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Investigation of metal organic frameworks for the adsorptive removal of hydrochloride from dilute aqueous solution

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ABSTRACT

In this paper, six kinds of reported water-stable MOFs, MIL-101(Cr), MIL-100(Cr, Fe), UiO-66, MIL-96(Al), and MIL-53(Cr) were evaluated as adsorbents for removal of hydrochloride from dilute aqueous solution. The as-synthesized products were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The results showed that UiO-66 exhibited excellent stability towards hydrochloride and the highest adsorption capacity among the six studied MOFs. Further researches on kinetics, thermodynamics, isotherms of adsorption process of hydrochloride on UiO-66 and its stability towards acid were investigated in detail. Moreover, a simple method was developed to free hydrochloride and recycle UiO-66 for repeated adsorption process, which showed UiO-66 may work as a good adsorbent for removal of hydrochloride from dilute aqueous solution.

1. Introduction

Vast amounts of spent dilute hydrochloric acid are generated in chemical, pharmaceutical, and iron and steel industries every year [1]. Spent dilute hydrochloride is a major concern due to its highly corrosive and polluting nature. With an urgent need to dispose dilute hydrochloride for economic and ecological benefits, an effective method is intensively pursued in industries and academia.

Several methods are suggested for separating hydrochloride from wastewater, including roasting, extraction, evaporation, distillation, membrane separation and so on, among which adsorption is a promising way when dilute hydrochloride with concentration less than 5 wt% is involved. Some adsorbents for hydrochloride adsorption have been reported, such as diatomite, activated carbon and zeolite, but disadvantages including low adsorption capacity (usually lower than 20 mg g^{-1}) [2,3] or difficulty in regeneration greatly impede their applications. MOFs are crystalline compounds consisting of metal ions or clusters coordinated to rigid organic molecules to form one-two-, or three-dimensional pore structures [4]. These materials hold very high adsorption capacities, and their porosities are much higher than that of their inorganic counterpart zeolites (up to 90%). High adsorption capacities and easy tunability have crystallized in perspective applications in gas storage, separation and molecular sensing [5–9]. Though gas phase separation using MOFs has been extensively studied and reviewed, studies on liquid phase separation are scarce.

Water adsorption capacities of MOFs are known for substantially exceeding those of traditional porous materials [10,11]. Although notorious instability towards water, good performances of MOFs in dealing with wastewater such as removing drug macromolecule, organic dyes, pharmaceuticals, alcohols, aromatic compounds, heavy metal ions and inorganic ions [12] have been reported. But none of the desirable results in dealing with HCl solutions has been reported. It should be noted that most MOFs are characterized by structural degradation on either immediate or prolonged exposure to moist environments, not to mention in strong acid solutions like HCl solutions [10]. Therefore, the focus of this paper is the adsorptive ability of HCl from water with several MOFs and their stabilities towards strong acid solution.

Herein, six MOFs which have been reported that show high stability in water, even in acid, including MIL-101(Cr), MIL-100(Cr, Fe), MIL-53(Cr), UiO-66, MIL-96(Al) with various surface areas, functions, and pore dimensions were screened for adsorbing HCl from water by experiments. And further researches on kinetics,

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thermodynamics, isotherms of adsorption process of hydrochloride on UiO-66 and its stability towards acid were investigated in detail.

2. Experimental

2.1. Preparation of MOFs

All of the reagents used in this paper are all A.R. Grade, including chromium (Cr, Aladdin, 99.5%), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, Aladdin, 99.99%), iron powder (Fe, J&K scientific Ltd., 99%), chromium (III) nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9H_2O$, Aladdin, 99.95%), Zirconium (IV) chloride ($ZrCl_4$, Macklin, 99.9%), 1,3,5-benzenetricarboxylic acid ($C_9H_6O_6$, TCI, 98.0%), terephthalic acid ($C_8H_6O_4$, TCI, 99.0%), acetic acid glacial (CH_3COOH, Guangfu Ltd., 99.0%), N,N-dimethylformamide (C_3H_7NO, Aladdin, 99.5%), hydrofluoric acid (HF, J&K scientific Ltd., 40 wt%), hydrochloric acid (HCl, Yuanli Ltd., 36–38%), and NaOH (Yuanli Ltd., 0.01 N).

The MOFs were synthesized by hydrothermal synthesis method and activated according to the reported ones [13–18].

2.2. Adsorption experiments

All the experiments were carried out with 50 mL flask. For each experiment, 0.2 g of MOFs was added to 40 mL HCl solutions with different initial concentrations and continuously stirred for 24 h. In the adsorbing stage, about 0.3 mL of solution was sampled for specified intervals up to 24 h and then treated with centrifugation for solid-liquid separation. The HCl concentration was measured by titration method using 0.01 M NaOH solutions.

The amount of HCl adsorbed on MOFs Q_t, was calculated by equation (1)

$$Q_t = \frac{(C_0 - C_t)*V*M*1000}{m} \quad (1)$$

where C_0 and C_t (mol L^{-1}) are the liquid-phase concentrations of HCl at the initial point and sampled time, respectively; V (L) is the volume of HCl solution; M (g mol^{-1}) is the relative molecular mass of HCl; and m (g) is the mass of the adsorbent used.

2.3. Characterization

The crystal form of the MOFs were characterized by SEM (Nanosem 430, America). XRD of the MOFs samples was performed by an X-ray diffractometer (D/MAX-2500, Japan) using Cu K_α radiation. Besides, TGA analysis (TGA/DSC 1 SF/1382, Switzerland) was also introduced to characterize the MOFs.

3. Results and discussion

3.1. HCl adsorption capabilities of MOFs

Six kinds of MOFs: MIL-101(Cr), MIL-100(Cr, Fe), MIL-53(Cr), UiO-66, MIL-96(Al) were chosen from reported high structural stability in aqueous media and acid environments. In order to determine the optimal adsorbent, each of them with the same dosage was investigated for HCl removal. In Fig. 1, UiO-66 presented outstanding adsorption capacity among these six MOFs, which reached as high as 289.81 mg/g. So it was selected as an optimal adsorbent for further study.

3.2. Effect of contact time and adsorption kinetics

Equilibrium time is an important parameters affecting the design of wastewater treatment systems [19]. The effect of adsorption time for HCl with UiO-66 was investigated to determine equilibrium time. The result is shown in Fig. 2, from which we can see that the adsorption capacity increased with time, until the adsorption reached the equilibrium, but no significant increase in adsorption efficiency after the equilibrium time. Because of the competition of water adsorption on UiO-66, the adsorption capacity at the sampled time were larger than that of the equilibrium time. Besides, it is can be seen that the time reaching equilibrium state is less than 4 h with the HCl initial concentration of 0.1–1.0 mol L^{-1} at 298 K.

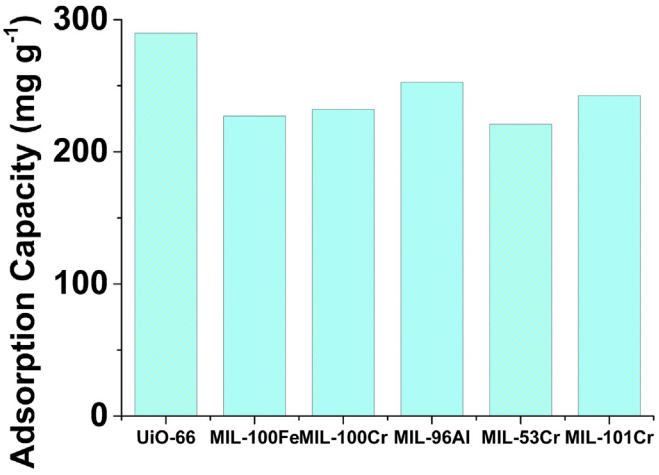

Fig. 1. Adsorption capacities of six MOFs for HCl solutions with 1.0 mol L^{-1} as initial concentration at 298 K

Herein, three kinetics models were applied to study the adsorption kinetics of HCl on the solid surface of UiO-66, which are the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

Pseudo-first-order Model. The pseudo-first-order rate expression based on capacity is generally expressed as follows [20]:

$$\frac{dQ_t}{dt} = k_{1.ad}(Q_e - Q_t) \quad (2)$$

where Q_t (mg g^{-1}) is the amount of HCl adsorbed per unit weight of the adsorbent at time t, while Q_e (mg g^{-1}) is the adsorbance at equilibrium; $k_{1,ad}$ (g mg^{-1} h^{-1}) is the pseudo-first-order rate constant. The linear form of equation (2) can be given as [21].

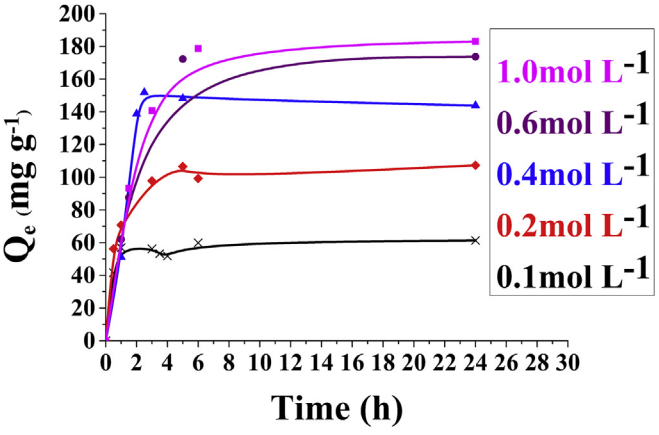

Fig. 2. Effect of contact time on adsorption of HCl on UiO-66.