Preparation of cellulose/sodium alginate/sepiolite porous microspheres and their adsorption properties for methylene blue

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Abstract. To improve the feasibility of cellulose microspheres for application in wastewater treatment, microcrystalline cellulose/sodium alginate/sepiolite (MSS) composite porous microspheres were synthesized via a two-step method of self-assembly and suspension droplet. The as-prepared MSS microspheres were characterized by SEM, FT-IR and XRD analyses, and the results display that the MSS microspheres possess a layered cross-linked porous structure. Parameters affecting dye uptake (such as pH and sepiolite content) were evaluated, and pH of 7 and MSS-30 microsphere were taken as the optimal removal environment and adsorbent. The maximum adsorption capacity of MSS-30 microsphere was found to be 319.5 mg/g, indicating an efficient and feasible adsorbent for MB removal from wastewater.

1. Introduction

Nowadays, dye wastewater from various industries, including leather, synthesis, dyeing and electroplating and so forth, has become a major source of environmental pollution in terms of its volume, complexity, high toxicity and non-biodegradability [1, 2]. Methylene blue (MB), a cationic phenothiazine dye, is commonly treated by flocculation, biological oxidation, chemical precipitation, and adsorption [2-4], etc. Among these methods, adsorption by porous microspheres has shown the advantages of high efficiency, eco-friendliness and simplicity, receiving increasing attention in recent years.

Cellulose, the most abundant renewable polysaccharide on earth, is composed of α-glucose molecules linked by β-1,4 glycosidic bonds. Three hydroxyl groups on each glucose unit endows the cellulose chains good binding ability with pollutants, such as MB, Cu$^{2+}$ and phosphopeptides, etc [5-7]. However, it is still defective for the wide application of pure cellulose microspheres in dye wastewater treatment, owing to the weak mechanical strength and low adsorption capacity. Sodium Alginate (SA) is an abundant natural anionic polysaccharide with a large number of carboxyl groups, which can adsorb positively charged MB dye through electrostatic attraction [8]. Herein, a dual network structure can be formed through self-assembly of hydrogen bond driven by the active groups of cellulose and SA, which will reinforce the network structure of microspheres. Moreover, sepiolite powder (Si$_{12}$Mg$_8$O$_{30}$(OH)$_4$(OH$_2$)$_4$·8H$_2$O) (SP), is a natural porous clay mineral with a formula of magnesium hydrosilicate. The unique fibrous structure of SP allows the penetration of pollutant ions into its channels, making it a great potential ion-exchanger for dyes removal from industrial wastewater [9]. Marrakchi et al. fabricated chitosan/SP composites with epichlorohydrin as a cross-linker. They found
that the interconnectivity, porosity and adsorption capacity were optimal when the composite was composed of 50% chitosan and 50% SP [10].

In this work, a dual network structure is constructed by microcrystalline cellulose (MCC) and SA molecule chains, in which MCC is used as the cellulose source. Then, SP is added to support the dual network and form the MCC/SA/SP (MSS) composite microsphere. The micromorphology, chemical structure and crystal morphology of the porous microsphere were studied, respectively. Also, the adsorption performance of MSS microsphere in different conditions for MB was tested.

2. Experimental

2.1. Materials
Sodium alginate (SA, medium viscosity) and Methylene blue (MB) were obtained from Aladdin Industrial Co., Ltd. Microcrystalline cellulose (MCC, 20-80 μm), sepiolite powder (SP), urea, sodium hydroxide (NaOH), calcium chloride (CaCl₂) and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Pretreat of sepiolite powder
The sepiolite powder was firstly filtered by a 200 mesh standard sieve, and then treated by 6 mol/L HCl for 6h. Thereafter, the sepiolite powder was washed to neutral and dried to the constant weight.

2.3. Preparation and characterization of MSS microspheres
Firstly, a solution of NaOH/urea/H₂O (7:12:81, by weight) was prepared and precooled to -12℃. 1 g MCC and 1 g SA were immediately added to precool solvent under vigorous stirring for 5 min to obtain a 2 wt% transparent MCC/SA hybrid solution. Then, 0.86 g SP was added and kept stirring to obtain a homogeneous suspension, and the suspension was added dropwise by a 5 mL syringe into a 5 wt% HCl solution containing 5 wt% CaCl₂ for 12 h to cure. The resulting MCC/SA/SP (abbreviated as MSS-30, according to the mass ratio of SP) microspheres were filtered and washed in deionized water until neutral. Finally, the MSS microspheres were obtained after freeze-drying.

The surface morphology was studied with Hitachi S-4800 scanning electron microscope (SEM). The chemical and crystalline structures were recorded with Nicolet 5700 Fourier transform infrared (FT-IR) spectroscopy and Bruker D8 X-ray diffractometer (XRD). The MB concentration was measured by Shanghai Unico UV-4802S UV–visible spectrophotometer.

3. Results and Discussion

3.1. Characterization of MSS microspheres
The surface morphology was observed by optical and SEM photos in Fig. 1. As shown in Fig. 1a, all of them displayed a milky white sphere with the size of ~4 mm, which is typically Ca²⁺-crosslinked alginate beads prepared via suspension droplet method. Fig. 2b revealed the rough and laminated surface and the porous internal structure, and the further magnified photo was shown in Fig. 2c. A layered cross-linked porous structure can be clearly observed, suggesting the strong interaction between components, which can help to improve the adsorption performance.

Figure 1. Optical (a) and SEM images (b, c) of MSS microspheres.
Fig. 2 shows the FT-IR spectra of SA, MCC, SP and MSS microspheres. The characteristic peaks at 1637 and 1059 cm\(^{-1}\) corresponded to the vibration of C–C aromatic skeletal and C–O bond of the MCC [4]. The bands of SA at 3417 and 1617 cm\(^{-1}\) can be assigned to asymmetric stretching vibrations of –OH and –COO\(^{-}\) [5]. In the spectrum of SP, the peaks at 3424 and 1636 cm\(^{-1}\) can be attributed to the stretches and the OH bending, corresponding to zeolitic water. Typical bands appearing at 1035 and 518 cm\(^{-1}\) are due to the characteristic vibrations of the tetrahedral (Si–O–Si) and Mg–O bond. For MSS microsphere, the bands of 3442 and 1633 cm\(^{-1}\) exhibit slight discrepancies as compared to the components likely due to the hydrogen bond interaction between components. Furthermore, the weak peak of 2924 cm\(^{-1}\) and obvious peak of 1032 cm\(^{-1}\) can be attributed to the limited C–H stretching and enhanced C–O–C stretching, demonstrating the Ca\(^{2+}\)-crosslinked MSS microspheres [6].

To confirm the crystalline properties of MSS microsphere, XRD patterns of SA, MCC, SP and MSS microspheres are shown in Fig. 3. The strong peak of 14.80°, 16.64°, 22.76° and 34.77° of MCC are characteristic of cellulose I crystal structure [4]. Broad peak of SA at 13.6° displays the generally amorphous state [5]. The diffraction reflections occurring at 2\(\theta\) = 6.35°, 20.15°, 22.1° and 26.8° show the characteristic reflections of SP [6]. For MSS microsphere, the characteristic peaks of components can be generally observed, indicating the well interaction within these components.
Figure 3. XRD patterns recorded of MCC, SA, SP and MSS microsphere.

3.2. Adsorption performance of MSS microspheres

The solution pH is a considerable factor in the adsorption process, due to variation of the surface charge of the adsorbents and the adsorbates. Fig. 4 shows the adsorption behavior of MB over a pH range of 3-10, while keeping the constant concentration of each dye (500 mg/L), temperature (25°C), time (240 min) and mass of MSS-30 microsphere (0.1 g/L). As shown in Fig. 4, the adsorption capacity of MB increases from 247.9 to 308.4 mg/g when pH increases from 3 to 10. This can be explained that the competition adsorption occurs between the hydronium ions H$^+$ and the positively charged MB at acidic pH [11]. At the basic pH, the density of the negatively charged MSS microsphere surface groups increases, which promotes the adsorption of MB by electrostatic attraction [12, 13]. Further observation shows that the adsorption capacity increased slowly when pH was greater than 7, so pH of 7 was chosen for further research.

Figure 4. Effect of initial pH on the adsorption capacity of MB on MSS-30 microsphere.

To further explore the effect of SP content on MB adsorption performance, the adsorption capacities of MSS microspheres with various SP contents were characterized in Fig. 5. The MSS microsphere shows a relatively low adsorption amount of 210.7 mg/g. The adsorption capacity enhances rapidly with increasing the SP content to 30% (319.5 mg/g), and no significant change was observed with the further increase of SP, which is consistent with Marrakchi’s report [10]. Therefore, MSS-30 is considered as the optimal microsphere with a desired adsorption capacity. The incorporation of SP increases not only the surface area of MSS microspheres, but also the adsorption sites and functional groups, which further improves the adsorption amount of MSS microspheres.
4. Conclusions
A novel MCC/SA/SP (MSS) ternary composite microsphere was prepared by a two-step method of self-assembly and suspension droplet, in which MCC and SA were selected as the components of dual network. Also, the SP served as the supporting unit and functional additive. Adsorption experiments showed that MSS-30 microsphere can be chosen as the optimal adsorbent for MB and pH of 7 can be taken as the best adsorption environment. Benefiting from the porous network structure of microsphere and functional groups of components, the maximum adsorption capacity of MSS-30 microsphere at pH 7 was found to be 319.5 mg/g, which was higher than most previously reported biomass-based adsorbents. These results suggest that this MSS microsphere is an efficient and promise adsorbent for MB removal from wastewater.

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