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Adsorptive removal of 1-naphthol from water with Zeolitic imidazolate framework-67

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A R T I C L E I N F O

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A B S T R A C T

1-Naphthol is widely used as an intermediate in the plastics, dyes, fibers and rubbers production areas, leading to the increasing detection of 1-naphthol in the soil and water environment, which is of particular concern due to its acute toxicity and negative environmental impacts. Considering the high surface area and good stability of ZIFs (zeolitic imidazole frameworks) material, ZIF-67 (a representative cobalt-based ZIFs material) was synthesized and applied as an adsorbent for removal of 1-naphthol from aqueous solution. The obtained ZIF-67 was characterized by XRD, TEM, XPS, N_2 physisorption and TG, and the adsorption isotherm, kinetics, and regeneration of the adsorbent were studied in detail. The adsorption of 1-naphthol on ZIF-67 followed a pseudo-second-order equation kinetics and fitted Langmuir adsorption model with a maximum adsorption capacity of 339 mg/g at 313 K, which is much higher than that of the common adsorbents reported such as activated carbon and carbon nanotubes et al. The solution pH was found to be an important factor influencing the adsorption process, which could be explained by the predominant mechanism controlling the process, i.e. electrostatic attraction. In addition, the ZIF-67 showed desirable reusability toward 1-naphthol removal from alkaline aqueous solution.

1. Introduction

Water and soil pollution by synthetic aromatic compounds is one of the most serious environmental problems because these pollutants can easily migrate in the media and cause adverse effects on human and ecological receptors. 1-naphthol, as a derivative of aromatic compound, is widely used in the production of various industrial materials such as dyes, plastics, pharmaceuticals and rubbers et al. It can be easily released into the environment through discharge of industrial waste water or during the accidental leaks, thereby pose a threat to the ecosystem due to its acute toxicity [1–3].

Great efforts have been devoted into treatment of 1-naphthol containing waste water. Biological technique is a common method for wastewater treatment but it is inefficient for 1-naphthol removal due to its poor bioavailability [4]. The oxidation and membrane technology have also been developed but the process is costly [5,6]. By contrast, the adsorption method is a more favorable alternative, because of its low initial cost and simple operation, and the key of this technology is the development of excellent adsorbent. A number of adsorbents like activated carbon, carbon nanotubes, polymer resin and biochar et al. have been reported for 1-naphthol removal [7–11], however, the adsorption capacity of these materials were usually not high enough to remove 1-naphthol efficiently. Thus, it is still necessary to seek a new material with high adsorption capacity for the application of 1-naphthol removal.

In recent years, metal organic frameworks (MOFs), consisted of various transition metal ions or clusters interconnected by a variety of organics, has been extensively developed and used as adsorbent or catalyst in many areas with exceptional performances [12–16]. As one particular class of MOFs, zeolitic imidazole frameworks (ZIFs) received much attention recently because of its superior chemical and thermal stabilities. There have been numerous papers about the application of ZIFs as adsorbent for the removal of different pollutants from waste water and it showed great potential [17–23]. These studies also demonstrated that most of the ZIFs possessed hydrophobic surface and the material was stable in aqueous solution. Considering the above features, ZIFs could be a good candidate for the removal of 1-naphthol from waste water.

In this paper, we report the synthesis and application of ZIF-67 as a novel adsorbent for adsorptive removal of 1-naphthol from aqueous solution. ZIF-67 is a representative ZIFs material with the formula of $[Co(mim)_2]_n$ (mim=2-methylimidolate) and sodalite type zeolite structure. The adsorption isotherms, kinetics, and regeneration of the adsorbent were studied in detail. The obtained ZIF-67 exhibited

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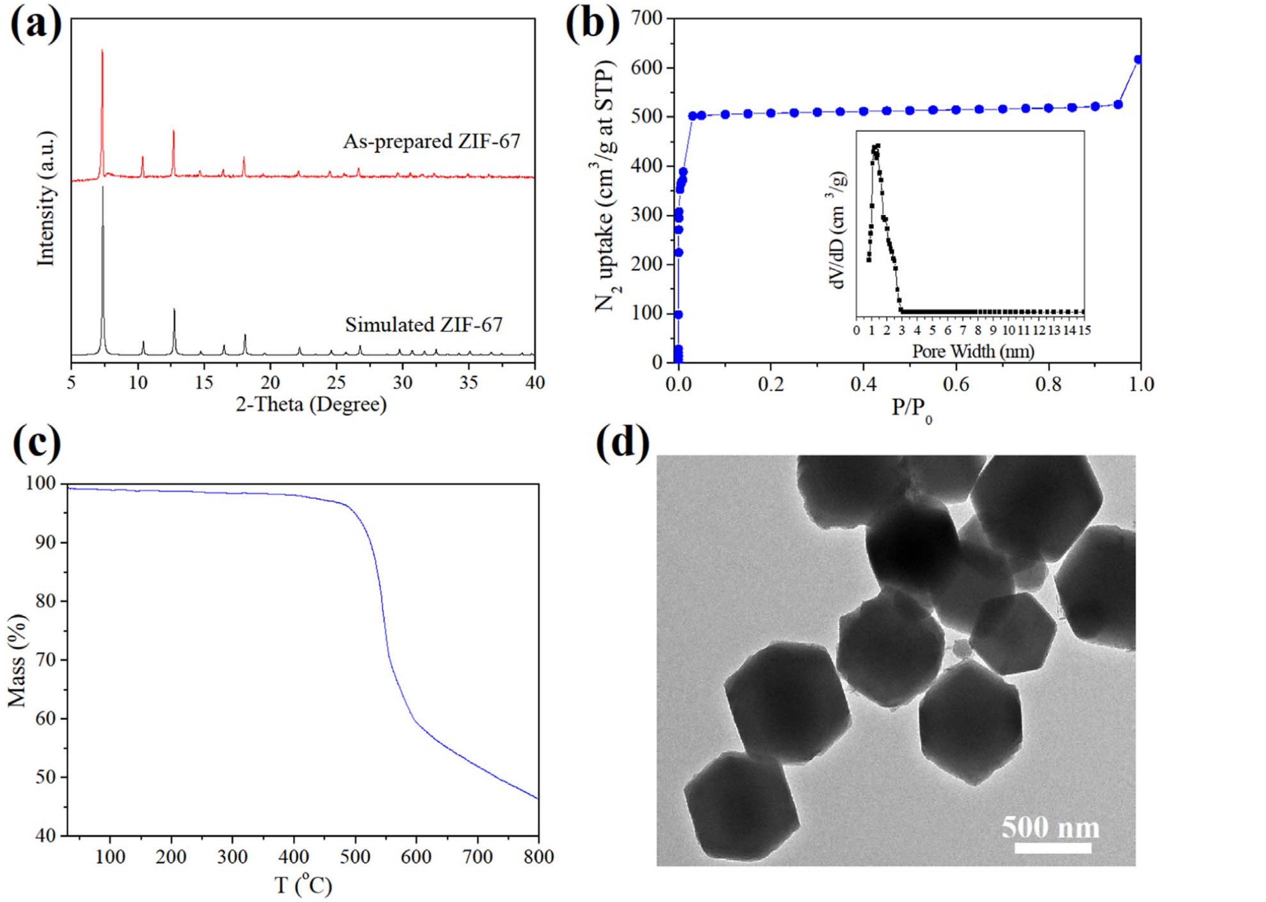

Fig. 1. Characteristics of the as-synthesized ZIF-67: (a) XRD patterns; (b) N_2 adsorption-desorption isotherms and pore size distribution (Inserted); (c) TG curve; (d) TEM image.

superior adsorption capacity (339 mg/g at 313 K) compared with common sorbents such as activated carbons, making it a potential adsorbent for the adsorptive removal of 1-naphthol from waste water.

2. Experimental

2.1. Materials

$Co(NO_3)_2{\cdot}6H_2O$, 1-naphthol, methanol and ethanol were obtained from Sinoreagent. 2-methylimidazole was purchased from J & K Scientific Company. All reagents used were of analytical grade and without further purification.

2.2. Synthesis of ZIF-67

Zeolitic imidazole framework-67 was prepared according to the reported procedure with minor changes [24]. Typically, cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) (4 mmol) and 2-methylimidazole (16 mmol) were dissolved in separate 100 mL portions of methanol. The above two clear solutions were mixed together under vigorous stir at room temperature for about 2 h and sealed for 6 h, during which time the mixed solution became cloudy due to precipitation of ZIF-67 nanoparticles. Then, the purple precipitate was collected by filtration and washed several times with methanol and ethanol, respectively. The as-prepared sample was dried at 50 °C overnight for further evaluation.

2.3. Characterization

Powder XRD pattern was recorded on a Bruker D8 ADVANCE diffractometer with Cu Kα radiation (40 kV, 30 mA). N_2 adsorption-desorption isotherms were measured at 77 K after degassing at 150 °C overnight by IQ2 Quantachrome porosimeter. Total pore volume was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.99. Morphology of ZIF-67 was characterized by Transmission Electron Microscope (TEM) (FEI Tecnai G2 F20) at 200 kV. Thermal decomposition behavior of ZIF-67 was determined using a thermogravimetric analyzer (Netzsch STA 449 F5) with a temperature ramp of 10 °C min^{-1} under a nitrogen atmosphere. X-ray photoelectron spectrum (XPS) was collected on a Thermo Scientific Escalab 250Xi instrument equipped with Al Kα radiation.

2.4. Adsorption experiments

The adsorption of 1-naphthol was performed by batch adsorption experiments. Firstly, stock solution was prepared by dissolving 200 mg/L 1-naphthol and 400 mg/L NaN_3 (to inhibit the degradation by incidental bacteria) in deionized water, and the solutions with other desired concentrations were obtained by further dilution before test.

For equilibrium adsorption, 5 mg of pre-dried ZIF-67 were added in 50 mL of the 1-naphthol solution with a known concentration and stirred for 10 min. The pH values were adjusted with minute quantity of HCl or NaOH solution. Then, the mixture was transferred to a glass tube, sealed and stewing for 48 h. After that, the mixture was taken and filtered through a 0.45 µm filter membrane for analyzing 1-naphthol concentration.

The adsorption kinetic tests were performed using a static adsorption method to avoid introducing oxygen into the solution during the taken of the samples. Specifically, 12–15 copies of glass tube which contained 100 mg of ZIF-67 and 50 mL of 1-naphthol solution with a known concentration were placed in a water bath with a predetermined temperature of 30 °C. At a given time point, one of the tubes was opened and the solution was taken and filtered for analyzing.