



# Efficient capture of nitrobenzene from waste water using metal–organic frameworks



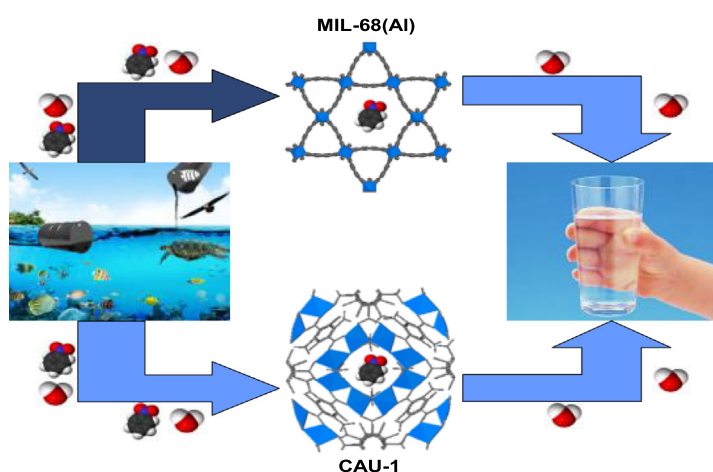
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## HIGHLIGHTS

- This work investigates a series of water-stable MOFs for NB capture.
- Adsorption capacities of CAU-1 and MIL-68(Al) are highest in reported materials.
- The  $\mu_2$ -OH in the Al–O–Al units plays a key role in the adsorption performance.
- CAU-1 and MIL-68(Al) have high stability and good reusability for NB removal.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 18 December 2013  
Received in revised form 18 February 2014  
Accepted 20 February 2014  
Available online 3 March 2014

### Keywords:

Adsorption  
Aluminum-based MOFs  
Environment  
Nitrobenzene  
Regeneration

## ABSTRACT

In this work, a series of metal–organic frameworks (MOFs) are systematically screened for the capture of nitrobenzene (NB) from water for the first time. The results show that the adsorption capacities of two aluminum-based MOFs, CAU-1 and MIL-68(Al), can reach around  $970 \pm 10$  and  $1130 \pm 10$   $\text{mg g}^{-1}$  respectively, which are much higher than the experimental values of other porous materials reported so far. The  $\mu_2$ -OH in Al–O–Al units of Al-MOFs may play a key role in the adsorption process of NB. Langmuir isotherm was found to be suitable for depicting the NB adsorption process on these two MOFs, and the adsorption kinetics appropriately matched the pseudo-second-order model. Moreover, the Weber–Morris intraparticle diffusion model demonstrates that intraparticle diffusion is not the only rate-limiting step, and film diffusion also plays an important role in the adsorption for NB on MOFs. In addition, the regeneration of CAU-1 and MIL-68(Al) could be fully achieved using methanol without secondary pollution. These results indicate that MOFs are promising adsorbents for efficient capture of NB from waste water, and further in-depth investigations deserve to be performed.

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## 1. Introduction

As an important chemical raw material as well as a product of industry, nitrobenzene (NB) has been widely used in the manufacture of dyes, plastic, pesticides, explosives, pharmaceuticals and

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lubricating oil [1]. Due to its high solubility ( $S = 1900 \text{ mg L}^{-1}$  at  $20^\circ\text{C}$ ), large density ( $\rho = 1.2 \text{ g cm}^{-3}$  at  $20^\circ\text{C}$ ) [2] and high toxicity, NB poses a potential threat to ecological and human health [3], and has been listed as one of the 129 priority pollutants by the U.S. Environmental Protection Agency [4]. Consequently, it is highly necessary to seek effective methods for the removal of this injurant. At the moment, the related technologies can be generally divided into two categories: one is the chemical method by destroying the structure of NB molecules, such as oxidation [5] and biodegradation [6], which have limited applications because of the expensive cost and secondary pollution [7]; the other one is the physical method, such as adsorption, which is considered as the relatively more economical and efficient technique owing to its easy operation and the universality of the adsorbents. Recently, many studies have been conducted to examine the adsorption of NB in various porous materials including activated carbon [8–16], zeolite [17–19], lipid adsorption material (LAM) [20], organoclay [21,22], bentonite [23], sediment [4,24], activated sludge [25,26], nanocrystalline hydroxyapatite (HAP) [27], silica aerogel [28], p(4-vinylpyridine) hydrogel [29], and  $\beta$ -cyclodextrins [30]. Nevertheless, the high cost for regeneration, the low adsorption efficiency and poor selectivity make these materials less feasible as excellent adsorbents, especially for the high concentration waste water of NB ( $C > 100 \text{ ppm}$ ) [31]. Therefore, efficient adsorbents are highly needed.

With the development of supramolecular coordination chemistry and combinatorial chemistry, metal–organic frameworks (MOFs) have emerged as a novel class of nanoporous solids, exhibiting remarkable properties compared to other porous materials [32,33]. To date, MOFs have been shown promising applications in a wide range of fields, such as gas storage and separation [34–36], catalysis [37], and drug delivery [38]. Especially, several studies claimed that MOFs have excellent performance in the adsorptive removal of hazardous substances because of their unique characteristics, for instance, the desulphurization and denitrogenation from petroleum [39–42], the removal of organic contaminants from water [43–47], and the separation of aromatic compound systems [48]. However, to the best of our knowledge, the relevant studies on NB capture using MOFs are still very scarce up to now [49] compared to the rich study in adsorption of other organic molecules. Therefore, in this work several water-stable MOFs were selected to investigate their performance for separating NB from its aqueous solutions, aiming to preliminarily screen promising adsorbents as well as evaluate the optimal operational conditions. The obtained results can provide useful information for the use of MOFs in efficient capture of hazardous substances.

## 2. Material and methods

### 2.1. Synthesis of MOFs

In order to meet the industrial demand for the removal of NB from water, it is essential for the MOFs to have the following characteristics: (i) excellent water stability, (ii) pores large enough to accommodate the NB molecule, (iii) large affinity and capacity, (iv) easy preparation with a relatively low cost, and (v) good ability of regeneration. Considering these requirements, we chose thirteen diverse MOFs with different metals, topologies, pore sizes and chemical characteristics, including MIL-53(Al, Fe) [50,51], MIL-100(Cr, Fe) [52,53], MIL-68(Al, In) [54,55], UiO-66(Zr), UiO-66(Zr)(–NH<sub>2</sub>, –NO<sub>2</sub>) [56], ZIFs-7, -8 [57,58], and CAUs-1, -6 [59,60]. These MOFs were synthesized by the hydrothermal method as reported in references, and the details are summarized in [supplementary data](#), with their structural parameters listed in [Table S1 of the supplementary data](#).

### 2.2. Characterization of MOFs

The powder X-ray diffraction pattern (PXRD) of the synthesized MOFs were recorded on a D8 ADVANCE X-ray diffractometer using monochromatic Cu K $\alpha$  radiation under 40 kV and 30 mA with a scan speed of  $5^\circ/\text{min}$ , a step size of  $0.02^\circ$  in  $2\theta$ , and a  $2\theta$  range of  $5\text{--}50^\circ$ . The structural properties of these materials were determined by an Autosorb-IQ-MP surface area analyzer. Approximate 50 mg sample of each MOF was placed in a 9 mm sample cells with large bulb for the measurement of the N<sub>2</sub> adsorption isotherms at 77 K. Prior to adsorption experiments, samples were initially out-gassed at 473 K for 12 h. The Fourier transform infrared (FTIR) spectra of the pure samples and those loaded with guest molecules were performed on Nicolet 6700 FTIR spectrometer. In these measurements, the samples were first grounded into powders with KBr by a proportion of 100 g KBr per gram of the material, and then the spectrum for each of them was recorded in the range of  $400\text{--}4000 \text{ cm}^{-1}$  with a resolution of more than  $0.09 \text{ cm}^{-1}$ .

### 2.3. Adsorption experiments

In order to quickly screen the MOFs with the best adsorption performance for NB, the adsorption measurements were firstly conducted at 303 K. A series of different initial concentrations of NB solution from 100 to 250  $\text{mg L}^{-1}$  were put into 250 mL stoppered conical flask with 25 mg MOF, respectively. After magnetic stirring for 2 h, the slurry was withdrawn and filtrated by using a syringe and a PTFE millipore filtering film with  $0.22 \mu\text{m}$  pore size. Then the residual concentration of NB was determined at  $\lambda = 267.5 \text{ nm}$  with UV–Vis spectrophotometer (TU-1901).

After the preliminary screening of MOFs, batch experiments of the optimal MOFs were performed to investigate the effects of various parameters including the contact time, temperature, pH value, ionic strength, and the initial NB concentration. The effect of contact time on NB adsorption was studied on 300 and 800  $\text{mg L}^{-1}$  NB solution at 303 K. The experiments were carried out by mixing 20 mg MOFs with 100 mL aqueous solution in 100 mL stoppered conical flask. For studying the effect of temperature, 800  $\text{mg L}^{-1}$  NB solution was chosen, and the measurements were performed in a temperature-controlled water bath magnetic stirrer from 303 K to 333 K. Then, the effect of pH value was measured. It should be pointed out that the pH of the NB solution was adjusted with  $0.1 \text{ mol L}^{-1}$  NaOH and  $0.1 \text{ mol L}^{-1}$  HCl solution. The effect of ionic strength was carried out by separately added 5 mL  $1 \text{ mol L}^{-1}$  NaCl, 5 mL  $0.1 \text{ mol L}^{-1}$  NaCl, 5 mL  $0.01 \text{ mol L}^{-1}$  NaCl solution and 5 mL deionized water. The adsorption isotherms were obtained by mixing 20 mg MOFs with 100 mL NB solution of different concentrations from 200  $\text{mg L}^{-1}$  to 1000  $\text{mg L}^{-1}$  at a constant temperature of 303 K, with stirring for 4 h.

The amount of NB adsorbed on the MOFs was calculated using the mass balance with Eq. (1):

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where  $Q_e$  ( $\text{mg g}^{-1}$ ) is the equilibrium adsorbed amount;  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial and equilibrium concentrations of solution;  $V$  (L) is the volume of solution;  $M$  (g) is the mass of MOF. In order to assure the accuracy of measurements, all the experiments were repeated at least three times, and we took the average of the results as the final values to reduce the random error. The relative standard deviation was approximately less than 3%. Moreover, all the materials were dried overnight under vacuum at 423 K before use.

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