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Adsorption and removal of phthalic acid and diethyl phthalate from water with zeolitic imidazolate and metal–organic frameworks

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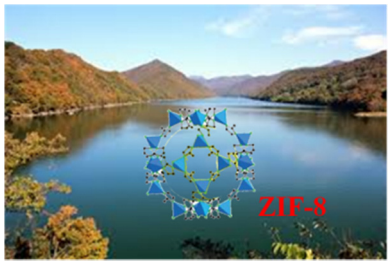
HIGHLIGHTS

- Electrostatic interaction is important for high adsorptions over ZIF-8.
- Acid–base interaction also can contribute to the adsorption of phthalic acid.
- ZIF-8 can be used to remove phthalic acid even though positivity was not high.
- Used ZIF-8 can be recycled for the adsorptions by simple methanol washing.

GRAPHICAL ABSTRACT



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ABSTRACT

ZIF-8 (zinc-methylimidazolate framework-8), one of the zeolitic imidazolate frameworks (ZIFs), has been used for the removal of phthalic acid (H_2-PA) and diethyl phthalate (DEP) from aqueous solutions via adsorption. The adsorption capacity of the ZIF-8 for H_2-PA was much higher than that of a commercial activated carbon or other typical metal–organic frameworks (MOFs). Because the surface area and pore volume of the adsorbents showed no favorable effect on the adsorption of H_2-PA, the remarkable adsorption with ZIF-8 suggests a specific favorable interaction (electrostatic interaction) between the positively charged surface of ZIF-8 and the negatively charged PA anions. In addition, acid–base interactions also have a favorable contribution in the adsorption of H_2-PA, based on the adsorptive performances of pristine and amino-functionalized MOFs and adsorption over ZIF-8 at acidic condition (pH = 3.5). The reusability of ZIF-8 was also demonstrated after simple washing with methanol. On the other hand, ZIF-8 was not effective in adsorbing DEP probably because of little charge of DEP in a water solution.

1. Introduction

Environmental pollution by hazardous organics is one of the most problematic issues worldwide because of its effect on human health and ecological systems [1–9]. Recently, much attention has been given to emerging organic contaminants (EOCs) from both analysis and reduction/elimination standpoints [1–3]. Currently, it is more important to establish efficient methodologies to remove EOCs from surface water and/or waste water because previous studies have focused mostly on the occurrence and fate of EOCs in the environment. Phthalic acid (H_2-PA) and its esters are present in waste water, soil and natural water because of their extensive use in agricultural, industrial and domestic applications [10–13]. Phthalic acid is the source and main degradation product of phthalic acid anhydride and various phthalate esters (dimethyl phthalate, diethyl phthalate, dibutyl phthalate, bis(2-ethylhexyl) phthalate, and so on), and exists as a neutral acid or negatively charged anions ($H\text{-}PA^-$ and PA^{2-}) in solution depending on the pH since the pK_a values of H_2-PA are 2.9 and 5.4 [14]. Moreover, hydrolysis of the phthalate esters in an acidic medium can easily produce

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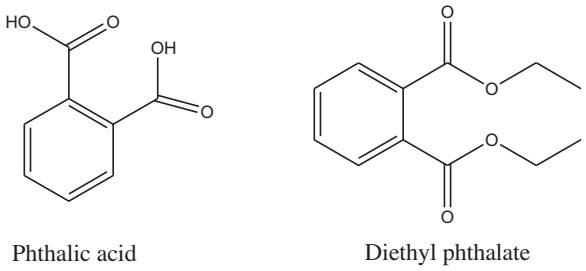
phthalic acid and alcohols. Phthalates have been used mainly as plasticizers in polymer-based industries. Phthalates are also used in ceramics, toys, paper, medical products, synthetic fibers, cosmetics, and inks, and in paint industries. Because of their widespread use, the annual worldwide production of phthalates goes over four million tons [12]. Large amounts of phthalates leach to the environment by industrial discharge in waste water and therefore, are suspected as important environmental pollutants. The concentrations of phthalates in waste water from chemical plants/nearby rivers and plasticizer producing factories was 100 mg/L [15,16]. Because of their large production and extensive distribution, phthalates have been classified as endocrine disruption compounds and as priority pollutants by the European Environment Agency and US Environmental protection agency [12]. Therefore, removal of phthalates and H_2-PA (an intermediate for phthalic anhydride or esters, and hydrolysis product of phthalates) from waste water is very important before discharging to a municipal system or sewage sludge.

So far, a number of methods have been used in the removal of phthalates or H_2-PA [14] from water including bioconversion [17,18] or destruction/biodegradation [16,19–22] by microorganisms and activated sludge, surface complexation at the hematite/water interface [23,24], adsorption [14,25–28] and so on. Due to their high water solubility and consequently high concentrations in industrial waste water, adsorption/separation has been considered as the most competitive method for the removal of phthalates or H_2-PA from waste water. Moreover, adsorptive processes have the general advantages of low cost, simple operation, ambient temperature/pressure for operation, etc. Among the numerous porous adsorbents, activated carbon (AC) [14,26], alumina [28], biochar [25], and polymeric resins [27] have been studied. High porosity/surface area [26], surface functionality [14,28] of adsorbents and adsorbent–adsorbate interactions like hydrogen bonding [25,27] or π–π stacking [27] have been suggested for the efficient adsorption of phthalates and H_2-PA.

Recently, remarkable progress on porous materials has been achieved because of the development of mesoporous materials [29–33] and metal–organic framework materials (MOFs) [34–37]. The importance of MOF-type materials is because of their huge porosity and easy tunability of their pore size and shape from a microporous to mesoporous scale by changing the connectivity of the inorganic moiety and the nature of the organic linkers [34–37]. MIL-101(Cr) [38], MIL-53(Cr) [39], MIL-100(Cr) [40], MIL-100 (Fe) [41] and UiO-66 [42] are some of the well studied MOFs (MIL and UiO stand for Material of Institut Lavoisier and University of Oslo, respectively). Very recently, MOF based adsorbents [43–45] have shown very promising results in liquid phase adsorption/removal of organic pollutants from water [46–52] or liquid fuel [53–59]. Zeolitic imidazolate frameworks (ZIFs) are a class of MOFs that offer similar pore topologies with zeolites and show good chemical and thermal stability [60,61]. Among the numerous ZIFs reported so far, one of the most topical solids is the porous ZIF-8, with the formula of Zn(2-methylimidazole)$_2$ with a sodalite-related zeolitic structure. The ZIF-8 framework composed of narrow six membered-ring pore windows (3.4 Å) and much larger pores (11.4 Å) [62,63] has been used successfully as potential adsorbents for adsorption/separation purposes [61,62,64–68] and as a heterogeneous catalyst in various catalytic reactions [69–73].

Even though the adsorptive removal of H_2-PA and its esters using a few porous solids has been reported, there is no trial using the robust and highly porous MOFs or ZIFs structures in this respect, so far. Herein, for the first time, we report the adsorption of H_2-PA and diethyl phthalate (DEP) (as a model phthalate compound, see Scheme 1) from water on various MOFs (including UiO-66, MIL-101(Cr), MIL-53(Cr), and MIL-100(Cr, Fe)) and ZIF-8 materials. Adsorptions and zeta potentials of ZIF-8 were also investigated at various pHs to suggest a plausible adsorption mechanism over ZIF-8. Kinetic constants for the adsorption of H_2-PA on ZIF-8 and AC adsorbents were also evaluated. Moreover, ZIF-8 could be used several times for the adsorption of H_2-PA, suggesting its potential application in the purification of spent water.



Phthalic acid Diethyl phthalate

Scheme 1. Chemical structures of phthalic acid and diethyl phthalate.

2. Experimental

2.1. Materials

Phthalic acid ($C_8H_6O_4$, 99.5%), diethyl phthalate ($C_{12}H_{14}O_4$, 99.5%) and 2-methylimidazole (99%) were purchased from Sigma Aldrich. Zinc acetate ($Zn(CH_3COOH)_2{\cdot}2H_2O$, 99%), activated carbon (granular, 2–3 mm) and sodium hydroxide (NaOH, 93%) were obtained from Duksan pure chemicals. Methanol (CH_3OH, 99.6%) and hydrochloric acid (HCl, 35%) were purchased from OCI chemicals. All the chemicals used in this study were analytical grade and used without further purification.

2.2. Preparation and characterization of the adsorbents

ZIF-8 was synthesized at room temperature from zinc acetate, 2-methylimidazole and methanol similar to a previously described method [74]. Before syntheses, zinc acetate dihydrate was heated at 110 °C for 6 h to remove the crystallized water of the salt. An exact amount of zinc acetate (178 mg) and 2-methylimidazole (263 mg) was separately dissolved in 20 mL of methanol. Then the two solutions were mixed together, and further stirred for 5 min. After that, the solution was aged for 24 h at room temperature. The precipitated white powders were collected by filtration and washed carefully with methanol and dried overnight. MIL-101(Cr), MIL-53(Cr), MIL-100(Cr, Fe), UiO-66 and NH_2-UiO-66 adsorbents were prepared similar to the reported procedures [38–42].

The phase of the adsorbents was determined with an X-ray diffractometer (D2 Phaser, Bruker, Cu*K*α radiation). The nitrogen adsorption isotherms were obtained at −196 °C with a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation of the adsorbents at 150 °C for 12 h. The surface area was calculated with the BET equation. The zeta potential of the ZIF-8 adsorbent was measured at various pHs with a Zetasizer Nano zs90.

2.3. Adsorption experiments

H_2-PA and DEP solutions with the desired concentrations were prepared with deionized water. The H_2-PA and DEP concentrations were determined with the absorbance (at 280 nm and 275 nm, respectively) of the solutions after obtaining the UV spectra with a spectrophotometer (Shimadzu UV spectrophotometer, UV-1800). Before adsorption, the adsorbents were dried overnight under vacuum at 100 °C, and an exact amount of the adsorbents (5.0 mg) was put in the aqueous H_2-PA or DEP solution (50 mL) having a fixed concentration. The H_2-PA or DEP solution containing the adsorbent was mixed well with magnetic stirring and maintained for a fixed

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