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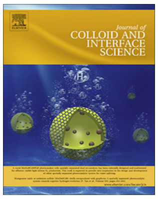

Regular Article

Understanding the adsorption of sulfonamide antibiotics on MIL-53s: Metal dependence of breathing effect and adsorptive performance in aqueous solution

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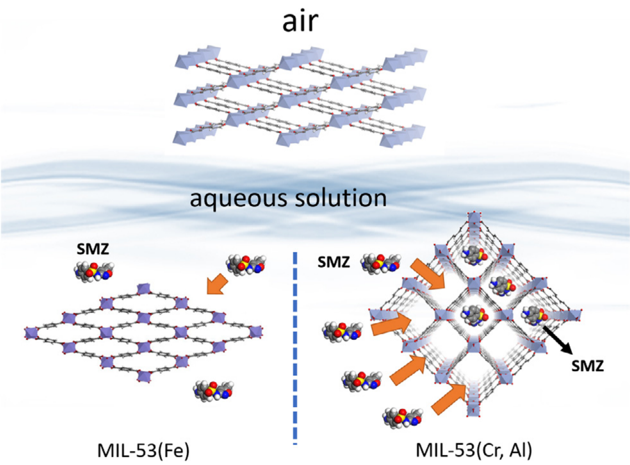
GRAPHICAL ABSTRACT



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ABSTRACT

This investigation is based on experimental data to deeply understand the unusual adsorption behavior of the flexible MIL-53s in aqueous solution. In contrast to the strongly flexible MIL-53(Cr) and MIL-53(Al) with large pore form (*lp*) in water and in their anhydrous state, MIL-53(Fe) exhibits narrow pore form (*np*) or very narrow pore form (*vnp*), indicating that breathing effect depends on the nature of the metal. Sulfamethoxazole (SMZ) adsorption results demonstrated that the maximum adsorption capacities predicted by Langmuir model were 1.85, 1.78 and 0.314 mmol/g for MIL-53(Cr), MIL-53(Al), and MIL-53(Fe), respectively. The adsorption equilibrium was rapidly reached within 60 min and the kinetic data best fitted with the pseudo second order model. The *lp* form of MIL-53(Cr) and MIL-53(Al) in aqueous solution provided the easy entrance for contaminants, lead to lower binding energy and caused modifications of the hydrophobic/hydrophilic character, which all enhanced their adsorption capacities for SMZ. However, the *np* form of MIL-53(Fe) with small inner pores and hydrophilicity compromised its adsorption capacity for SMZ. The experimental results revealed electrostatic interactions, hydrogen bonding, and π-π interaction/stacking contributed to the adsorption of SMZ on MIL-53s as well. In summary, the complexation

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of different metal nodes to MOFs is accompanied by the diversity of properties, which significantly affect their adsorptive performance.

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1. Introduction

Porous Metal-organic frameworks (MOFs), consisting of organic ligands and metal clusters, have received increasing attention since the past few years for their wide range of potential applications [1–4]. Because of their unique characteristics such as superior surface area, high tunability, and versatile functionality, MOFs are regarded as promising materials in gas storage, catalysis, adsorption, sensing and drug delivery [5–15]. An exceptional property of some MOFs depends on their ability to adjust their pore size to accommodate guest molecules [16,17]. The flexibility, also named as "breathing effect", can produce a dramatic decrease or increase in pore size and cell volume without loss of crystallinity. Typical examples are MIL-53 series of MOFs constructed by terephthalate and metal nodes. They have shown outstanding stability, unique breathing effect and tunable pores [18–20]. Several isoreticular MOFs with the same topology and ligand connected by different metal nodes (Al, Cr, Fe, Ga, In, V) have been reported, and different flexible modes have been described, suggesting metal composition is a potential factor influencing the flexibility of MOFs [21,22]. In these studies, the different breathing behavior of MIL-53s significantly affected their performance during the gas adsorption process [23]. The breathing effect may be very different under liquid and gas phase conditions. However, despite lots of applications of MIL-53s for the water purification, the relationship between breathing effect and adsorptive performance of MIL-53s in aqueous solution remains understudied.

The widespread use of antibiotics has caught public attention as their residues can enter into the aquatic ecosystem via wastewater treatment discharges and pose a potential threat to the environment and human health [24]. Sulfonamide antibiotics, used in human medicine and cattle farming, are considered as typical and representative antibiotics. The sulfonamide antibiotics in wastewater have been evaluated as a class of highly studied emerging pollutants in recent years [25–27]. Among them sulfamethoxazole (SMZ) is one of the most commonly used broad-spectrum antibacterial agents, especially for the treatment of urinary tract infections and avian cholera. Due to the high consumption of SMZ and its potential risk, it is highly recommended that SMZ should be eliminated it in wastewater treatment [28–30]. In addition to traditional processes such as coagulation and advanced oxidation, novel adsorbents and catalysts have also been used for the removal of sulfonamides in recent years [31–33]. Adsorption has emerged as an economical and effective method for the removal of SMZ. However, most of the regular adsorbents, e.g., activated carbon, resin and zeolites, are not very effective due to their small, irregular pores [34–36]. Therefore, flexible MIL-53s with tunable pore size provide a possibility for the effective adsorption of SMZ [37]. However, to the best of our knowledge, to date there is no study in sulfamethoxazole removal by MIL-53s.

Therefore, in this work isomorphous MIL-53(Cr), MIL-53(Al), and MIL-53(Fe) were synthesized and used for the adsorption of SMZ. We determined the flexibility of different MIL-53s by combining thermogravimetry analysis-differential scanning calorimetry (TGA-DSC) measurements and powder X-ray diffraction (PXRD) patterns. In that way, the breathing effect of MIL-53s in solution and gas phase was detected respectively. Then the adsorption kinetics, isotherms, and effect of pH were studied in detail. Indeed, different adsorption abilities of MIL-53(Cr), MIL-53(Al), and MIL-53(Fe) have been observed, suggesting that metal nodes play an important role in adsorption. Toward this end, a combination of adsorption results and structural analysis was used to establish a correlation between the adsorptive performance and the breathing effect of the MIL-53s. The study contributes to the understanding of adsorption behaviors of MOFs in aqueous environment and has significant implications for developing MOFs that are effective for wastewater treatment.

2. Materials and methods

2.1. Materials

Dimethylformamide (DMF) and *p*-phthalic acid were purchased from Peking Reagent (China) and Sigma-Aldrich (USA), respectively. $Cr(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $FeCl_3 \cdot 6H_2O$ of analytical grade were offered by Sinopharm (China). Sulfamethoxazole was obtained from Sigma-Aldrich (USA). All solutions were prepared with ultrapure water (resistivity > 18 MΩ) prepared with a Mill-Q system (Milli-pore, Billerica, USA).

2.2. Synthesis of MIL-53s

The isoreticular MIL-53(Cr), MIL-53(Al), and MIL-53(Fe) were synthesized according to a previously reported solvothermal method [38,39]. Briefly, $Cr(NO_3)_3 \cdot 9H_2O$, or $Al(NO_3)_3 \cdot 9H_2O$, or $FeCl_3 \cdot 6H_2O$ was mixed with *p*-phthalic acid and DMF. The resulting suspension was introduced into a Teflon-lined stainless autoclave and heated to 493 K for 72 h. The as-synthesized products were collected by centrifugation and washed thoroughly with DMF and methanol. Finally, all of the MOFs were dried in a vacuum oven at 150 °C for 12 h prior to use.

2.3. Characterization of the MOFs

The functionality of MOFs was studied using Fourier Transform Infrared (FTIR) spectroscopy. The spectra were scanned from 400 to 4000 cm^{-1} using an attenuated total reflectance (ATR) technique on a Thermo Nicolet Nexus 870 FT-IR spectrometer system (Thermo Fisher, USA). The morphology of MIL-53s was studied using Scanning Electron Microscope (SEM) (Zeiss, Germany) operating at 10 kV with magnification of 3000–5000. TGA-DSC was carried out under a N_2 atmosphere on a TGA-DSC 1 STARe instrument (Mettler Toledo, Switzerland) at a heating rate of 5 °C/min. The MOF sample was loaded into an alumina pan (150 μL). The surface area was measured using N_2 adsorption/desorption isotherms on Autosorb-1MP (Quantachrome, USA). The PXRD spectra of MOFs were collected on an X-ray diffractometer (Bruker, Germany), with accelerating voltage and current of 40 kV and 40 mA, respectively (Supplementary Material, X-ray diffraction experiments).

2.4. Adsorption experiments

2.4.1. Adsorption kinetics

The adsorption kinetics of SMZ on MIL-53s were revealed as follows. 5 mg adsorbent was added to 50 mL of target contaminant (20 mg/L) solution with constant magnetic stirrers at 298 K. Then, 1.0 mL of solution sample was collected at predetermined time intervals and filtered to remove the adsorbent by a 0.22 μm filters.