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Adsorption of dyes in aqueous solutions by chitosan–halloysite nanotubes composite hydrogel beads

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ABSTRACT

Composite hydrogel beads containing chitosan and halloysite nanotubes (HNTs) with a well defined structure were prepared by the dropping and pH-precipitation method. The influence of HNTs on the appearance, diameter, microstructures, and thermal stability of the chitosan beads was characterized. The composite hydrogels exhibit slightly increased diameter and improved thermal stability. A rough surface and high concentration of the nanotubes in the bead core are found in the composite beads. The hydrogel beads were employed as absorbents for removal of methylene blue and malachite green from aqueous solutions and the fundamental adsorption behavior was studied. Both Langmuir isotherm and Freundlich isotherm models can fit the isotherm absorption data well. The addition of HNTs can significantly increase the adsorption rate of chitosan beads for the two dyes. Moreover, with the increase of the amount of hydrogel beads in the dye solution, the removal ratio of dyes increases but the absorption amount per unit absorbent weight gradually reduces. The adsorption kinetics closely follows pseudo-second order model. The regeneration experimental shows that the adsorption ability of all the beads can be recovered especially for methylene blue. So the chitosan–HNTs composite hydrogels can be potentially used for the removal of dyes from wastewater.

1. Introduction

It is important to find an effective way of dyes pollution treatment for our environment, because dyes are harmful to human beings and toxic to microorganisms [1]. The dyes can cause the decrease of water transmittance and hinder the growth of bacteria and other micro-organisms simultaneously. Furthermore, the dyes can disturb the aquatic photosynthesis and damage the ecosystem [2,3]. To address this problem, various natural or synthesized materials have been used for treatment of the wastewater by adsorption of the dyes.

Chitosan, a cationic polysaccharide, contains amino groups and hydroxyl groups, which generates strong adsorption and complexation interactions with dyes via the hydrogen bonding, electrostatic attraction, ion exchange and van der Waals force, etc [4–6]. The adsorption types include physical adsorption, chemical adsorption and ion exchange adsorption, so chitosan-based adsorbent materials can absorb all kinds of dye molecules [7,8]. Although chitosan has many advantages as an adsorbent for dyes wastewater [9–15], the dye adsorption amount and adsorption rate of chitosan needs to be further improved for practical applications [16].

One routine for solving this problem is to design and prepare chitosan nanocomposites. There are strong interactions between chitosan and nanoparticles [17–20], which is responsible for the enhancement of the adsorption properties. For example, the adsorption performance of chitosan hydrogel beads was improved by the incorporation of multiwalled carbon nanotubes (MWNTs) for removal of congo red [21]. Graphene oxide (GO) was added into the porous spongy chitosan by the freeze-drying method. The chitosan–GO composite sponges could be used as adsorbents for methyl orange and Cu^{2+} ions [22]. Chitosan intercalated montmorillonite (Chi-MMT) was prepared by Monvisade et al. and the adsorption capacities of Chi-MMT for all basic dyes increased [23]. Copello et al. synthesized chitosan composite hydrogels by adding SiO_2 hybrid mesoporous materials via the sol–gel method, and the prepared composites had potential applications as biosorbents [24].

Halloysite is a clay mineral composed of myriad thin tubular or fibrous crystals, which is a product by weathering and depositing [25–27]. The application of halloysite is similar to that of kaolinite, including ceramic raw materials, catalysis, and polymer nanofillers. Halloysite shows short tubular structures with high aspect ratio (ca. 20), thus it is usually called as "halloysite nanotubes (HNTs)" [28]. HNTs are widely used in the areas of electronics, catalysis, biological and functional materials due to their

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submicron hollow tubular structure, rich reactive groups, and large surface/volume ratio [29]. Compared with other tubular nanomaterials (such as carbon nanotubes (CNTs)), natural HNTs are cheap and environmentally friendly [30–32]. Due to these excellent properties, HNTs can be used as cheap and efficient adsorbents for dyes wastewater (such as methylene blue) [32,33]. However, the direct application of HNTs powder as dye adsorbent is limited, since HNTs will swell and form a highly stable colloidal suspension upon contacting with water, making their separation from water very difficult. In addition, the use of HNTs powder as an adsorbent material in columns is limited due to the low permeability of the compacted HNTs [34]. As a result, constructing composite bead adsorbent by combing HNTs and biopolymers is critical for practical applications, since they exhibit improved mechanical strength and dye adsorption performance.

The individual features of chitosan and HNTs have inspired us the feasibility of combining them to make an effective composite material for dyes removal. Based on the interactions between chitosan and HNTs [35,36], this work prepared chitosan–HNTs composite hydrogel beads by the dropping and pH-precipitation method [37,38]. The influence of HNTs on appearances, size, microstructure, thermal stability of the chitosan was investigated firstly. Methylene blue and malachite green were selected as models to evaluate the capacity of chitosan–HNTs hydrogel beads for the removal of dyes from aqueous solutions [39,40]. This work provides a novel routine for preparing dye adsorption materials by simple fabrication method with high performance as well as low cost.

2. Experimental

2.1. Raw materials

Chitosan (CS) was supplied by Jinan Haidebei Marine Bioengineering Co. Ltd (China). The deacetylation and viscosity-average molecular weight were 95% and 600,000 g mol^{-1} respectively. Halloysite was mined from Hunan province, China. Before using, halloysite was purified according to the reference [27]. The elemental composition of purified HNTs by X-ray fluorescence (XRF) was determined as follows (wt.%): SiO_2, 54.29; Al_2O_3, 44.51; Fe_2O_3, 0.63; TiO_2, 0.006. The Brunauer–Emmett–Teller (BET) surface area of HNTs was 50.4 m^2 g^{-1}. Methylene blue (MB) and malachite green (MG) were analytical grade and used as received without further purification (Scheme 1). Ultrapure water from Arium 611 Ultrapure Water Systems (Sartorius, Germany) was used to prepare the aqueous solutions.

2.2. Preparation of chitosan–HNTs composite hydrogel beads by using dropping and pH-precipitation method

The pure chitosan and chitosan–HNTs composite hydrogel beads were prepared by the dropping and pH-precipitation method. The procedure was as follows: 2 g chitosan powder and 2 mL acetic acid were added to 100 mL deionized water. By stirring for 6 h, 2 wt.% chitosan solution was prepared. Then 0.5, 1, 2, 4 g HNTs powder was added into the solution under stirring for 6 h to obtain homogenously dispersed chitosan–HNTs dispersion. The drop-wise addition of the dispersions into a precipitation bath containing 1 mol L^{-1} NaOH solution under mild stirring gave rise to the chitosan–HNTs composite hydrogel beads. Pure chitosan bead was prepared with similar procedure but without addition of HNTs. The beads were extensively washed with deionized water and preserved in an aqueous environment for future use. The weight ratio of chitosan and HNTs was 2:1, 1:1, 1:2, 1:4, and which was referred to CS2N1, CS1N1, CS1N2, and CS1N4, respectively.

2.3. Structure characterization of chitosan–HNTs composite hydrogel beads

2.3.1. Determining the diameter of the hydrogel beads

The diameters of the hydrogel beads were determined by using the optical microscope. At least, 100 beads were tested for every group and the averages were calculated.

2.3.2. Scanning electronic microscopy (SEM)

The hydrogel beads were soaked in ethanol solution and dried under room temperature. Afterward, the samples were cut by using a blade to observe the structures using of SEM (Ultra55, ZEISS).

2.3.3. Thermogravimetric analysis (TGA)

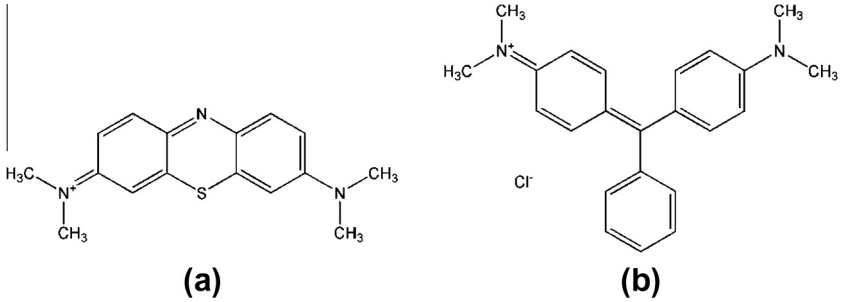
TGA of the dried chitosan and chitosan–HNTs hydrogels was carried out with a NETZSCH TG 209 F3 Tarsus® from 30 °C to 600 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere. This experiment was used to study the thermal degradation behavior of the hydrogel beads.

2.4. Dyes adsorption properties of chitosan–HNTs hydrogel beads

Batch adsorption experiments were conducted and equilibrated using a thermostatic shaker bath operated at 90 rpm at room temperature (30 °C). All adsorption experiments were repeated at least three to ensure accuracy of the obtained data. The dye concentrations in the solutions were determined at the wavelength of 630 nm by using MK3 microplate reader (THERMO LABSYSTEM, USA). The amount of MB and MG adsorbed on hydrogel was calculated by the following equation:

$$q_e = \frac{(C_O - C_e)V}{W} \quad (1)$$

where q_e is the amount of dye adsorbed onto the unit amount of the hydrogel (mg g^{-1}), c_0 is the initial concentration of dye (mg L^{-1}), c_e is the final or equilibrium concentration of dye (mg L^{-1}), V is the volume of the dye solution (L) and W is the weight of hydrogel bead (g).



Scheme 1. Chemical structures of methylene blue (a) and malachite green (b).