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Adsorptive removal of methylchlorophenoxypropionic acid from water with a metal-organic framework

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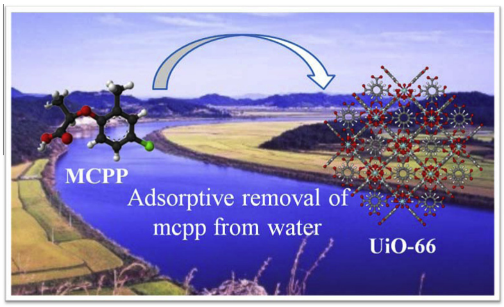
HIGHLIGHTS

- Methylchlorophenoxypropionic acid can be adsorbed effectively over UiO-66.
- The adsorption capacity and rate over UiO-66 are remarkably high.
- The used UiO-66 can be recycled by simple washing with solvents.
- The adsorption mechanism can be explained with electrostatic and π–π interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time, the adsorptive removal of methylchlorophenoxypropionic acid (MCPP) from water, using a metal-organic framework (MOF), namely Zr-benzenedicarboxylate (UiO-66), was investigated to determine the applicability of MOFs in the removal of hazardous herbicides/pesticides from contaminated water. Compared with activated carbon, UiO-66 has a very high adsorption rate (kinetic constant ~30 times that of activated carbon). This rapid adsorption is remarkable because the pore size of UiO-66 is smaller than that of activated carbon. Moreover, the adsorption capacity of UiO-66 is higher than that of activated carbon especially at low MCPP concentrations (~7.5 times at 1 ppm of MCPP). These rapid and high uptakes by UiO-66 suggest that there is a special mechanism for interactions between MCPP and UiO-66. Additionally, the adsorbent can be reused for adsorptive removal by washing the spent adsorbent with a simple solvent. MOFs such as UiO-66 are therefore potential adsorbents for use in the adsorptive removal of MCPP from contaminated water. A plausible adsorption mechanism is suggested based on the effects of pH on the zeta potential of the adsorbent and on adsorption. For the adsorption of MCPP by UiO-66, electrostatic and π–π interactions might both be important.

1. Introduction

Phenoxyacids such as methylchlorophenoxypropionic acid (MCPP or Mecoprop), 2,4-dichlorophenoxyacetic acid (2,4-D), and 2-methyl-4-chlorophenoxyacetic acid are widely used in agriculture, and these acids are some of the most frequently detected herbicides/pesticides in groundwater [1–3]. MCPP is one of phenoxyacids whose structure is shown in Scheme 1, and is a widely used acidic herbicide with high toxicity [1–3]. MCPP is one of the common household weed killers and may be lawn fertilizers based on a “weed-and-feed” process. Because of the toxicities of pesticides/herbicides, the permitted concentrations in drinking water are 0.1 and 0.5 µg/L, respectively, for a single chemical and all materials [1,2]. Therefore, efficient methods for removing MCPP are required for a safe environment. So far, various methods,

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including photocatalytic degradation and advanced oxidation processes, have been used [1,2,4]. The adsorptive removal of MCPP is one of the most attractive methods, if suitable adsorbents are available, because it is a low cost and simple process with mild operating conditions. Several adsorbents such as carbonaceous materials including activated carbons [2] and iron oxides [3] have been studied for the adsorptive removal of MCPP from water. Sorption by sand filters also increases the efficiency of MCPP removal from ground water [1]. However, MCPP is one of the most difficult phenoxyacids to remove using adsorption [2].

Recently, significant progress has been made in nanoporous materials because of new materials [5–13] including metal-organic frameworks (MOFs) [9–13]. MOFs have attracted much attention because of their high and regular porosities. Additionally, MOFs have many potential applications, including adsorption, storage, and separation of organic molecules [9–13]. MOFs have also been studied for adsorptive removal of hazardous materials, including adsorptive desulfurization [14–17] and adsorptive denitrogenation [18–21] processes.

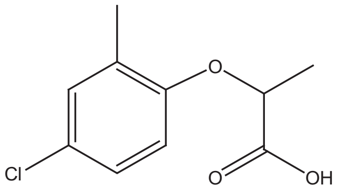
Even though MOFs have been used in the removal of several organics such as dyes [22–25], bisphenol-A [26,27], organic arsenic acids [28,29], and PPCPs (pharmaceuticals and personal care products) [30,31] from water, to the best of our knowledge, there has been no report on the use of MOFs in the adsorptive removal of MCPP from contaminated water. There is only one report [32] on MCPP adsorption over Basolite Z1200 (ZIF-8, a sub-group of MOFs). However, the adsorption was performed from an ethanolic solution rather than an aqueous solution of MCPP, and there is little detailed explanation of the adsorption such as mechanism and adsorption capacity.

In this work, we report the first adsorptive removal of MCPP from water with a MOF to investigate the possibility of using MOFs as adsorbents for the removal of MCPP, one of the typical anionic herbicides/pesticides with high toxicity, from contaminated water. Among the numerous MOFs reported so far, a porous zirconium-benzenedicarboxylate (Zr-BDC) called UiO-66 (UiO stands for University of Oslo) was used for the adsorption. UiO-66, which contains hexanuclear zirconium clusters linked by terephthalates [33], is an interesting material, because of its stability [34] and possible applications in adsorption [27,35,36] and catalysis [37]. Because MCPP and UiO-66 both have benzene rings, UiO-66 might have favorable interactions (such as π–π interactions) with MCPP for adsorptive removal. Moreover, UiO-66 can be synthesized cheaply from terephthalic acid, which is produced in huge amounts for polyesters. A possible adsorption mechanism is also suggested, based on the zeta potential of UiO-66 and adsorptions at various pHs.

2. Experimental

2.1. Materials and adsorption procedure

UiO-66 was prepared solvothermally under conventional electric heating, using reported methods [33,34] with minor modifications. The detailed synthetic procedures have been reported elsewhere [38]. The synthesized UiO-66 was characterized using X-ray diffraction (XRD) and nitrogen adsorption measurements (shown in Supporting Fig. S1); the results for the obtained UiO-66 were similar to reported values [33,34]. Activated carbon (granule, size: 2–3 mm) was purchased from the Duksan Chemical Company. The textural properties of the adsorbents were examined using a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation at 150 °C for 12 h. The BET surface area and pore volumes were calculated using nitrogen adsorption isotherms. The zeta potential of UiO-66 was measured at various pHs, using a Zetasizer Nano zs90 instrument.



Scheme 1. Chemical structure of MCPP.

An aqueous stock solution of MCPP (200 ppm) was prepared by dissolving MCPP (molecular formula: $C_{10}H_{11}ClO_3$, molecular weight: 214.65 g/mol, Sigma Aldrich, PESTANAL®, analytical standard) in deionized water. Aqueous MCPP solutions of concentrations 20–170 ppm were prepared by successive dilution of the stock solution with deionized water. The concentrations of MCPP were determined using the absorbances (at 279 nm) of the solutions after getting the UV spectra of the solutions with a spectrophotometer (Shimadzu UV spectrophotometer, UV-1800). A calibration curve was obtained from the spectra of the standard solutions (2.5–100 ppm) at a pH 4.0.

Before adsorption, the adsorbents were dried overnight under a vacuum at 150 °C, and kept in a desiccator. Exact amounts of adsorbent (2 mg) were added to aqueous solutions (20 mL) with fixed MCPP concentrations of 20–170 ppm. The aqueous MCPP solutions containing the adsorbents were mixed well using a magnetic stirrer for a fixed time (1–24 h) at 25 °C. After adsorption for a pre-determined time, the solution was separated from the adsorbent with a syringe filter (polytetrafluoroethylene, hydrophobic, 0.5 μm), and the MCPP concentration was calculated using the absorbance obtained from the UV spectrum.

To determine the adsorption capacities at various pHs, the pH of the MCPP solution (20 ppm) was adjusted with 0.1 M HCl or 0.1 M NaOH aqueous solution. The adsorption capacities at various pHs were measured at 25 °C after mixing the MCPP solution and the UiO-66 for 12 h. The reusability of the adsorbents was determined after simple washing of the used adsorbents with water and ethanol, filtration, drying, and evacuation. The washing of the used adsorbent was carried out by adding 10 mL of water three times and 20 mL of ethanol three times during filtration of the used adsorbent.

2.2. Analysis of adsorption data

The adsorption data were analyzed using a pseudo-second-order non-linear kinetic model [39], Langmuir isotherms [40], and separation factors [41]. Details of the methods are given in the Supporting information.

3. Results and discussion

3.1. Adsorption rates

Fig. 1 compares the relative performances of several adsorbents, including MOFs and a typical adsorbent (activated carbon), in the adsorption of MCPP (20 ppm in water) for 12 h. UiO-66 and activated carbon showed the highest and second highest uptakes, respectively, of MCPP. It is interesting that MIL-101, with a huge surface area of 3900 m^2/g [42], had negligible adsorption capacity. Moreover, the result for MIL-53(Cr), which showed remarkable result in the adsorptive removal of another phenoxyacid (2,4-D) [43], was also poor. Further work is needed to understand why these two MOFs showed very poor results for MCPP adsorption. In this