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Novel Al-doped carbon nanotubes with adsorption and coagulation promotion for organic pollutant removal

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ABSTRACT

Al-doped carbon nanotubes (Al-doped CNTs) were prepared as a multifunctional integrated material of adsorbent and coagulant aid for organic pollutant removal from aqueous solution. It was observed that aluminum species were dispersed homogeneously on the surface of CNTs, and mainly anchored onto defect structures of the CNTs. The introduction of aluminium efficiently improved adsorption ability for methyl orange (MO) onto the CNTs, and maximum adsorption capacity calculated from the Langmuir isotherm model can reach 69.7 mg/g. The MO adsorption kinetics can be better described by the pseudo-second-order and pore diffusion kinetic models, and the diffusion of MO anions into pores of the Al-doped CNT adsorbent should be the rate-determining step. Thermodynamic analyses indicated that the adsorption of MO onto Al-CNTs-2.0 was endothermic and spontaneous. Moreover, adsorption capacity for MO on the Al-doped CNTs was evidently dependent on the CNT dose, solution pH and adsorbent dose. From the perspective of low-cost and multifunctional, suspension obtained during the Al-doped CNT adsorbent preparation, was tested as coagulant to remove humic acid (HA). A significant observation is that the suspension exhibited an excellent coagulation performance for HA, because abundant aluminous polymer and Al-doped CNTs existed in the suspension.

Introduction

Water pollution caused by organic pollutants has been a worldwide and serious environmental issue in recent years. The main organic pollutants, such as humic substances, pharmaceuticals, dyestuffs, pesticides, and other aromatic pollutants, have aroused serious public concern because of their high biotoxicity and chemical stability in water. Methyl orange (MO), one of the most commonly used synthetic organic dyes in textile and printing industries, could cause water pollution and harm human health when it enters into aqueous environments (Jing et al., 2014). Thus, there is an urgent demand for removal of such pollutants. Up to now, various methods have been devoted to remove organic dyes in water, including adsorption (Xi and Chen, 2014; Zhong et al., 2006), coagulation–flocculation (Han et al., 2016; Nourmoradi et al., 2016), chemical oxidation (Quan et al., 2013; Xing et al., 2011), and photodegradation (Vaiano et al., 2015; Zhou et al., 2012b), *etc.* Among these methods, adsorption has been considered as one of the most promising methods for organic dye removal in terms of efficiency, simplicity and cost. A wide range of adsorbents such as chitosan (Chen et al., 2013), metal

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oxides (Wang et al., 2014c), SiO_2 (Guo et al., 2014; Zhang et al., 2011), and carbon-based materials (Xie et al., 2012; Zhuang et al., 2009) have been developed for organic dye removal. However, low adsorption capacity and removal efficiency have imposed significant challenges in employing them as adsorbents to remove organic pollutants from water. In view of pollutant control at present, it is still urgent to develop new adsorbent materials with high adsorption capacity and removal efficiency.

Aluminium based adsorbents, including Al_2O_3 (Cai et al., 2012; Zhou et al., 2012a), AlOOH (Xiao et al., 2014), polyaluminum chloride (PACl) (Mertens et al., 2012), and alumina impregnated with various oxides (Li et al., 2014b; Shan et al., 2014), are found to be one of the most suitable candidates for water treatment, due to its availability of high porosity and abundant surface active sites when compared to other materials (George et al., 2010). Recently, carbon nanotubes (CNTs) have stimulated researchers' great interests and shown promising applications in many fields, because of their high conductivity, unique tubular structure, extraordinary thermal and chemical stabilities, and good mechanical property (Apul and Karanfil, 2015). Owing to their large surface areas, porous structures and π–π electrostatic interactions, the CNTs have been proven to possess huge potential as adsorbents for removing organic dyes (Wei et al., 2014) as well as heavy metal ions (Li et al., 2014a; Mubarak et al., 2014). Nevertheless, the adsorption capacity of CNTs remains limited. Provided that the aluminium based materials are used to modify the CNTs, a promising novel material could be obtained, which simultaneously possess the unique properties of CNTs (large surface area and good mechanical properties), and aluminium based materials (high adsorption capability). It is reasonable to assume that high adsorption capacity and removal efficiency will be obtained, when the synthesized Al-doped CNT nanocomposites are used in water treatment.

In this paper, a novel multifunctional material of Al-doped CNTs was facilely fabricated by hydrothermal method. When the as-prepared material was tested as adsorbent for MO removal, it presented high adsorption capacity and remove efficiency. From the perspective of low-cost and multifunctional, suspension obtained during the Al-doped CNT adsorbent preparation, was used as coagulant for humic acid (HA) removal. A significant observation is that the suspension exhibited an excellent coagulation performance for HA. To the best of our knowledge, there have been no reports on efficient removal of organic pollutants from aqueous solution using such a novel multifunctional material. Application of such a multifunctional integrated material may provide useful information for material design and an efficient way for organic pollutant removal in practical applications.

1. Experimental section

1.1. Materials

The CNTs and HA were purchased from DK nano Beijing Co., Ltd. and Sigma, respectively. Other chemical reagents used in this study were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., including aluminum chloride ($AlCl_3{\cdot}6H_2O$), anhydrous sodium carbonate (Na_2CO_3) and methyl orange (MO, $C_{14}H_{14}N_3SO_3Na$). All of the reagents are of analytical purity and used as received without further purification. Deionized water was used throughout the synthesis and treatment processes. The chemical structure of MO was displayed in Fig. 1.

1.2. Material synthesis

The Al-doped CNTs were synthesized *via* a facile hydrothermal method. Firstly, 60 mmol $AlCl_3{\cdot}6H_2O$ was dissolved in 60 mL deionized water to form a clear solution under ultrasonication. Then, 60 mmol Na_2CO_3 and a certain amount of the pristine CNTs were added into the solution. Then the mixture was transferred into a teflon-lined stainless steel autoclave (100 mL capacity) and maintained at 80°C for 12 hr. Afterwards, suspension of the resulting product was reserved as coagulant for coagulation study. The precipitate was separated by centrifugation, and washed with anhydrous ethanol and deionized water in sequence, and dried in air at 60°C for 24 hr to obtain the final product of Al-doped CNTs. Similar experiments were performed by varying the amount of CNTs from 0.5 to 3.0 g. For sake of simplicity, the sample was denoted as Al-CNTs-*X*, where *X* is the amount of the CNTs.

1.3. Material characterization

The size and morphology of the obtained product was observed by an S-4800 scanning electron microscope (SEM) operating at 10 kV (Hitachi, Japan). The phase formation and crystallographic state of the product were characterized by X-ray diffraction (XRD) using a D/max 2500 diffractometer (Rigaku, Japan) at a voltage of 40 kV and a current of 200 mA with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å), employing a scanning rate 0.02°/sec in the 2θ ranging from 3° to 80°. The specific surface area was measured by nitrogen (N_2) adsorption–desorption Brunner–Emmet–Teller (BET method) using an automated gas sorption analyzer autosorb-iQ (Quantachrome, USA). The pore size distribution was determined by using the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALab220i-XL (Thermo Scientific, USA) electron spectrometer from VG Scientific using 300 W Al $K\alpha$ radiation. ^{27}Al solid-state Nuclear Magnetic Resonance (NMR) spectrum was obtained on an AVANCE III 400 spectrometer (BRUKER, Switzerland) operating at 104.01 MHz equipped with a 4 mm rotor spun at 12 kHz.

1.4. Adsorption experiments

Batch adsorption experiments were conducted in 150 mL conical flasks containing 50 mL anion solution and shaken at 200 r/min in a thermostatic shaker at (25 ± 1)°C for 24 hr. The adsorbent dose was kept as 1 g/L for the experiments, unless otherwise stated. Adsorption isotherm experiments were carried out with varying initial MO concentration (10–100 mg/L). The procedure of adsorption kinetics were kept similar to the isotherm experiments, except for the MO concentrations which were withdrawn from the conical flask at predetermined time intervals during adsorption. The effect of solution pH ranged from 4.5–11.0 on MO removal was studied by adjusting solution pH with 0.1 mol/L HCl