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Adsorption behaviors of methyl orange dye on nitrogen-doped mesoporous carbon materials

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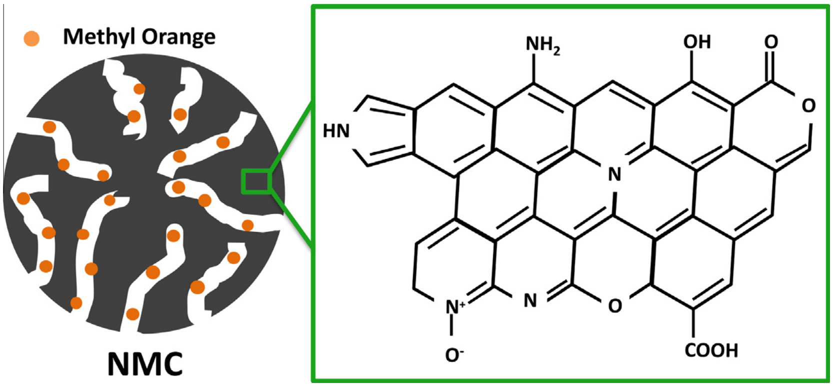
GRAPHICAL ABSTRACT



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ABSTRACT

A series of nitrogen-doped mesoporous carbon materials (NMC) with different nitrogen contents (from 9.1 to 11.3 wt.%) were prepared using urea and ammonia as economical nitrogen resources by sol–gel method. The NMC materials possessed high surface areas (from 659 m^2/g to 912 m^2/g) as well as large number of oxygen-containing and nitrogen-containing groups. The adsorption behaviors of NMC materials for anionic dye methyl orange (MO) were investigated, which are fit excellent for the Langmuir isothermal adsorption equation. All the materials exhibited high adsorption capacity for MO at room temperature. Their adsorption capacity can be adjusted by changing the nitrogen contents in NMC materials. Moreover, treating the NMC material at higher temperature can significantly improve the adsorption capacity for MO. According to the results of characterization, the main features of NMC materials, like large pore size and abundant basic nitrogen-containing groups on the surface, should be related to the excellent adsorption property for MO.

1. Introduction

Removal of organic dyes in wastewater is one of the major environmental problems in the world due to the dangers of natural environment and human health [1,2]. Adsorption method is one

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of the most effective techniques for the removal of organic dyes from wastewater [1–5]. Among various adsorbent materials, active carbon materials have shown great advantages over other adsorbents for its higher adsorption capacity to different dye molecules [5–11]. It is well known that the porosity and surface chemical groups of carbon materials are two key factors for influencing the adsorption behaviors of organic dyes [4,12,13]. In order to further improve the adsorption property of carbon materials for various dye molecules, more recent work has been focused on developing novel carbon materials with high specific surface area, effective pore size and suitable surface properties [14–19].

As a new type of carbon materials, nitrogen-doped carbon material has been attracting great attention due to its excellent mechanical, electrical, physical and chemical properties [20]. The incorporated nitrogen species may be present in the form of various N-containing groups, which can significantly change the polarity and/or acidic–basic property of the carbon materials. A few recent works showed that N-doped mesoporous carbons have strong ability for the adsorption of dyes in wastewater [21–23]. For instance, Hu and coworkers [22] reported that the ammonia-tailored mesoporous carbon CMK-3 showed much higher uptake rate for a few anionic dyes including methyl orange (MO) than that of microporous active carbon. The strong adsorption capacity was mainly attributed to the existence of ordered mesoporous structure and the electron-donating effect of the incorporated nitrogen-containing functional groups.

Previously, our group reported a simple and efficient sol–gel route to prepare a kind of nitrogen-doped nanoporous carbon (NNC) material by using in situ-formed aluminum phosphate as template, citric acid and hexamethylene tetramine (HMT) as carbon or nitrogen sources. The resultant NNC materials contain different types of oxygen- and nitrogen-containing groups, and could be used as active catalysts for the transesterification of dimethyl oxalate with phenol [24].

In present work, we tried to prepare another kind of nitrogen-doped mesoporous carbon materials (NMC) using sucrose and urea as substitute of HMT via a similar sol–gel strategy. It was found that changing the content of urea in the reactant solution could bring significant effect on the structure and surface properties of the resulting NMC materials. A variety of techniques have been employed in the characterization of these samples, including X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectrometer (XPS), N_2 adsorption/desorption isotherms, Fourier Transform infrared (FT-IR) spectra, and the temperature-programmed desorption (TPD). The adsorption behaviors of the NMC materials were studied for the removal of organic dye MO from water.

2. Experimental section

2.1. NMC materials preparation

NMC materials were prepared by a sol–gel method developed from the synthesis of nanoporous carbon described in the literatures [25]. Analogously, H_3PO_4 (85 wt.%) was dropped into a mixed aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$, urea (U), sucrose (Su) and citric acid (CA) under vigorous stirring at ambient temperature, leading to a composition in molar ratio of U/CA/Su/P/Al = x/0.5/1.0/1.0/1.0 (x = 0.8, 1.0, 1.2,1.5). The solid composite was formed after removing water at 80 °C. After that, the composite was pretreated at 300 °C in open air for a few minutes, and then carbonized at 800 °C under argon for 6 h. The black carbonized composite was treated with finite concentration of HNO_3 solution at 60 °C to remove AlPO component, and was filtered and dried at 110 °C to obtain the resulting NMC materials, which are denoted as NMC-1 (x = 0.8), NMC-2 (x = 1.0), NMC-3 (x = 1.2), NMC-4 (x = 1.5), respectively. In addition, the NMC-3 sample was separately treated at 600 °C and 800 °C under argon for 6 h to obtain two thermally treated samples, which are denoted as NMC-3-600 and NMC-3-800, respectively.

2.2. Characterization of materials

N_2 adsorption/desorption isotherms were measured by Micromeritics ASAP 2010 N analyzer. Samples were degassed at 250 °C for 8 h before measurements. Specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) model. Pore volumes were estimated at a relative pressure of 0.94 (P/P_0), assuming full surface saturation with nitrogen. Pore size distributions were evaluated from desorption branches of nitrogen isotherms using the Barret–Joyner–Halenda (BJH) model.

The morphology of the samples was observed on a ShimadzuSS-550 scanning electron microscope (SEM) and FEI Tecnai F20 EM (TEM).

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA) using Ni-filtered Cu Ka radiation.

The FT-IR spectra were recorded on a Thermo Nicolet 6700 spectrometer. The spectra were recorded using KBr wafers containing 1% of the sample at ambient conditions with a resolution of 4 cm^{-1} in the region from 400 to 4000 cm^{-1}.

Elemental analyses were performed with a Thermo Quest FlashEA1112 analyzer.

XPS was used to provide information on the surface composition of the materials. Analysis were performed on an ESCALAB250 X spectrometer with an Al Ka source (1 486.6 eV). The internal reference was the C 1s line at 284.6 eV.

The concentration of basic and acidic groups on the surface of materials was determined by acid–base titration method with 0.05 M solution of HCl and NaOH.

The TPD experiments were carried out on an online mass spectrometer (Balzers, OmniStar). The concentrations of loss of molecular were determined by the intensities of m/z respectively.

2.3. Adsorption experiments

The concentration of MO in the solution was determined by UV–vis spectrophotometer at maximum absorbance (λ_{max} = 464 nm). A calibration curve was plotted between absorbance and concentration of the dye to obtain the absorbance–concentra tion profile of the MO based on Beer–Lambert's law. For high concentration dyes, dye samples were diluted before absorbance measurements.

Adsorption experiments of different NMC materials were conducted by a batch method. In general, 0.025 g of NMC material was added into a 50 mL conical flask containing 25 mL solution of MO (100 mg/L), and the flask was shaken by a shaker for 23 h under ambient temperature conditions. The adsorption isotherm experiments were conducted in 50 mL conical flasks. The solutions of known initial concentrations (25–300 mg/L) were shaken for 23 h using 0.025 g of adsorbent under ambient temperature conditions. The kinetics studies were conducted to measure the time dependent uptake of MO on representative materials. The studies were carried out in 500 mL conical flasks containing 400 mL of adsorbent solutions with the initial MO concentration 300 mg/L. To each flask, 0.4 g of adsorbent was added. It was then equilibrated in a shaker under ambient temperature conditions at predetermined time interval (30–720 min).

The adsorption capacity values (q) were calculated by using the following equation (1) :