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Regular Article

A metal-organic framework with large 1-D channels and rich —OH sites for high-efficiency chloramphenicol removal from water

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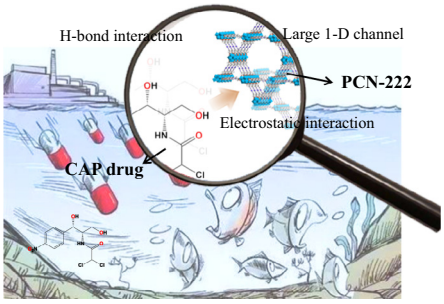
GRAPHICAL ABSTRACT



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ABSTRACT

High-efficiency removal of chloramphenicol (CAP) drug from waste water still faces a large challenge up to date. Herein, we report the first metal-organic framework-based adsorbent (PCN-222) for CAP and effective removal was achieved. PCN-222 exhibits a large adsorption capacity of 370 mg g^{-1}, superior to some other MOFs and various reported adsorbents; and more importantly, the adsorption equilibrium can be quickly obtained at only 58 s. Besides, ~99.0% of CAP can be removed from water in the low concentrations (including the concentrations found in real water). Further investigation indicates that H-bond interaction, electrostatic interaction and the special pore structure of PCN-222 all play important effects on the high-efficiency removal of CAP. Therefore, our work may provide a novel perspective for removing CAP or other antibiotic drugs from contaminated water.

1. Introduction

Nowadays, antibiotic drugs are paid large interests in the treatment of human health. However, heavy use of these drugs can lead to serious water pollution. In particular, large drink of water containing chloramphenicol (CAP) can induce human diseases due to its side effects such as fatal bone marrow depression and aplastic anemia [1,2]. Therefore, efficient removal of this antibiotic drug is of great importance to keep human healthy and environment safe. Up to date, some methods have been explored to remove chloramphenicol from water such as degradation and adsorption [1,3–7]. In particular, adsorptive removal is gaining large attentions for few by-products, high efficiency and low operation cost.

Over the past years, several porous materials such as carbon nanotubes, ordered mesoporous carbon and mesoporous sol-gel have been explored for CAP adsorption [6–8]. However, these

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reported materials face the drawbacks in adsorption capacity or adsorption rate. Therefore, further discovery of novel high-efficiency adsorbents is necessary. In general, abundant adsorption sites can promote effective adsorption especially in lower concentration range. For CAP molecules containing large amounts of organic functional groups, introduction of H-bonds interaction may be an effective strategy. On the other hand, for the adsorption of CAP, large pore size is necessary in the construction of porous adsorbents, which can be beneficial for the fast diffusion of guest molecules.

In this respect, metal-organic frameworks (MOFs) have exhibited large potentials due to their special pore structures, large specific surface areas and pore volumes, and designable activated sites [9–11]. Up to date, MOFs as adsorbents have been widely used in adsorptive removal of pollutants from water such as dyes, ions, explosives, and drugs [12–17], while MOFs-based adsorbents for CAP are not reported so far.

In this work, a water stable MOF, PCN-222 was prepared on large scale at reflux condition and systematically studied for its removal performances of CAP from aqueous solution. PCN-222 owns two types of 1-D channels, both far larger than the molecular size of CAP [12]; in addition, the inorganic cluster of PCN-222 ($Zr_6(\mu\text{-}OH)_8(OH)_8(CO_2)_8$) can provide high density of hydroxyl groups, which can bind with CAP molecules via H-bonds interaction [18,19]. As expected, PCN-222 demonstrates to be a fast and high-capacity adsorbent for CAP in aqueous solution. To the best of our knowledge, PCN-222 is the first MOF-based adsorbent for CAP up to date. Our work may provide an effective strategy in design of MOFs for antibiotic drugs removal.

2. Materials and methods

2.1. Materials and reagents

Zirconium oxychloride octahydrate ($ZrOCl_2{\cdot}8H_2O$), 2-aminophthalic acid ($H_2BDC\text{-}NH_2$), 1,4-dicarboxybenzene (H_2BDC), N,N-dimethylformamide (DMF), formic acid and other common salts were purchased from HWRK Chem. and were used without further purification. The ligand tetrakis(4-carboxyphenyl)porphyrin (TCPP) was synthesized according to the literature [20].

2.2. Preparation of MOFs

In this work, PCN-222 was prepared on a large scale by heated reflux under normal pressure. In a 2 L flask, $ZrOCl_2{\cdot}8H_2O$ (2.86 g) and TCPP (2.34 g) were solved in the mixture of DMF (800 mL) and formic acid (560 mL). Then the solution was stirred and refluxed at 135 °C for three days. In the activation process, the collected solid was dispersed in DMF (400 mL) containing hydrochloric acid (3 mL, 1.5 M) and stirred at 120 °C for 24 h. The activation process was repeated twice. At last, the resulting solid was washed with acetone and then dried at 100 °C overnight. The yield of the material is 2.14 g (62% based on TCPP, higher than 46% in the previous report [20]). Other MOFs including MIL-101(Cr), MIL-101 (Cr)-NH_2, MIL-53(Al) and MIL-68(Al) were synthesized according to the reported works [21–24].

2.3. Characterization techniques

The powder X-ray diffraction (PXRD) patterns of the MOFs were recorded on a D8 Advance X diffractometer equipped with Cu Kα radiation (λ = 1.54178 Å) at room temperature. The 2θ range from 3° to 30° was scanned with a step size of 0.02°. Nitrogen adsorption–desorption measurements at 77 K were performed on an Autosorb-iQ-MP surface area analyzer. The morphologies and element mapping of the MOFs were characterized using a Hitachi S-4700 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray system. The FT-IR spectroscopy was recorded on a Nicolet iS50 FTIR spectrophotometer. The spectra data were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. In addition, the zeta potential of the sample was obtained through a Zetasizer Nano ZS Zeta potential analyzer. Thermal stability of sample was investigated by thermal gravimetric analysis (TGA) using a METTLER TOLEDO TGA/DSC 1/1100 SF simultaneous thermal analyzer. Heating rate was 5 °C min^{-1} and air flow speed was 10 mL min^{-1}.

2.4. Adsorption of CAP

The CAP adsorption by MOFs in this work was performed at the form of batch adsorption. It is noted that the MOF samples were dried at 100 °C for 12 h before the adsorption process to remove the guest water molecules in the pores. In the adsorption experiments, MOF sample (5 mg) was added into the CAP aqueous solution (5 mL). After adsorption in a shaker at 25 °C, the suspension was filtrated using a microfiltration membrane (0.22 μm) and the collected clear filtration solution was measured for the CAP concentration by a UV–vis spectroscopy (TU-1901, Persee, China).

3. Results and discussion

3.1. Characterization of PCN-222

Similar to other Zr-based MOFs, PCN-222 also exhibits excellent water stability [25]. Meanwhile, as shown in Fig. 1a, PCN-222 framework contains large 1D channels with the sizes of 3.7 nm and 1.3 nm, demonstrated by the pore size distribution (PSD) measurement (Fig. 2a). On the other hand, as shown in Fig. 1b and c, the $Zr_6(\mu\text{-}OH)_8(OH)_8(CO_2)_8$ clusters of PCN-222 can provide abundant hydroxyl groups, which play the adsorption sites via H-bonds interaction with various organic groups in CAP molecules (e.g. —OH, —NO_2, and —C═O). Therefore, these characteristics may

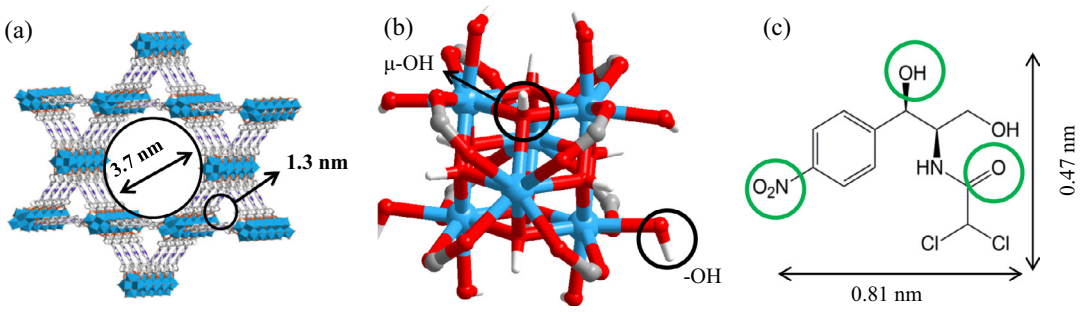

Fig. 1. (a) The pore structure and (b) the inorganic clusters $Zr_6(\mu\text{-}OH)_8(OH)_8(CO_2)_8$ of PCN-222; (c) the molecule structure and size of CAP. (Color: blue, Zr; grey, C; red, O; white, H.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)