), and methylene blue (MB, $\lambda_{\text{max}} = 662$ nm) were purchased from Aladdin Chemistry Co. All other reagents were analytical grade and used as received without further purification. Deionized water was used throughout the experiments.

2.2. Characterization

Fourier transform infrared (FTIR) spectra of the materials were carried out using Nicolet 205 spectrophotometer in the range of $400\text{--}4000\text{ cm}^{-1}$ (KBr disk). The magnetic moment was recorded at 300 K on a MPMS XL-7 vibrating-sample magnetometer (VSM). Scanning electron microscopy (SEM) images were obtained using JSM-6380 LV microscope. UV–vis spectra were recorded on a UV-3600 UV–vis spectrophotometer (Shimadzu). Transmission electron microscope (TEM) images were recorded on a JEOL-2010 TEM at 160 kV. TEM microtome specimens were cut using a diamond knife. The samples of 90–100 nm thickness were collected on hexagonal 400 mesh copper grids.

2.3. Synthesis of mCMS/PVA composite gels

To investigate the effect of reaction conditions on the properties of mCMS/PVA composite gels, a series of mCMS/PVA samples were prepared by adjusting the feed amounts of CMS and PVA (see

Table 1
Reaction conditions for magnetic mCMS/PVA composite gels.

| Sample | C_{PVA} (mg mL^{-1}) | C_{CMS} (mg mL^{-1}) | $C_{\text{Fe(II)}}$ (mM) | $C_{\text{Fe(III)}}$ (mM) |
|--------|--|--|--------------------------|---------------------------|
| S1 | 150 | 0 | 77.5 | 155 |
| S2 | 120 | 30 | 77.5 | 155 |
| S3 | 100 | 50 | 77.5 | 155 |
| S4 | 75 | 75 | 77.5 | 155 |

Table 1). In a typical procedure, PVA and CMS powder were dissolved in 30 mL of water at 95°C . After adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (the molar ratio of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was kept as constant at 2:1), the mixture was stirred for 30 min at room temperature to form a homogeneous solution. Subsequently, ammonia solution (1.5 mL) was added and a black mCMS/PVA composite gel was gradually formed. After reaction for 24 h, the composite gel was transferred to a freezer with temperature of -15°C and maintained for 12 h and unfrozen at 25°C for 1 h. The above freezing–thawing process was repeated for three times. After freezing–thawing treatment, the solid was dried under vacuum for 24 h at 50°C to afford the final mCMS/PVA composite gel.

The swelling ratio of mCMS/PVA gel was calculated as follows:

$$\text{swelling ratio} = \frac{(W_s - W_d) \times 100\%}{W_d} \quad (1)$$

where W_d and W_s are the weight of dried mCMS/PVA composite gel before and after immersing in water, respectively.

2.4. Dye adsorption

The dye adsorption experiments were carried out in a batch system. Typically, 30 mg of mCMS/PVA adsorbent was added in 3 mL of dye solution of known concentration and the mixture was agitated at 25°C . The solution pH was adjusted with HCl (0.1 M) or NaOH (0.1 M). The ionic strength of solution was manipulated by adding NaCl. The dye solution sample was withdrawn at predetermined time interval until adsorption equilibrium was achieved. The adsorbent was separated from the dye solution by magnetic separation. To minimize random error, all adsorption experiments were carried out in triplicate. Dye concentration was determined by UV–vis spectrophotometer. Calibration curves were plotted between absorbance and concentration of the standard MB solution.

The adsorption capacity was calculated from the following equation [36]:

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

where Q_e (mg g^{-1}) is the adsorption capacity of the adsorbent, C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of MB in the solution respectively, and V (L) is the volume of the MB solution, and m (g) represents the dose of the adsorbent.

2.5. Adsorbent regeneration

Regeneration experiments were performed by immersing the dye-adsorbed sample S4 adsorbent into 20 mL of ethanol. After stirring for 1 h, the S4 adsorbent was separated by a magnet and then was reused for adsorption again. The ethanol solution was analyzed by UV–vis spectrophotometer.

3. Results and discussion

3.1. Synthesis and characterization of mCMS/PVA composite gels

The synthetic route to the mCMS/PVA composite gel is illustrated in Scheme 1. As soon as the addition of ammonia solution, the

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