



# Development of nanoscale zirconium molybdate embedded anion exchange resin for selective removal of phosphate



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## ABSTRACT

Development of a selective adsorbent with an enhanced removal efficiency for phosphate from wastewater is urgently needed. Here, a hybrid adsorbent of nanoscale zirconium molybdate embedded in a macroporous anion exchange resin (ZMAE) is proposed for the selective removal of phosphate. The ZMAE consists of a low agglomeration of zirconium molybdate nanoparticles (ZM NPs) dispersed within the structure of the anion exchange (AE) resin. As major results, the phosphate adsorption capacity of the ZMAE (26.1 mg-P/g) in the presence of excess sulfate (5 mM) is superior to that of the pristine AE resin (1.8 mg-P/g) although their phosphate uptake capacity was similar in the absence of sulfate and these results were supported by the high selectivity coefficient of the ZMAE toward phosphate over sulfate ( $SP_{PO_4/SO_4}$ ) more than 100 times compared to the pristine AE resin. This superior selective performance of the ZMAE for phosphate in the presence of sulfate ions is well explained by the role of the ZM NPs that contributed to 69% of the phosphate capacity which is based on an observation that the phosphate adsorption capacity of the ZM NPs is not affected by the presence of sulfate. In addition, the behavior of the selective phosphate removal by the ZMAE was well demonstrated by not only in the batch mode experiment with simulated Mekong river water and representative wastewater effluent but also in a column test.

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## 1. Introduction

The occurrence of excess phosphate is one of the main sources causing the eutrophication of lakes, rivers, and coastal regions. Eutrophication has become a widespread problem deteriorating water quality which has led to an accumulation of organic matters (plants and algae) and the development of color and odor in water as well (Su et al., 2013; Yang et al., 2014).

Therefore, developing effective technologies for reducing phosphate in wastewater going into river and lake waters has been one of the urgent strategies for controlling the eutrophication problem in recent decades. Among current technologies, adsorption technologies have been an alternative to biological and

chemical precipitation processes due to their simple operation, environmental friendliness, and effective removal of low level phosphate concentrations (Li et al., 2014; Su et al., 2013).

Thus, developing selective adsorbents for improving the efficiency of the adsorption process has become a critical issue. In recent years, organic-inorganic nanocomposites based adsorbent, which consist of inorganic nanoparticles (NPs) and organic support matrix, have been considered as alternative adsorbents due to their selective performance toward target ions. In addition, this approach for hybrid adsorbents is presumed to be one of the solutions for overcoming the inherent problems of NPs, such as poor mechanical/hydraulic properties, clogging the column, and separation difficulty (Pan et al., 2009a, 2014).

For this purpose, various composite adsorbents have been synthesized and examined for phosphate adsorption, which consist of metal oxides NPs (e.g., hydrated ferric oxide and zirconium oxide) dispersed into a porous structure of an organic host (e.g., activated carbon/graphite (Xu et al., 2015; Yao et al., 2013; Zhang et al., 2015), mesoporous silica (Zheng et al., 2016), chitosan

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(Jiang et al., 2013; Liu and Zhang, 2015), zeolites (Guaya et al., 2015; Xie et al., 2015), or functional polymer (Blaney et al., 2007; Pan et al., 2009c; Song et al., 2016; You et al., 2016)). Particularly, ion exchange polymers have been reported as good candidates for a polymer matrix of a hybrid adsorbent due to their Donnan effect resulting from the fixed charges (Cumbal and SenGupta, 2005; Pan et al., 2013).

Despite the limited success of the anion exchange resin as a matrix for the enhancing adsorption capacity and efficiency for phosphate removal (Cumbal and SenGupta, 2005; Du et al., 2013), selective adsorption for phosphate removal remains a challenging issue because the anion exchanger resin in a hybrid adsorbent rapidly loses its adsorption capacity in the presences of excess sulfate ions, which is inevitable in wastewater conditions (Awual and Jyo, 2011; Pan et al., 2009b). Thus, developing a selective adsorbent is urgently required to achieve a high removal efficiency of phosphate from wastewater (Pan et al., 2009b).

Therefore, the aim of this study was to develop a novel molybdate-based nanocomposite adsorbent for selective phosphate removal, which was a hybrid of nanoscale zirconium molybdate and a macroporous anion exchange resin (ZMAE). The performance of the ZMAE was evaluated by adsorption studies in the absence/presence of excessive sulfate (5 mM) compared with that of the pristine AE resin. Furthermore, the ZMAE was used with simulated Mekong river water in batch mode and simulated waste effluent in a fixed-bed column test to test its practical use.

## 2. Experiments and methods

### 2.1. Materials and chemicals

All chemicals including the (pristine) AE resin used in this study were purchased from Sigma-Aldrich (St. Louis, MO, USA). Zirconium molybdate (ZM) NPs, ammonium heptamolybdate tetrahydrate  $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O})$  and zirconium (IV) oxychloride octahydrate  $(\text{ZrOCl}_2\cdot 8\text{H}_2\text{O})$  were used as received. The anion exchange (AE) resin used in this study was a macroporous strong base anion exchange resin with a polystyrene-divinylbenzene matrix (a Dowex™ Marathon™ MSA,  $640 \pm 50 \mu\text{m}$ ). Prior to use, the resin was washed with a hydrochloric acid solution replacing the anionic form with chloride ions and then rinsed with ethanol for 24 h and dried at room temperature.

### 2.2. Synthesis of the ZMAE adsorbent

In this study, the ZMAE was fabricated as follows: To fabricate the ZMAE, 10 g of the AE resin was added to a 100 mL of 0.05 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  solution with shaking for 8 h. This treated AE resin was immersed in a 100 mL of 0.2 M  $\text{ZrOCl}_2$  solution (containing 5% sodium chloride) with shaking for 24 h to precipitate the ZM NPs inside the AE resin. This AE resin containing the ZM NPs was washed with deionized water and ethanol. Finally, the ZMAE was obtained after drying at 50–55 °C.

The ZMAE was compared with the zirconium oxide embedded AE resin (ZAE) for the purpose of examining the potential role of Mo component in the ZMAE for the phosphate adsorption. The ZAE only containing zirconium oxide instead of zirconium molybdate was synthesized, following the method reported in the previous studies (Padungthong et al., 2015; Pan et al., 2013), which was similar with the synthetic procedure for the ZMAE. The only difference was that the hydrated zirconium oxide was precipitated with a 5% NaOH solution instead of the  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  solution.

### 2.3. Analytical methods

The phosphate concentration was analyzed with the molybdenum blue method using a UV–Vis spectrometer (8453 E UV/Vis, Agilent, USA) (Murphy and Riley, 1962; Tsang et al., 2007). Low concentrations of phosphate, below 0.05 mg/L, were analyzed with an ICP analyzer (ICP-MS, Varian 820-MS, Varian, Australia). The contents of Zr and Mo loaded in the hybrid adsorbents (ZMAE and ZAE) were determined with ICP-AES after digesting with mixed acids (HCl,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$ ).

The morphology and surface characteristics of the ZMAE were analyzed with a scanning electron microscope (SEM, JSM-6700F, Jeol, Japan), high resolution transmission electron microscope (HR-TEM, JEM 3010, Jeol, Japan), high resolution X-ray diffractometer (XRD, D8 Discover, Bruker, Germany), Fourier Transform Infrared Spectroscopy (FT-IR 200, Jasco, Japan), and X-ray photoelectron spectroscopy (XPS, Sigma Probe, ThermoVG, U.K.). The specific surface area and pore volume of the ZMAE adsorbent were measured with a BET analyzer (ASAP, 2000; Micromeritics, USA). The  $\text{pH}_{\text{pzc}}$  (point of zero charge) of the ZMAE was determined by the drift method (Fan et al., 2011).

### 2.4. Batch adsorption experiments

Phosphate adsorption isotherm experiments with the ZMAE (0.5 g/L) were carried out in the batch mode with a shaking glass bottle (100 mL) containing 50 mL of a phosphate solution (5–50 mg/L of  $\text{P-PO}_4$ ) at an initial pH of 5.5 (without adjusting during adsorption) for 24 h and compared with the ZAE and the pristine AE resin. All batch mode experiments were conducted in a shaker at a constant temperature (25 °C).

These experiments were conducted in the absence and presence of excess sulfate ions (5 mM). In addition, a kinetic study with ZMAE (0.5 g/L) in the absence and presence of high sulfate (5 mM) was performed in phosphate solution (10 mg/L of  $\text{P-PO}_4$  (0.31 mM), 200 mL) and compared with the pristine AE resin. At the pre-determined time, 0.5–2 mL of this solution were withdrawn to measure the phosphate concentration.

Regeneration of the ZMAE was successively examined with adsorption-desorption experiments of phosphate ion. For adsorption step, the experiments with the ZMAE (50 mg/50 mL) were carried out in the batch mode containing 10 mg/L  $\text{P-PO}_4$  with shaking (200 rpm) at pH of 5.5 for 24 h. The desorption step was performed in the condition of 0.1 M NaOH (5 mL) for 2 h at 200 rpm shaking. The adsorption and desorption efficiencies were calculated as follows:

$$\text{PO}_4 \text{ adsorbed}(\%) = \frac{[\text{PO}_4]_{\text{removed}}}{[\text{PO}_4]_{\text{initial}}} \times 100$$

$$\text{PO}_4 \text{ desorbed}(\%) = \frac{[\text{PO}_4]_{\text{desorbed}}}{[\text{PO}_4]_{\text{removed}}} \times 100$$

### 2.5. Determination of the selectivity coefficient of ZMAE

The selectivity of the ZMAE (0.5 g/L) for phosphate ions over sulfate ions was measured in mixed solutions of equal concentrations of phosphate and sulfate ions for three different conditions (0.25, 0.75, and 2.0 mM) at pH 5 for 24 h (equilibrium condition) and compared with that of the pristine AE resin.

The selectivity coefficient ( $S_{\text{PO}_4/\text{SO}_4}$ ) for either the ZMAE or the pristine AE resin was defined as the ratio of the distribution coefficients of the two respective ions between solution and

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