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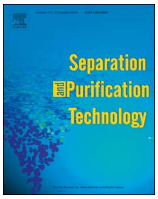

Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks

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ABSTRACT

With the rapid development of industrialization, removing heavy metal ions of wastewater from the discharge of industrial sewage is a very important topic, because it will severely affect our environment and water ecosystem. In this work, we synthesize two porous adsorbents of ZIF-8 and ZIF-67 and further investigate their performance of removing Pb^{2+} and Cu^{2+} from wastewater. Results indicate that saturated adsorption capacities of ZIF-8 and ZIF-67 for Pb^{2+} reach 1119.80 and 1348.42 mg/g, while they are 454.72 and 617.51 mg/g for Cu^{2+}, respectively, which are greatly higher than almost all other porous materials. If we use the excessive adsorbents to treat wastewater, more than 99.4% Pb^{2+} and 97.4% Cu^{2+} can be removed by ZIF-8 and ZIF-67 adsorbents. Moreover, the two adsorbents also show fast adsorption kinetics, and only need several decade minutes to reach adsorption equilibrium. These features indicate that ZIF-8 and ZIF-67 are excellent candidates for removal of heavy metal ions from wastewater.

1. Introduction

With the rapid development of industrialization, the environment has been heavily polluted by wastewater emitted from industry. Among various organic and inorganic pollutants, heavy metals are of most danger. The heavy metal ion pollution in the water ecosystems mainly from the discharge of industrial sewage has become a severe issue because of the increasing damage to humanity and other living organisms. Once taken into the human body, even in small amounts, heavy metals can result in a terrible harm because they can be neither detoxified nor eliminated effectively. So they must be removed from wastewater for public health. The main sources of heavy metals include mining, smelting, electroplating, battery manufacturing, textile printing and leather industries [1,2]. Actually, lead, mercury, cadmium, chromium, zinc and copper ions have been considered to be the pollutants that must be removed from wastewater. In particular, lead can destroy the hematopoietic system and cause damage to central brain, kidney and liver, thus leading to anemia, encephalopathy, hepatitis and so on [3]. Although copper is one of the essential trace elements in the human body, the excessive copper will harm nervous system and organisms, especially liver and gallbladder, leading to neuritis and cirrhosis. Therefore, removing lead and copper ions from wastewater is a very important project.

Various conventional methods have been adopted to remove heavy metals from wastewater. These methods include chemical precipitation with hydroxides, sulfides and chelating precipitations, ion exchange, adsorption by porous carbon materials, bioadsorbents, membrane filtration, electrodialysis, coagulation and flocculation, flotation and electrochemical treatment [4,5]. Among these methods, adsorption technique is the most widely applied owing to its convenience, economy and high efficiency for removing heavy metals at low concentration, especially in the range of 1–100 mg/L. Other methods often cause some side effects. For example, chemical precipitation can produce large amount of sludge to be treated with great difficulties and is ineffective when metal ion concentration is very low, while flotation and electrochemical technology involve high initial investment and operation costs [4].

In previous studies, using porous materials to remove lead and copper ions from wastewater has been widely explored. Ronda et al. adopted olive tree branch treated by NaOH to adsorb Pb^{2+} and its adsorption amount is 16.04 mg/g [6]. Maleki et al. successfully grafted ethyl acrylate to chitosan, the maximum Pb^{2+} removal efficiency of 92% were achieved [7]. Lee et al. found that the self-assembled flower-like TiO_2-graphene oxide (GO-TiO_2) hybrid could adsorb Pb^{2+} of 65.6 mg/g [8]. Al-Zboon et al. used amorphous polymer from waste coal fly ash to achieve Pb^{2+} uptake of 81.0 mg/g at pH = 5 and 298 K

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[9]. Pap et al. used Langmuir equation to predict that the maximum adsorption capacity of Pb^{2+} on lignocellulosic raw materials (sweet/sour cherry kernels) carried out by thermochemical conversion is 180.3 mg/g [10]. Ramirez et al. reported that adsorption amount of Pb^{2+} on 4-vinylpiridine (26.74%)-grafted poly-acrylic acid network (net-PAAc-g-4VP 26.74%) reaches 117.9 mg/g in 24 h [11]. Niu et al. used composite modified adsorbent (CSTEC) as novel fibrous materials for the adsorption of Cu^{2+} and Pb^{2+} ions from water, CSTEC showed better performance (Cu^{2+}, 95.24; Pb^{2+}, 144.93 mg/g) than most of other adsorbents [12]. Deng et al. found that adsorption capacity of Pb^{2+} on the functionalized graphene (GNS^{PF6}) prepared by electrolysis method is 406.6 mg/g at pH = 5.1 [13]. Zhao et al. reported that adsorption amount of Pb^{2+} on few-layered graphene oxide synthesized by using the modified Hummers method reaches 842.0 mg/g (pH = 6.0 and 293 K), 1150 mg/g (313 K) and 1850 mg/g (333 K), respectively [14].

Acheampong et al. reported that a maximum uptake of Cu^{2+} on the pretreated coconut shell is 53.9 mg/g at pH = 7 and 303 K [15]. Anirudhan et al. found that the maximum monolayer adsorption capacity of Cu^{2+} on humic acid-immobilized-amine modified polyacrylamide/bentonite composite (HA-Am-PAA-B) is 106.2 mg/g at pH = 5 and 303 K [16]. Kizilkaya et al. reported that adsorption capacity of Cu^{2+} on fish bones pretreated with NaOH is 150.7 mg/g at pH 5.0 and 323 K [17]. Wang et al. found that chitosan-grafted-poly (acrylic acid) shows a maximum adsorption capacity of 262.25 mg/g for Cu^{2+} at pH = 5.50 and 303 K [18]. Jeong et al. reported that adsorption capacity of Cu^{2+} on the tetrakis (4-carboxyphenyl) porphyrin-functionalized mesoporous silica reaches the 823.56 mg/g at 298 K due to the chelating nature [19].

Since highly porous frameworks, including metal-organic frameworks (MOFs) [20,21], covalent-organic frameworks (COFs) [22–27] and zeolitic imidazolate frameworks (ZIFs) [28–30], were reported, these frameworks have been widely applied to gas adsorption and separation [21–22,24,26,31–33], electrochemistry [30,34–37] and luminescent probe, etc. [25,29,38,39]. As a family member of the crystalline porous frameworks, ZIFs have been proved to not only have exceptional hydrothermal stability and chemical stability in refluxing organic solvents and aqueous alkaline solution, but also hold the large pore volume and high specific surface area, which suggests that ZIF is a promising candidate for wastewater treatment. However, few studies have been reported on MOFs and ZIFs as adsorbents. Ke et al. investigated adsorption of Hg^{2+} on the thiol-functionalized $[Cu_3(BTC)_2]_n$ and found that its uptake achieves 714.29 mg/g [40]. Wu et al. studied the removal capacity of As^{5+} on five kinds of ZIF-8 prepared through different methods, among which hierarchical ZIF-8(H-ZIF-8-14) reaches maximum capacity of 90.92 mg/g [41,42]. Pan et al. reported that adsorption capacity of ZIF-67 for phenol is 378.89 mg/g at pH = 9 and 303 K [43].

Therefore, here we would use ZIF-8 and ZIF-67 as adsorbents to investigate their performance in removing heavy metal ions from wastewater. In particular, the emphasis is placed on removal of Pb^{2+} and Cu^{2+} from wastewater. And their adsorption kinetics mechanism would be also explored.

2. Experimental section

All chemicals and reagents were commercially available in analytical grade without further purification.

2.1. Preparation of adsorbents

ZIF-8 was synthesized by the solvothermal reaction of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and 2-methylimidazole in solvent of N,N-dimethylformamide (DMF) [28]. A solid mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (2.3888 g, 8.03 mmol) and 2-methylimidazole (0.6002 g, 7.31 mmol) was dissolved in DMF of 216 ml in a 250-ml vial. The vial was sealed and heated to 140 °C at a rate of 5 °C/min in a programmable oven and held at this temperature for 24 h, then cooled to room temperature at a rate of 0.4 °C/min. After filtration, the crystal was washed by DMF (3 × 10 ml) and dried in air.

ZIF-67 was synthesized by the solvothermal reaction of cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and 2-methylimidazole in a DMF solvent [44]. A solid mixture of $Co(NO_3)_2{\cdot}6H_2O$ (2.6193 g, 9 mmol) and 2-methylimidazole (2.2167 g, 27 mmol) was dissolved in DMF of 216 ml in a 250 ml vial. The vial was sealed and heated at constant 100 C for 72 h, then cooled naturally in air.

The dry ZIF-8 and ZIF-67 were immersed in chloroform (3 × 20 ml) at ambient temperature for 72 h. Then, they were evacuated at 200 °C in vacuum for 24 h to yield samples.

2.2. Preparation of heavy metal solutions

Heavy metal solutions were prepared by dissolving analytical grade $Pb(NO_3)_2$ and $Cu(NO_3){\cdot}3H_2O$ in distilled water to obtain 200 mg (metal ion)/l solutions. The pH of the solutions was measured to be 5.1 ± 0.4 for Pb^{2+} and 5.2 ± 0.2 for Cu^{2+} at ambient temperature and no chemicals were added to change the pH value.

2.3. Batch adsorption experiments

Batch adsorption studies were carried out by mixing a certain amount of adsorbent and a certain volume of metal ion solution with the magnetic stirrer at room temperature (298 K). The initial concentrations for the two metal ions were around 200 mg/l and the amount of adsorbent was in the range of 0.1–2.0 g/l. The volume of metal ion solution was in the range of 50–800 ml, which was determined according to the amount of adsorbent to ensure that it could reach 0.05 g minimum. In the first five minutes, magnetic stirrer was operated at 700 rpm to make adsorbent dissolved adequately and then it was set as 400 rpm. Preliminary experiments showed that almost all adsorption processes were fast and the adsorption amount basically keeps unchanged after 120 min. Therefore, 120 min were used as the equilibrium time for most batch experiments except for a few of special experiments with a longer equilibrium time. 7 ml sample solution was taken out from the bottle at a given time interval and filtered by filter paper (0.22 μm) to remove the adsorbent for finally analyzing the concentration of metal ions in the solution.

2.4. Characterization of materials

Powder X-ray diffraction (PXRD) measurements were carried out with D8 ADVANCE X-ray diffactometer (Cu Kα, 40 kV, 20 Ma, λ = 1.54178 Å) to analyze ZIF structures. The adsorption-desorption isotherms of N_2 at 77 K were measured by a Micromeritics ASAP 2020 analyzer and then the specific surface area and pore size distribution were also determined. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) elemental analysis were carried out with S-4700 of HITACHI and AMETEK at 20 kV. The concentrations of metal ions were measured with Sequential Plasma Spectrometer, which was ICPS-7500 from SHIMADZU at wavelengths of 220.351 and 327.396 nm for Pb^{2+} and Cu^{2+} respectively.

3. Results and discussion

Fig. 1(a) and (b) shows the typical PXRD patterns of the ZIF-8 and ZIF-67, which are the same with the simulated one in previous literature, respectively [45,46]. The good agreement of experimental PXRDs and simulated ones indicates that the synthesized ZIF materials have the same structure as the single crystal.

The N_2 adsorption-desorption isotherms at 77 K and pore size distributions of the ZIFs are shown in Fig. 1(c) and (d). The as-synthesized