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Adsorption interaction between a metal–organic framework of chromium–benzenedicarboxylates and uranine in aqueous solution

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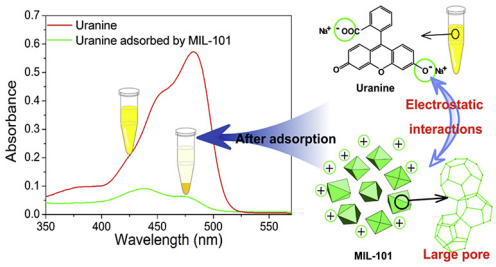
HIGHLIGHTS

- The adsorption interaction between MIL-101 and uranine was studied.
- The adsorption kinetics, mechanism, and thermodynamics were investigated.
- The adsorption mechanism involved the electrostatic interactions and the large pore aperture.
- MIL-101 can be applied to adsorb uranine with good regeneration.

GRAPHICAL ABSTRACT

The adsorption interaction between a metal-organic framework of chromium-benzenedicarboxylates (MIL-101) and uranine in aqueous solution was studied, it showed that MIL-101 can be employed as an effective and reusable adsorbent for removal of uranine from aqueous solution.



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ABSTRACT

Metal-organic frameworks as novel functional materials, have enjoyed extensive exploration, with applications ranging from gas storage to sensing to adsorbents. Here, the adsorption interaction between a metal-organic framework of chromium-benzenedicarboxylates (MIL-101) and uranine in aqueous solution was studied. The influences of various factors on their adsorption interaction were discussed in view of pH value, contact time and initial concentration of uranine, and then the adsorption kinetics and isotherms were investigated. It was found that the adsorption kinetics obeyed the pseudo-second-order kinetic model and the adsorption isotherms followed the Langmuir model. In addition, the zeta potential of MIL-101 decreased obviously after adsorbing uranine and the adsorption capacity of MIL-101 was greater than that of the zeolitic imidazolate framework of $Zn(MeIM)_2$ [MeIM = imidazolate-2-methyl] (ZIF-8), showing the importance of the electrostatic interactions between MIL-101 and uranine as well as the importance of the large pore aperture of MIL-101 for the adsorption interaction, respectively. The results of the adsorption thermodynamics and related parameters including free energy, enthalpy and entropy changes revealed that the adsorption of uranine on MIL-101 was a spontaneous and endothermic process.

1. Introduction

Uranine ($C_{20}H_{10}Na_2O_5$) (the structure is shown in Fig. 1), as a dye material, is mainly applied in detergent, soap, silk, woolen and cosmetic industries. However, it brings some serious problems. As a topical ophthalmic solution, this dye synergizes dermatitis to sensitive skin and causes irritation to eyes [1]. Moreover, the highly colored uranine can change the color of water and highly influence water quality. Therefore, choosing the suitable adsorbent to remove uranine from aqueous solution and studying the adsorption interaction between adsorbent and uranine are of great importance.

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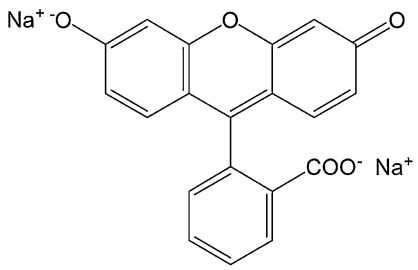


Fig. 1. The structure of uranine.

Up to now, many adsorbents such as activated carbon [2,3] and zeolites [4,5] have been widely investigated for the removal/adsorption of different industrial dyes. Interestingly, industrial and agricultural wastes such as solid wastes [6–8], lemon [9], banana and orange peel [10] have also been used as adsorbents. Additionally, magnetic particles have been dispersed/incorporated in the adsorbent to separate adsorbent from liquid after adsorption [11–13]. In the past three years, metal-organic frameworks (MOFs), as a new kind of adsorbent, have been applied for the adsorption of dye materials [14–22].

MOFs are generally composed of two main components of inorganic vertices (metal ions or clusters) and organic linkers/struts with infinite crystalline lattices [23]. Thanks to their large surface area, tunable pore sizes, high thermal stability, as well as magnetic, electrical, optical, and catalytic properties, MOFs attract considerable attention and show potential applications in gas purification and separation [24–26], chromatogram separation [27], catalysis[28], sensing [29], luminescence [30,31] and so on.

In 2010, Jhung et al. reported the adsorption of dye material on MOFs for the first time [14]. MIL-101 was applied for adsorption removal of methyl orange (MO) [14] and xylenol orange (XO) [15] from aqueous solution due to its giant cell volume, extra-large pore sizes, surface charges and so on [16]. The adsorption mechanism for MO and XO on MIL-101 was considered to be related to the electrostatic interactions [14] and $-SO_3^-$ group of dye [15], respectively. In addition, iron-terephthalate (MOF-235) was investigated to adsorb MO and methylene blue (MB) from aqueous solution [17]. A highly porous MOF of $Fe_3F(H_2O)_2O[C_6H_3(CO_2)_3]_2{\cdot}nH_2O$ [MIL-100(Fe)] was used for adsorption of malachite green (MG) from aqueous solution [18]. However, so far, there are still only a few reports about the dye adsorption on MIL-101, and more work and examples are needed to study the details of adsorption interaction between dye and MIL-101. In this paper, the adsorption interaction between uranine and MIL-101 was investigated (Scheme 1). We studied the factors, adsorption kinetics, thermodynamics and characteristics of the adsorption process.

2. Materials and methods

2.1. Apparatus

A U-3010 spectrophotometer (Tokyo, Japan) was used for recording the absorption spectra. A pH 510 precision pH meter (California, USA) was used to measure the pH values. An S-4800 scanning electron microscope (SEM) (Hitachi, Japan) was used to scan the SEM images. A QL-901 vortex mixer (Haimen, China) was used to mix the solution. A XD-3 X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å) was used to collect powder X-ray diffraction (PXRD) patterns at a scan rate of 2.00 min^{-1} (Purkinje, China). A ZEN3600 laser particle size analyzer (Malvem, Britain) was used to measure the zeta potential of the adsorbent.

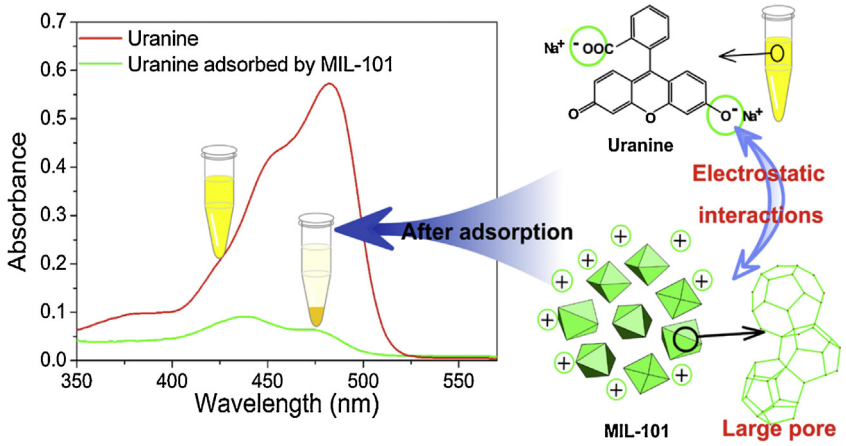
2.2. Chemicals and materials

Chromium(III) nitrate nonahydrate (99%), hydrofluoric acid (HF) (48%) and terephthalic acid (99%) was purchased from Aladdin chemistry Co., Ltd. (Shanghai, China). Uranine (99%) was purchased from China Pharmaceutical Group Shanghai Chemical Co., Ltd. (Shanghai, China). ZIF-8 was purchased from Sigma-Aldrich Co., LLC. (St. Louis, MO, USA). Activated carbon was purchased from Tanggu Binghai Chemical Factory. (Tianjin, China).

The stock solution of 5.0×10^{-3} mol/L uranine was prepared by dissolving uranine with water and then stored in the dark. Milli-Q water (18.2 MΩ at 25 °C) was used throughout the experiment.

2.3. Preparation of MIL-101

MIL-101 was synthesized according to the previous literature [32,33]. Briefly, $Cr(NO_3)_3{\cdot}9H_2O$ (2.00 g, 5.0 mmol), HF (48 wt%, 5.0 mmol), terephthalic acid (0.82 g, 5.0 mmol), and 24 mL of water were added into a hydrothermal bomb and then put it in an autoclave held at 220 °C for 8 h. After the mixture was naturally cooled, the mixture was filtered by using a large pore fritted glass filter to eliminate a significant amount of recrystallized terephthalic acid. Then, the MIL-101 powder was separated from the solution with a small pore filter and washed thoroughly with water and ethanol. After being soaked in ethanol (95% ethanol with 5% water) at 80 °C



Scheme 1. A scheme to illustrate the changes of absorbance and color of the uranine aqueous solution before and after adsorption on MIL-101 (left) and the adsorption mechanism of uranine on MIL-101 (right).