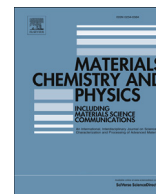




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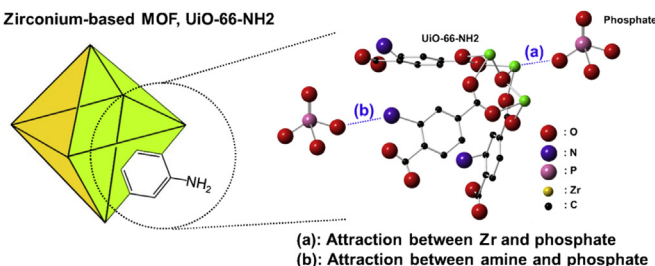
Zirconium-based metal organic frameworks: Highly selective adsorbents for removal of phosphate from water and urine

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HIGHLIGHTS

- UiO-66 as the first type of MOFs was used to remove phosphate from water and urine.
- The amine group in UiO MOFs was found to enhance the phosphate adsorption.
- UiO-66 exhibited a high adsorption selectivity towards phosphate over other anions.
- UiO-66 could be easily regenerated and re-used with 85% regeneration efficiency.

GRAPHICAL ABSTRACT

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ABSTRACT

Phosphate is one of the most concerning compounds in wastewater streams and a main nutrient that causes eutrophication. To eliminate the phosphate pollution, Metal Organic Frameworks (MOFs) are proposed in this study as adsorbents to remove phosphate from water. The zirconium-based MOF, UiO-66, was selected as representative MOF given its exceptional stability in water. To investigate the effect of an amine functional group, UiO-66-NH₂ was also prepared using an amine-substituted ligand. The adsorption kinetics and isotherm reveal that UiO-66-NH₂ exhibited higher adsorption capacities than UiO-66 possibly due to the amine group. However, the interaction between phosphate and zirconium sites of UiO MOFs might be the primary factor accounting for the phosphate adsorption to UiO MOFs. UiO MOFs also exhibited a high selectivity towards phosphate over other anions such as bromate, nitrite and nitrate. Furthermore, UiO MOFs were found to adsorb phosphate and to completely remove diluted phosphate in urine. We also found that UiO MOFs could be easily regenerated and re-used for phosphate adsorption. These findings suggest that UiO MOFs can be effective and selective adsorbents to remove phosphate from water as well as urine.

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1. Introduction

Phosphates are one of the most widely-used chemicals in industries such as fertilizer, detergent, and food and beverage.

Production and consumption of phosphate-containing products inevitably releases a large quantity of phosphates into the environment commonly via municipal and industrial water effluents. Unfortunately, excess phosphate in water can cause rapid growth of aquatic plants and algae, or eutrophication. Eutrophication worsens water quality and disturbs the balance of aquatic ecology. Thus, removal of phosphate from water has been considered an essential process in wastewater treatment.

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Phosphate is typically removed from water using precipitation [1,2], flotation [3], biological [4] and adsorption methods [5–8]. Although each method possesses its own advantage, adsorption appears to be the most employed process owing to its simplicity and relatively low initial cost [9,10]. Therefore, development and evaluation of high-capacity and efficient adsorbents for phosphate has been a research focus in wastewater treatment [11,12].

Recently, “Metal Organic Frameworks (MOFs)”, a new type of organic-inorganic hybrid materials, have been developed. MOFs possess tunable crystalline network structure [13–15], which allows them to be exceptional adsorbents owing to the guest-to-host mechanism [16–20]. MOFs have been intensively studied for gaseous applications such as hydrogen storage and CO₂ capture [18–20]. MOFs have also been evaluated for drug delivery [21], catalysis [22–24] and sensors [25]. Until recently, researchers start to investigate the capability of MOFs as adsorbents in the wastewater treatment. It is found that several types of MOFs are stable in water and exhibit promising adsorption capacities for the removal of pollutants from water such as metal ions [26], toxic dyes [27,28], herbicides [29], oil droplets [30], humic acid [31], phenols [32], halogen ions [33,34], etc. Some MOFs reveal even higher adsorption capacities than conventional adsorbents, like granular activated carbon [30,35–37]. Nevertheless, to our knowledge, few studies have been conducted to investigate the removal of phosphate from water by MOFs via the adsorption and the adsorption mechanism has not been determined. Thus, in this study, we propose to use MOFs to remove phosphate from water and investigate the underlying adsorption mechanism.

Zirconium-based MOFs are selected in particular because of their exceptional stability. Since MOFs can be functionalized by selecting different ligands, the effect of amine functional groups, which have been reported to enhance phosphate adsorption [38], should be investigated. Therefore, two Zr-MOFs, UiO-66 and UiO-66-NH₂, were synthesized with and without amine groups to examine the effect of amine on the phosphate adsorption. UiO-66 and UiO-66-NH₂ denote the Zr-MOFs consisting of terephthalic acid and aminoterephthalic acid, respectively, which were developed at the University of Oslo (Universitetet i Oslo). The as-synthesized UiO-66 and UiO-66-NH₂ were characterized by scanning electronic microscopy (SEM), powder X-ray diffraction (PXRD), FT-IR, thermogravimetric analysis (TGA), diffuse reflectance spectroscopy and X-ray adsorption spectroscopy (XAS). Factors affecting the phosphate adsorption were examined, including solid-to-liquid ratio, mixing time and temperature. Adsorption kinetics and isotherms were determined and competition adsorption between phosphate and other anions was also studied. A potential mechanism for the phosphate adsorption was proposed. Since urine is a major source of phosphates, the removal of phosphate from urine has been an interesting treatment to eliminate phosphate pollution or to recover phosphate [39,40]. Thus, we also studied the removal of phosphate from urine via adsorption using UiO MOFs. To re-use UiO MOFs for phosphate adsorption, recyclability of UiO MOFs was also evaluated.

2. Experimental

2.1. Synthesis and characterization of UiO-66 and UiO-66-NH₂

Fig. 1 illustrates the syntheses of UiO-66 and UiO-66-NH₂ based on reported methods with slight modifications [41,42]. To prepare UiO-66, 4.0 mmol of Zirconium chloride (ZrCl₄) (Acros Organics, USA) and 4.0 mmol of terephthalic acid (H₂BDC) (Acros Organics, USA) were added to 20 ml of N,N-dimethylformide (DMF) (Aencore Chemical, Australia). The resulting mixture was

stirred for 1 h and then poured into a 100-ml Teflon-lined autoclave, which was placed into a temperature-controllable oven at 120 °C for 24 h. The mixture was then cooled to the ambient temperature, and the precipitate was collected and washed thoroughly with DMF and ethanol. Subsequently, the precipitate was dried and activated at 150 °C under reduced pressure for 24 h to obtain UiO-66. Preparation procedure of UiO-66-NH₂ was the same as that of UiO-66 except that H₂BDC was replaced by aminoterephthalic acid (NH₂-H₂BDC). Characterization methods for the as-synthesized UiO MOFs can be found in the supporting information (see ESI).

2.2. Adsorption of phosphate to UiO-66 and UiO-66-NH₂

Adsorption behaviors of phosphate to UiO MOFs were studied using batch-type adsorption experiments. A certain amount of UiO MOFs was added to 0.02 L of phosphate solution with a given initial concentration (C_0). The resulting mixture was then placed in a temperature-controllable orbital shaker at 250 rpm to begin the adsorption. Adsorption capacity (q_t) of UiO MOFs after a mixing time (t) was calculated using the following equation (Eq. (1)):

$$q_t = V(C_0 - C_t)/M \quad (1)$$

where M (g) is the weight of UiO MOFs and V represents the total volume of solution. The adsorption capacity at equilibrium was denoted as q_e (mg g⁻¹). The concentration of phosphate in water was analyzed by an ion chromatography system (Dionex ICS-1100 Basic Integrated IC System, USA) with IonPac AS9-HC column. The mobile phase was 9 mM of sodium carbonate with a flow rate of 1 ml min⁻¹.

In this study, the effect of solid-to-liquid (S/L) ratio was first studied by varying the S/L ratio from 0.1 to 1.0 (g L⁻¹). In addition, the adsorption kinetics of phosphate was determined by mixing 0.01 g of UiO MOFs with a 0.02 L of phosphate solution with $C_0 = 50$ mg L⁻¹ at 20, 40 and 60 °C. The adsorption isotherm, on the other hand, was measured by fixing the amount of UiO MOFs (i.e., 0.01 g) while C_0 was varied from 5 to 100 mg L⁻¹. The adsorption isotherm experiments were performed for 120 min to ensure that the adsorption reached the equilibrium.

2.3. Effect of co-existing ions and adsorption of phosphate from urine

To examine the effect of co-existing anions on the adsorption of phosphate to UiO MOFs, solutions containing equal concentrations of bromate, nitrite, nitrate and phosphate were prepared and the concentration ranged from 30 to 100 mg L⁻¹. Since the removal (or recovery) of phosphate from urine was also examined, fresh synthetic human urine was prepared based on the reported composition [43] which contained 3 g L⁻¹ of urea (Sigma–Aldrich, USA), 2.57 g L⁻¹ of sodium chloride (Showa chemicals, Japan), 2.13 g L⁻¹ of sodium sulfate (Showa chemicals, Japan), 2.98 g L⁻¹ of potassium chloride (Showa chemicals, Japan), 0.81 g L⁻¹ of magnesium chloride hexahydrate (Sigma–Aldrich, USA), 0.04 (or 1.41) g L⁻¹ of sodium monohydrogen phosphate heptahydrate (Sigma–Aldrich, USA) and 0.58 g L⁻¹ of calcium chloride dihydrate (Showa chemicals, Japan).

To represent the diluted and concentrated concentrations of phosphate in urine, we prepared 14 mg L⁻¹ and 500 mg L⁻¹ of phosphate in urine, respectively. Concentrations of nitrate, nitrite and bromate were also determined using the same IC system and column as for phosphate.

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