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Magnetic carbon nanospheres: Synthesis, characterization, and adsorbability towards quinoline from coking wastewater

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HIGHLIGHTS

- Magnetic carbon nanospheres (MCNSs) were synthesized.
- KOH activation and HNO_3 acidification of MCNSs were carried out.
- MCNSs-KH exhibited the best saturated adsorption capacity.
- Pore structure and acid–base interaction are the key factors for adsorption.

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ABSTRACT

Magnetic carbon nanospheres (MCNSs) dotting with Fe_3O_4 nanoparticles were synthesized by a simple solvothermal method. Furtherly, KOH activation and HNO_3 acidification of MCNSs were carried out to tune surface structure and property of MCNSs for the sake of adsorption improvement. The results show that both MCNSs and modified MCNSs (MCNSs-KH) have magnetic properties, and can be used as adsorbents for rapid separation and reutilization towards quinoline in coking wastewater. After KOH activation and HNO_3 acidification, the saturated adsorption capacity of MCNSs-KH is improved to 297.21 mg g^{-1}, much better than that of MCNSs (99.43 mg g^{-1}). According to BET and NH_3-TPD characterizations, KOH activation introduced a large number of pore structures, which significantly increased the specific surface area of MCNSs; HNO_3 acidification further increased the surface acidity of MCNSs, especially C=O functional group, which promoted the acid–base interaction with weakly basic quinoline. From the results of adsorption kinetics, isotherm and thermodynamics, the spontaneous and exothermic adsorption process conformed to pseudo-second-order and Langmuir–Freundlich models better.

1. Introduction

With the rapid development of economy and industrialization, water pollution has become an urgent environmental problem [1]. Coking wastewater, as a typical industrial organic wastewater, mainly comes from coking and gas purification process, and contains high concentrations of phenol, quinoline, pyridine and polycyclic aromatic hydrocarbons [2–4]. It always has the characteristics of large discharge, high toxicity, complex compositions and refractory degradation [5–8]. Quinoline, as one of the refractory organic pollutants in coking wastewater [9–10], still has a high content in the effluent of biochemical treatment process of coking wastewater [11–12]. As an endocrine interferon, quinoline from the direct discharge of quinoline-containing wastewater can cause irritation to respiratory system, liver injury and carcinogenesis [13–15]. Therefore, it is significant to study and realize the deep treatment of coking wastewater to reduce the discharge of ammonia-nitrogen organic pollutants.

Nowadays, the methods for deep treatment of coking wastewater mainly include chemical oxidation, coagulation, extraction and adsorption. Adsorption is widely used in advanced treatment of coking wastewater because of its simple operation and high efficiency. Activated carbon has been widely used in water treatment owing to its good adsorption performance [16], but its high cost and difficult separation limit its application [17–20]. Some researchers choose

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adsorbents such as carbon nanotubes, activated carbon fibers and biochar, which still have the problems of high cost, difficult desorption and regeneration, and poor adsorption performance. Rameshraja et al. [21] explored the adsorption behavior of quinoline on granular activated carbon and bagasse fly ash. They found that the saturated adsorption capacity of granular activated carbon towards quinoline was 160.03 mg g^{-1}, higher than that of bagasse fly ash. However, the granular activated carbon adsorbent had the problems of difficult desorption and poor regeneration. Liao et al. [22] used bamboo charcoal to investigate the adsorption kinetics, thermodynamics and regeneration behavior of nitrogen heterocycle compounds. Although bamboo charcoal as adsorbent had low cost and good regeneration, its saturated adsorption capacity for quinoline was only 32.50 mg g^{-1}. Thus, it is of great importance to develop an adsorbent with low cost, high adsorption capacity and easy separation and recovery.

At present, carbon nanosphere, as a functional carbon nanomaterial, has been widely used as adsorbents, drug carriers and hydrogen storage materials, because of its stable physical and chemical properties, large specific surface area, abundant porous structure, outstanding electrical conductivity and excellent biocompatibility. In wastewater treatment, carbon nanosphere adsorbents have been widely used to adsorb organic pollutants, heavy metal ions and dyes in aqueous solutions [23]. For example, Chen et al. [24] reported a mesoporous silica–carbon microsphere adsorbing Di-n-butyl phthalate in aqueous solution with a maximum adsorption capacity of 57.14 mg g^{-1}. Other researchers [25] reported that the Pb^{2+} adsorption capacity in aqueous solution of porous hollow carbon spheres@ZIF-8 was 152.4 mg g^{-1} higher than that of pure ZIF-8 adsorbent. To further improve the separation efficiency, magnetic nanoparticle Fe_3O_4 can be introduced into carbon nanospheres [26–30] since its superparamagnetism can promote adsorbent recovery under the action of external magnetic field [30–36]. Although many researchers have prepared various magnetic carbon nanospheres and used them to adsorb pollutants in water, it has been found that the adsorption performance of magnetic carbon nanospheres is not high. For example, Liu et al. [37] reported that a N-doped ferromagnetic mesoporous carbon nanosphere adsorbed acid red 57 and basic fuchsin with maximum adsorption capacity of 125 and 165 mg g^{-1}, respectively. Xie et al. [38] reported the adsorption of Pb (II) and Cu (II) on a Mg/Fe layered double hydroxide with Fe_3O_4-carbon sphere with maximum adsorption capacity of 3.66 and 5.33 mmol g^{-1}, respectively. Nevertheless, the adsorption effects of adsorbents are closely related to their structural characteristics. The surface chemical properties and pore structures of carbon materials directly determine their adsorption performances [39]. Thus, it is urgent to design an adsorbent with appropriate structure characteristics and surface chemical properties for better adsorption towards quinoline from coking wastewater.

In this paper, magnetic carbon nanospheres (MCNSs) were synthesized by solvothermal method. KOH activation and HNO_3 acidification were further adopted to provide MCNSs with larger specific surface area and suitable surface chemical environment [39–40]. At the same time, the adsorption properties of MCNSs towards quinoline in coking wastewater were investigated before and after modification. The structural characteristics of MCNSs before and after modification were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), nitrogen adsorption (BET), X-ray photoelectron spectroscopy (XPS), Field emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM) and so on. The effects of pH, contact time and adsorption temperature on the adsorption performance of the adsorbents were investigated. The adsorption kinetics, isotherm, thermodynamic behavior and regeneration performance of MCNSs before and after modification were discussed [41].

2. Experimental section

2.1. Materials

Quinoline (99%) was purchased from Aladdin Reagent Company. 1,5-Dihydroxy naphthalene (98%) was purchased from Macklin Reagent Company. PF127 was purchased from Sigma–Aldrich Reagent Company. Ethanol (99.7%), potassium hydroxide (85%), methanol (99.5%) and acetic acid (99.5%) were supplied by Tianjin Guangfu Technology Development Co., Ltd. (China). Ferrocene (98%) was acquired from Tianjin Guangfu Fine Chemical Research Institute, and hydrogen peroxide (30%) was purchased from Tianjin Tianli Chemical Reagent Co., Ltd. (China). Nitric acid (68%) was purchased from China Medicine Group Chemical Reagent Co., Ltd. (China). All the reagents were not further purified. Deionized water was used in all experiments, and it was primary distilled water.

2.2. Preparation of magnetic carbon nanospheres

First, 0.1 g of 1,5-dihydroxy naphthalene, 0.5 g of PF127 and 0.3 g of ferrocene were added to 20 mL of ethanol. Then, 1 mL of hydrogen peroxide was added to the solution. Subsequently, the mixed solution was transferred to a 50 mL teflon-lined stainless autoclave. The reaction was proceeded for 24 h at 220 °C, then cooled to room temperature. The supernatant was removed, the precipitated product was centrifugally washed with ethanol and deionized water in turn, and then dried overnight in an oven at 50 °C. The dried product was annealed in N_2 flow at 500 °C for 1 h with a heating rate of 10 °C min^{-1}. Finally, the magnetic carbon nanospheres, named MCNSs, were obtained.

2.3. Modification of magnetic carbon nanospheres

After mixing MCNSs and KOH at a mass ratio of 1:1, the mixture was calcined in a tube furnace at 750 °C for 1 h in N_2 atmosphere (10 °C min^{-1}), then cooled to room temperature and centrifugally washed with deionized water until the pH of product was neutral. The product was named MCNSs-K. MCNSs-K was mixed with 50 mL of 8 mol L^{-1} nitric acid solution. After ultrasonication for 20 min, the mixture solution was stirred at 80 °C for 20 min. Then the product was collected after centrifugation and washed with deionized water for several times until the pH of product was neutral, named MCNSs-KH.

2.4. The characterization methods

The morphology and particle size of the sample was analyzed by field emission scanning electron microscopy (FESEM) on a JSM-6700F (Japan). The microstructure of the sample was analyzed by high resolution transmission electron microscopy (TEM) on a JEM-2010 (Japan). The magnetic property of the sample was measured on a vibrating sample magnetometer at room temperature (VSM; Versalab, Quantum Design Company, USA). The X-ray diffraction (XRD) pattern of the sample was obtained on a Rigaku-D/max-2005 X-ray diffractometer (Cu-Ka radiation, 6° min^{-1}, 2θ = 5–85°). The surface functional groups of the sample were characterized by Fourier transform infrared spectrometry over a range from 400 to 4000 cm^{-1} (FTIR; BRUKER TENSOR 27, German). The nitrogen adsorption–desorption was measured using a nitrogen adsorption apparatus (BET; ASAP2020HD88, USA) and the Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH) equation were used to calculate the surface area and pore size distribution, respectively. The samples were pretreated at 100 °C for 30 min and then at 300 °C for 4 h [39]. Thermogravimetric analysis (TGA) was achieved using German NETZSCH TG209F3 thermal analyzer from 100 °C to 900 °C at a heating rate of 10 °C min^{-1} in N_2 atmosphere. The acid content and acid strength of the sample were analyzed by programmed temperature desorption (NH_3-TPD; FINESORB-3010, Zhejiang). NH_3 was the adsorbate gas and