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Study on adsorption of copper ion from aqueous solution by MOF-derived nanoporous carbon

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ABSTRACT

Nanoporous carbons (NC) materials are synthesized by direct carbonization of zeolitic imidazolate framework (ZIF-8), a well-known metal organic framework (MOF). Here we study the efficiency of the obtained MOF-derived nanoporous carbon (MOF-NC) particles as adsorbent for the removal of copper (Cu) ions from an aqueous solution. The adsorption behavior is carefully studied from both kinetic and equilibrium point of view from which the obtained data can be described with different models. The efficiency of MOF-NC for removing Cu ion is compared with other carbonaceous adsorbents. The effect of solution pH and temperature on the removal percentage is also studied.

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1. Introduction

The presence of heavy metal ions in water, mostly originating from industrial activities, has a critical impact on the environment and indirectly affects human health and other organisms. Heavy metal ions are not biodegradable. Therefore, suitable methods are needed to remove these elements from water. So far, many attempts have been dedicated to the effective removal of heavy metal ions from aqueous solutions and different methods have been developed such as ion-exchange, chemical precipitation, nano-filtration, reverse osmosis, membrane technologies, oxidation/reduction and adsorption [1–5]. The adsorption process is one of the most promising methods for metal ions removal and has attracted considerable attention because of its simplicity and efficiency [1–5].

Cu is one of the heavy metal ions which may cause liver and eye damage at high uptakes [6]. The existence of heavy metals even with concentration of less than 0.1 ppm (μg per g) can be toxic to living organisms. According to World Health Organization (WHO) and Environmental Protection Agency (EPA) guidelines, the maximum allowed concentration of Cu ion in drinking water is 1.3 mg L^{-1} and 2.0 mg L^{-1}, respectively [7,8]. So far, various adsorbents have been used to remove copper (Cu) ions, such as polymer absorbents like poly(N-isopropylacrylamide-co-acrylic acid) hydrogels [9], polyaniline-grafted chitosan beads [10], poly-ethyleneiminemethylenephosphonic acid [11], alginate particles [12], calcium alginate immobilized kaolin [13], modified barley straw [14], cashew nut shell [15], and micro-structured ZnO thin films [3].

Nanoporous carbons (NC) materials with high surface area and large pore volume are useful, especially in the field of adsorption, separation, and gas storage [16,17]. Among NC materials, activated carbons are known to be good adsorbents, but their maximum adsorption capacity for removal of Cu ion relatively low [18,19]. Thus, finding new NC materials with high affinity for removing Cu ions from aqueous solution is a promising challenge. So far, various NC materials have been synthesized by several methods, e.g.,

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pyrolysis followed by physical or chemical activation of organic precursors, carbonization of polymeric aerogels, and nanocasting with hard-templates [20–22]. Lately, NC materials have been also prepared using metal organic frameworks (MOFs) or porous coordination polymers (PCPs) as precursors [23,24]. Yamauchi et al. have recently reported a facile way to prepare NC materials by direct carbonization of MOFs or PCPs without adding any other carbon precursors [25–28].

In this work, the use of MOF-derived NC (MOF-NC) for the removal of Cu ions is investigated for the first time. The MOF-NC used in this study is prepared by direct carbonization of zeolitic imidazolate framework (ZIF-8) which is a typical MOF. The adsorption study of Cu ions by MOF-NC is conducted and both equilibrium and kinetic aspects of the process are discussed. The effects of solution pH and temperature on the removal efficiency are also studied. This work demonstrates that the MOF-NC can be a good candidate as adsorbent for the removal of heavy metals ions from water.

2. Experimental

The NC adsorbent was successfully prepared from MOF accord to a method previously reported [27]. Briefly, about 500 mg of ZIF-8 was homogeneously dispersed in a ceramic boat. The sample was then put into a tube furnace and was exposed to a flow of nitrogen for an hour. After that, the furnace was heated to 800 °C with a rate of 5 °C min^{-1}, kept for 5 h and cooled down to room temperature. The resulting powder was washed with HF aqueous solution to completely remove the remaining Zn species. Finally, the carbon sample was rinsed with distilled water and then dried at 60 °C. The obtained nanoporous carbon is denoted as MOF-NC.

For the adsorption measurements, first, an aqueous solution of Cu (1000 ppm) was prepared by dissolving $CuSO_4$ in deionized water. Other concentrations were prepared by successively diluting the initial solution. The residual Cu ion concentration in both kinetic and equilibrium adsorption experiments was determined by complexometric method (with Zincon in buffer solution at pH = 7) [29], using UV/visible spectrophotometer (PG Instrument T80) at $\lambda_{max} = 600$ nm. For kinetics experiments, the adsorptions of Cu ions on MOF-NC were measured at desired time intervals (0–1200 min) with fixed initial concentration (50 ppm) at room temperature (25° C). In this experiment a series of 2 mg of MOF-NC added to 10 mL Cu ions solutions were stirred in a thermostated shaker. Each flask was sampled at the desired time to determine the residual concentration of Cu ion after centrifugation. For equilibrium adsorption experiments, 2 mg of the carbon adsorbent was added to a series of 10 ml of the aqueous Cu solutions with different concentrations ranging from 40 ppm to 1000 ppm. After 24 h, the concentration of residual Cu ions, collected by centrifugation, was measured in a similar manner.

To compare the removal efficiency of the prepared adsorbent with other activated carbons, 2 mg of each carbon was added to 10 ml Cu ion solution (100 ppm). The residual concentration of Cu ions was then measured after 0.5 h and 4 h. To investigate the effect of temperature on the adsorption process, experiments with fixed concentration of Cu ions (100 ppm) and fixed amount of carbon adsorbent (2 mg) were carried out at various temperatures ranging from 25 to 55° C. After 6 h, the residual concentration was determined. For the study of the pH effect on the removal percentage, 10 ml of Cu ions solution (100 ppm) in the pH range of 3.0–5.4 were prepared. The pH of Cu ions solution was adjusted by adding increments of 0.1 M HCl or 0.1 M NaOH solutions. Then, 2 mg of MOF-NC sample was added and the solutions were shaken for 6 h. The agitation speed and temperature were fixed at 150 rpm and 25° C respectively. Finally, the solution was analyzed with a UV/Vis spectrophotometer for determining the remaining Cu ions concentration. The pH of point of zero charge (pH$_{pzc}$) was determined according to a method reported by Faria et al. [30].

3. Results and discussion

3.1. Characterization

Fig. 1 shows the scanning electron microscopic (SEM) images of the obtained MOF-NC particles. The average particle sizes are *ca.* 2 μm. These images reveal the formation of MOF-NCs with polyhedron morphology similar to that of the parent ZIF-8 [27,28]. Thus, the carbonization at 800 °C does not change the morphology. During the carbonization, a network of NCs is formed through the thermal decomposition of ZIF-8 which acts both as sacrificial template and carbon precursor [27]. Our previous report has demonstrated that the MOF-NCs are built up from randomly assembled nanometer-sized sheets [27]. The formation of graphitic structures is confirmed by both wide-angle XRD and Raman measurements. The peak observed at 25° corresponds to a typical interlayer peak of graphite-type carbon nanosheets. The relative ratio of G bands to D bands (I_G/I_D) in the Raman spectra is almost the same as that of the commercially available activated carbon. N_2 adsorption–desorption isotherm of MOF-NC shows type I isotherms which is typical for microporous materials. The surface area, total pore volume, and pore size of MOF-NC are 1610 m^2 g^{-1}, 1.1 cm^3 g^{-1} and 1.07 nm, respectively.

3.2. Adsorption kinetics

The effect of the immersion time on the Cu ion adsorption by the MOF-NC was investigated and the results are depicted in Fig. 2a.
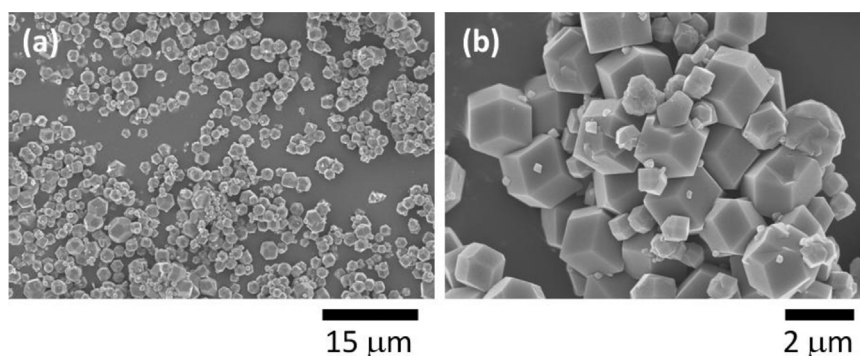

Fig. 1. SEM images of the prepared MOF-NC.