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A comparative study of rigid and flexible MOFs for the adsorption of pharmaceuticals: Kinetics, isotherms and mechanisms

Yanxin Gao[a], Kai Liu[b], Ruoxi Kang[a], Jing Xia[a], Gang Yu[a,*], Shubo Deng[a]

[a] *School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Tsinghua University, Beijing 100084, China*
[b] *Line and Robinson Laboratory Rm. 227, California Institute of Technology, 1200 E California Blvd, CA 91125, USA*

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ABSTRACT

Recently metal-organic frameworks (MOFs) have attracted great attention in the field of environmental remediation. In this article, rigid MIL-101(Cr) and flexible MIL-53(Cr) were synthesized and used for the adsorption of two typical pharmaceuticals, clofibric acid (CA) and carbamazepine (CBZ), from water. The adsorption equilibrium was rapidly reached within 60 min and the kinetics best fitted with the pseudo-second-order kinetic model. There was no significant difference in the maximum adsorption capacity of CA on MIL-101(Cr) and MIL-53(Cr), and electrostatic interaction was suggested to be the main factor in the adsorption processes. However, for the removal of CBZ, MIL-53(Cr) showed much better adsorptive performance (0.428 mmol/g) than MIL-101(Cr) (0.0570 mmol/g), indicating the adsorption of CBZ on MOFs is affected by the structural property. The Powder X-ray diffraction analysis revealed that MIL-53(Cr) was transformed into large pore form, leading to variations in cell volume up to 33%, lower binding energy and crucial modifications of the hydrophobicity/hydrophilicity. This unusual behavior enhanced its adsorption capacity for CBZ. Moreover, hydrogen bonding and π-π interactions/stacking also contributed to the adsorption of pharmaceuticals on the MOFs. The excellent adsorptive performance of MIL-53(Cr) and its structure/property switching might lead to the applications in water treatment.

1. Introduction

Pharmaceuticals and personal care products (PPCPs), as a class of contaminants of emerging concern, are ubiquitously detected in the aqueous environment [1]. Among those PPCPs with different properties, clofibric acid (CA) and carbamazepine (CBZ) (Table S1), which are used to treat high blood lipids and epilepsy, respectively, are considered as typical PPCPs with high environmental risk [2,3]. At present, their negative effect on reproduction, metabolism, and embryonic development have been reported [4–7]. When surface water is polluted with these compounds, aquatic life can be harmed even by trace amounts.

In general, removal methods for PPCPs include adsorption, membranes separation, advanced oxidation, and microbial degradation [8–11]. Among them, adsorption has been considered as a promising technique due to high efficiency, easy operation, and energy saving. The main challenge of developing adsorption techniques lies in the selection of adsorbent. Benefitted by high surface area and relatively low price, activated carbon has been demonstrated as the most commonly used material for the adsorptive removal of contaminants from water [12]. However, due to the limited adsorption capacity and short life cycles, activated carbon still suffers from considerable limitations in real applications. Therefore, it is of essential importance to develop new adsorption materials for the fast and efficient removal of PPCPs.

Metal-organic frameworks (MOFs) are a new family of crystalline porous materials which are constructed from coordinated organic linkers and metal ions/clusters. As MOFs can be systematically designed by changing the connectivity of the inorganic moiety and the nature of organic linkers, they hold great promise for various applications including gas capture, catalysis, separation, sensing and drug delivery [13–18]. Interestingly, the remarkably advantageous properties of MOFs, such as tenability of their pore size, intrinsic functionality, and flexible structures, endow them with excellent figures of merit for adsorption-related applications [19,20]. For example, the storage of hydrogen, carbon dioxide, and methane by MOFs has been extensively studied [21,22]. The removal of aqueous contaminants such as heavy metals, dyes and endocrine disrupting chemicals has also been investigated [23–25].

Among the numerous MOFs so far reported, the MIL series, with

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[*] Corresponding author.
E-mail address: yg-den@tsinghua.edu.cn (G. Yu).

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acid and base resistance and high thermal (> 300 °C) and aqueous stability, are largely studied for their potential applications [23,26]. The chemical stability of the MILs increases with increasing inertness of the central metal ions and the thermal stability can be explained by the strength of the metal-oxygen bond [27]. As Cr(III) is a well-known inert ion and can form strong Cr-O bond, the remarkable thermal and aqueous stability of Cr(III) MILs has been proven in previous reports [28–30]. Of those, two typical solids are MIL-101(Cr) and MIL-53(Cr) [26,31]. MIL-101(Cr) ($Cr_3O(F/OH)(H_2O)_2[C_6H_4(CO_2)_2]$), with extremely high specific surface area, has been used as a typical rigid MOF for studying adsorption for aqueous contaminants removal [32,33]. MIL-53(Cr) ($Cr(OH)[C_6H_4(CO_2)_2]\cdot nH_2O$), shows a three-dimension system with one-dimensional channels [34]. The most interesting property of MIL-53(Cr) is the flexibility, also named as "breathing effect", which can produce a dramatic increase or decrease in cell volume and pore size without losing crystallinity [35]. Unfortunately, the effects exerted by their flexibility and rigidity on adsorption behavior have not been compared. Furthermore, despite growing efforts in the research domain of aqueous compounds adsorption using MOFs, the mechanism, and the relationship between the mechanism and the MOF structural characteristics, are not well understood, which is largely due to the uncertainty in the structure of the flexible MOFs in the adsorption process.

Considering the aforementioned factors, we herein describe our attempt to synthesize rigid MIL-101(Cr) and flexible MIL-53(Cr) and compare their adsorption behavior. By controlling the same organic ligands and metal ions, the structural difference becomes the key factor affecting the adsorption. The aforementioned emerging contaminants CA and CBZ are used as model compounds. We have observed significant differences in adsorption performances of MIL-101(Cr) and MIL-53(Cr) for different adsorbates. The experimental data were fitted with different models to understand the solid-liquid adsorption processes. In addition, we complemented experiments on pH effect and structure analysis, not only to rationalize the differences in adsorption performance but also to interpret the adsorption mechanisms of both MOFs. Our study provides valuable insights into the understanding of the adsorption behavior of MOFs and the development of MOF-adsorbents for the removal of organic contaminants from wastewater.

2. Materials and methods

2.1. Materials

N,N-Dimethylformamide (DMF) and terephthalic acid (H_2bdc) were obtained from Peking Reagent (China) and Sigma-Aldrich (USA), respectively. $Cr(NO_3)_3\cdot 9H_2O$ of analytical grade and hydrofluoric acid (HF, 40%) was offered by Sinopharm (China). CA and CBZ were purchased from Strem Chemicals (USA) and Sigma-Aldrich (USA), respectively. All solutions were prepared with ultrapure water (resistivity > 18 MU) from a Mill-Q system (Milli-pore, Billerica, USA).

2.2. Synthesis of MOFs

MIL-101(Cr) was synthesized based on the published HF-free hydrothermal methods [36]. Briefly, H_2bdc and $Cr(NO_3)_3\cdot 9H_2O$ were added to ultrapure water. The resulting suspension was sonicated for 30 min at room temperature before being heated to 493 K for 18 h in a Teflon-lined autoclave. The crude product was firstly washed with DMF at 100 °C in an autoclave for 12 h and then washed with methanol. The resultant material was dried in a vacuum oven at 150 °C for 12 h.

MIL-53(Cr) was prepared from a mixture of $Cr(NO_3)_3\cdot 9H_2O$, H_2bdc, HF, and H_2O [33]. Reactants were introduced in this order and sonicated for a few minutes at room temperature before introducing the resultant suspension into a Teflon-lined stainless autoclave and heated to 493 K for 72 h. The crude product was collected by centrifugation and subsequently washed with methanol at 120 °C in an autoclave for several times. The resulting material was dried in a vacuum oven at 150 °C for 12 h to yield MIL-53(Cr) powder.

2.3. Characterization of the MOFs

The Fourier-transform infrared spectroscopy (FT-IR) can clearly show the presence of the functionalities of MOFs. The spectra were scanned from 400 to 4000 cm^{-1} via an attenuated total reflectance technique on a Thermo Nicolet Nexus 870 FT-IR spectrometer system (Thermo Fisher, USA). Powder X-ray diffraction (PXRD), performed in a D/MAX-RB (Rigaku, Japan) X-ray diffractometer equipped with a Cu-K_α radiation source, shows the crystal structures of MIL-101 and MIL-53. The morphology of MOFs was studied by Scanning Electron Microscope (SEM) (Zeiss, Germany) operating at 10 kV with magnification of 2000–5000. The BET surface area was measured by N_2 adsorption/desorption isotherms on Autosorb-1MP (Quantachrome, USA). Zeta potentials were analyzed by a zeta-potential analyzer (Delsa Nano C, Beckman Coulter, U.S.). MOF suspensions (0.1 wt%) were prepared with MOFs, ultrapure water and 2 mM NaH_2PO_4 at the desired pH and sonicated for a few minutes before test.

2.4. Adsorption experiments

The adsorption of CA and CBZ on MOFs was performed in a batch experiment. The stock solution was prepared by dissolving certain amount of pharmaceutical solids in ultrapure water. The experimental solution was obtained by diluting the stock solution with water to the desired initial concentration. In a typical adsorption procedure, certain amount of activated MOF powder was added into 50 mL of CA or CBZ solutions with predetermined initial concentrations and then placed in an orbital shaker at 150 rpm and 298 K. After adsorption for a predetermined time, the solution was separated by filter (0.45 μm). Kinetic experiments were done by mixing 5 mg of MOF sample and 50 mL 20 mg/L of CA or CBZ solution at pH 7 and agitated at room temperature. The adsorption isotherm experiments were carried out with the initial concentrations at the range of 5–100 mg/L. The effect of pH on adsorption was investigated over a pH range of 3.0–10.0 with a contact time of 5 h. The pH was adjusted by 0.1 M HCl or NaOH solution.

2.5. Pharmaceutical analysis

1 mL of solution sample was filtered through a 0.45 μm nylon syringe filter. Negligible adsorption of CA and CBZ onto filters was determined in a control experiment. A high-pressure liquid chromatography with a UV–vis detector (Shimadzu, Japan) and a 4.6250 mm TC-C18 column (Agilent Technologies, USA) was applied to detect the concentrations of pharmaceuticals. The concentrations of CA and CBZ were determined at their maximum absorption wavelength of 227 nm and 280 nm, respectively. The mobile phase was 70% methanol and 30% 20 mM 80 wt% H_3PO_4 at a flow rate of 1.0 mL/min. The amount of pharmaceutical adsorbed per unit mass of the adsorbent was calculated by the mass balance equation:

$$q = \frac{V(C_0 - C_e)}{mM} \tag{1}$$

where q (mmol/g) is the amount adsorbed per gram of adsorbent, C_0 and C_e are the initial and equilibrium concentrations of pharmaceuticals in the solution (mg/L), respectively; m is the mass of the adsorbent used (g); M (mg/mmol) is the molar mass of the adsorbate; and V (L) is the initial volume of the solution.

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