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Preparation and characterization of chitosan/purified attapulgite composite for sharp adsorption of humic acid from aqueous solution at low temperature

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ABSTRACT

In the adsorption treatment of water polluted with humic acid (HA), it is equally important to recover clean water with inexpensive raw materials, mild treatment environments and excellent adsorption capacity. Herein, a composite structured CPA (chitosan-modified purified attapulgite) composed of uniform PA (purified attapulgite) nanorods modified by chitosan was successfully fabricated under acetic acid conditions. Benefiting from the mesoporous structure of the PA nanorods and the carboxyl groups of chitosan, the prepared hybrid CPA exhibited a quick response and excellent adsorption capacity towards HA. The effects of pH, adsorbent dose, adsorption time, initial HA concentration and temperature were systematically studied using PA-90 (PA with purity of 90%) and CPA, respectively. The results show that CPA has a high capture affinity towards HA with a short response time (2 min for 80%) and the maximum adsorption capacity could reach 112.07 mg/g, which is superior to most results that have been reported. We believe CPA could be considered as an efficient and green heterogeneous adsorbent for the adsorption of humic acid, as well as provide a versatile platform for further development of functional hybrid composites for the adsorption of other pollutants.

1. Introduction

Humic acid (HA), which generally generates an undesirable color, odor and taste, has seriously polluted drinking water resources and poses an enormous threat to our health [1]. On the one hand, the excessive intake of HA may lead to some diseases, such as blackfoot and Kashin-Beck [2,3]. On the other hand, HA can produce by-products, specifically trihalomethanes and haloacetic acids, during the chlorination process that could possibly be carcinogenic to human beings [1]. In addition, HA also has a strong binding capacity for many contaminants, such as heavy metals, pesticides and herbicides, and thus could increase the contaminant concentration in water [4]. Polluted drinking water directly or indirectly entering human beings through the food chain could also cause great threat to our health. Therefore, sorbents with high adsorption capacity and quick response are desired for HA removal.

HA in drinking water has strict standards, which makes it urgent to develop appropriate technologies for HA removal. Adsorption is considered a promising method because of its advantages of simple fabrication, operability, efficiency and relatively low cost. A number of adsorption materials, such as zeolites [1], activated carbon [5], resins [6], chitosan [7], metal oxides [8], attapulgite [9], and organic or inorganic nanostructured fibers [10–13] have been successfully applied to dispose of sewage to improve water quality. Most of these adsorbents can only be effectively operated at high temperature, which is energy consuming [1,4,6,7,9]. Simultaneously, higher temperature is not always operable in practice, particularly in some severely cold areas. Therefore, the development of functional absorbents that could be operated at low temperature for effective HA removal is urgent.

Attapulgite has the potential to meet the above requirements owing to its unique layered chain structure with high specific surface area, moderate cation exchange capacity, good liquidity, and selective adsorption and is equipped with strong sterilization, deodorization, detoxification and insecticidal properties [9]. In our previous study, we found that natural attapulgite exhibited relatively higher adsorption capacity towards HA at low temperature

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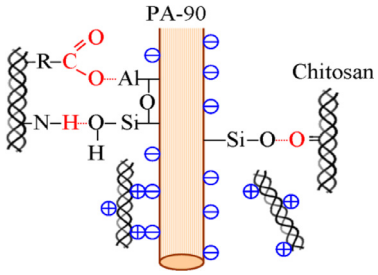

Fig. 1. Schematic diagram of interaction between PA-90 and chitosan.

compared with other adsorbents due to the adsorption process being exothermic in nature [14], but the limited adsorption capacity could not satisfy the increasing concentration of HA in practice. Therefore, it is critical to prepare purified attapulgite to improve the adsorption properties. Chitosan, generally extracted from the alkaline deacetylation of chitin, was chosen as a functional modifier polymer for the preparation of hybrid functional materials owing to its biocompatibility, biodegradability and high adsorption capabilities [15]. However, the raw material has a tendency to agglomerate in aqueous solution and can be easily dissolved in acidic media. The low specific gravity of chitosan makes itself difficult to separate from other aqueous solutions, which has limited its usage in either batch or column modes [16]. Until now, considerable effort has been devoted to modifying chitosan beads or chitosan immobilized on inorganic nanomaterials to enhance HA adsorption in aqueous solution [17–22]. To the best of our knowledge, no effort has been made to develop a promising strategy to fabricate chitosan-modified attapulgite hybrid functional materials for effective HA removal in water at low temperature.

In this contribution, we aimed to investigate the high adsorption capability of hybrid adsorbents for effective removal of HA from high-color water at low temperature. The as-prepared attapulgite was further functionalized by chitosan, and the fabrication process is illustrated in Fig. 1. More importantly, chitosan-modified porous attapulgite was used as a composite adsorbent for HA removal for the first time, and the initial motivation of this study was to develop an environmental composite adsorbent with high and ultrafast response to HA for potential applications in drinking water.

2. Materials and methods

2.1. Materials

Attapulgite (particle size: 200 mesh, compacted bulk density: 0.8–0.9 g/ml) was collected from the Xuyi City, Jiangsu Province, China. Chitosan (deacetylation degree of 90% and average molecular weight of 4×10^5) was purchased from Shanghai Boao Biotechnology Co. Ltd., China. HA powder was purchased from Jufeng Chemical Technology Company, Shanghai, China. Acetic acid, sodium hydroxide and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co. Ltd., China.

2.2. Preparation of PA and chitosan-modified PA

First, 5.0 g of raw attapulgite (RA) powder was dispersed in 95 g of distilled water with vigorous stirring at 10,000 r/min for 10 min, and then the sediment was filtered by gravity after 72 h and dried in an oven at 60 °C for 24 h; this sample is denoted PA-70 (purity, 70%). Subsequently, the dispersive clay mineral slurry (PA-70) was then precipitated in a high-speed centrifuge for further separation. The clay mineral slurry from the middle layer of the precipitated material was dried at 60 °C for 24 h and is denoted PA-90 (purity, 90%). Simultaneously, the sample with a ratio of attapulgite (PA-70) and distilled water in the initial mixing step at 1:99 is denoted PA-99 (purity, 99%).

Then, 2.50 g of chitosan was dispersed in 150 ml of 2 wt% acetic acid solution with continuous stirring at 60 °C for 4 h. Then, 50 g PA was slowly added to the above chitosan solution, and the mixture was stirred at room temperature for 3 h. Subsequently, the pH of the PA/chitosan mixture was neutralized using 0.1 mol/l NaOH solution. The chitosan-modified attapulgite powder was centrifuged, washed by deionized water at least three times, and then dried at 65 °C for 24 h. The obtained chitosan-modified PA-90 is denoted CPA.

2.3. Adsorption experiments

Detailed information on the preparation of the HA solutions and the pH value determination of zero point charge (pH_{zpc}) is given in the ESI. For the adsorption experiments, the designated adsorbents (PA and CPA) were added into the HA solution (5 mg/l, 100 ml) at the desired pH. Then, the mixtures in conical flasks were oscillated at 200 rpm in a bath shaker for a predetermined time. The obtained solution after oscillation was centrifuged and filtered through a 0.45 μm glass filter membrane. Subsequently, the residual concentration of HA was analyzed by UV–vis spectroscopy at $\lambda_{max} = 400$ nm. The experimental processes and corresponding conditions are listed in Table S1. The results were evaluated based on the adsorption efficiency (%) and the HA equilibrium adsorption capacity (q_e, mg/g), which can be calculated based on the following equation:

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

where V is the solution volume (l); C_0 and C_e are the initial concentration and the equilibrium adsorption concentration (mg/l), respectively; and M is the adsorbent dose (g).

To verify the stability of CPA, the adsorbents were tested using adsorption–desorption cycling, where 0.1 mol/l NaOH (25 ml) was employed in the HA desorption treatment. The adsorption capacity of CPA for HA adsorption was measured 6 times.

2.4. Characterization

The morphology of the relevant samples was examined by a scanning electron microscope (FE-SEM Hitachi S-4800). The crystal structure of the relevant samples was measured by an X-ray diffractometer (XRD, Rigku, Ultima IV). The specific surface area and pore diameter distribution of the relevant samples were derived from N_2 ad/desorption measurements using an automatic microspore physisorption analyzer (ASAP 2020). Fourier-transform infrared spectroscopy (FT-IR, PerkinElmer) was applied to detect the presence of clay mineral. The weight loss of RA, chitosan and CPA were obtained by thermogravimetric analysis (TGA) (Perkin-Elmer, USA).

3. Results and discussion

3.1. Morphology and structural characterization

Representative FE-SEM images of RA and PA of various purity fabricated from different treatment processes are shown in Fig. 2. A large amount of impurities, such as block SiO_2, could be observed, and nanorods with an average diameter of 50 nm and length of 200–300 nm were entangled and aggregated with each other. To the best of our knowledge, the aggregation of RA nanorods with impurities seriously limited the response rate and adsorption capacity towards HA [23]. Thus, it is very important to purify RA