



## Selective removal of phosphate in waters using a novel of cation adsorbent: Zirconium phosphate (ZrP) behavior and mechanism



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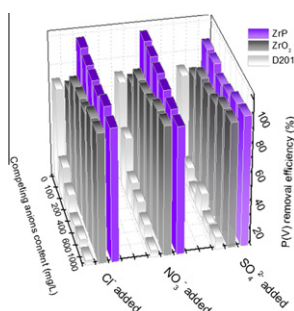
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### HIGHLIGHTS

- ▶ ZrP known as cation exchanger exhibits selective sorption towards  $P(V)$  anion.
- ▶  $P(V)$  uptake shows slight influences with other anions ( $SO_4^{2-}/NO_3^-/Cl^-$ ) at high levels.
- ▶ The exhausted ZrP were readily to efficient regeneration by 5% NaOH solution.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Control of excessive phosphates is a crucial environmental issue, resulting in eutrophication of water bodies. Among the available technology, adsorption stands out as the most attractive treatment option. Amorphous zirconium phosphate (ZrP), is generally acknowledged to be cation exchanger, little is known the sorption behaviors toward anionic pollutants. In the present study, ZrP was fabricated and the enhanced sorption properties towards anion-phosphate were explored. The uptake of phosphate onto ZrP was examined and common used anion-exchange resin (D201) and zirconium dioxide particles were introduced for references with coexistence of common anions ( $SO_4^{2-}$ ,  $NO_3^-$  and  $Cl^-$  ions), the results indicated that both ZrP and  $ZrO_2$  exhibited more favorable sorption performances than D-201, which might ascribed to the information of inner-sphere complex. FT-IR spectrum measurement validated that the immobilization of phosphate mainly driven through Zr–O bonds and phosphate complexation, while the sulfate, nitrate and chloride uptake onto ZrP might be attributed to the electrostatic interaction. XPS investigation further proved the strongly specific affinity between ZrP and phosphate over other common anions with larger binding energy shifts. Moreover, the fast sorption kinetic equilibrium was also observed and the data could be well described by the pseudo-first-order model. The used ZrP particles were readily to efficient regeneration by sodium hydroxide solution for repeated use at least five cycles. All the results suggest that ZrP is a promising adsorbent for enhanced sequestration of phosphates in waters.

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## 1. Introduction

Water pollution by phosphorus remains an important environmental issue associated seriously with eutrophication of water bodies due to the presence of excess amount of phosphate [1]. Up to now, various technologies including chemical precipitation [2], adsorption [3], biological treatment [4,5] are proposed to circumvent the serious problem, among the available methods, adsorption is technologically simple economical, enables efficient removal of even traces of phosphate ions and recognized as one of the most promising processes.

In the past decade, more and more inorganic materials, namely, metal oxides/hydroxides (containing  $ZrO_2$ ,  $Fe_2O_3$ ,  $CeO_2$ , etc.) were exploited as highly efficient adsorbents for phosphates or inorganic pollutants removal in waters [3,6–17]. For instance, mesoporous Zr-oxides and hydroxides were fabricated and their phosphate removal potentials were investigated in wastewater and seawater [7,9], Fe/Al/Mn/Ce/Nb oxides were also found to exhibit preferable sorption towards phosphate ions [18–20] and Fe–Zr and Mn–Zr binary oxides were also demonstrated as efficient hybrid adsorbents for trace phosphate retention [8,12]. Such satisfactory performance was mainly ascribed to the strongly sorption interactions between phosphate and metal oxides adsorbents, which has been studied extensively by researchers.

However, as a family of inorganic adsorbents, little is known about another important catalog by combining group IVB phosphate, i.e. Zr/Ti/Hf phosphates, and zirconium phosphate (abbreviated ZrP with structure presented in Fig. S1) as the most representative one has been extensively studied for catalytic reaction due to its solid acid properties [21]. As for the sorption performance, Clearfield and Alberti have investigated the ion-exchange behaviors toward Na(I), K(I), Li(I), etc. [22,23]. Besides, ZrP exhibits large sorption capacity, fast kinetics, extremely insoluble in acids and bases and environment-friendly. Unfortunately, most of relevant studies about ZrP mainly focus on the sorption mechanism and performances towards alkaline or alkaline earth metals [22,24,25]. In our previous study [26], amorphous zirconium phosphate was proved to be an efficient sorbent towards heavy metals with coexistence of common cations (K(I)/Na(I)/Ca(II)/Mg(II)) at high levels and growing researches were carried out on toxic metal decontamination for environmental propose [27,28]. Most researchers believe that ZrP is a typical cation exchanger, whereas the sorption behaviors and mechanism for anion-phosphate are not well concerned.

It is well recognized that zirconium exhibits highly sorption affinities towards phosphates. Thus, it is expected that ZrP could also present preferential sorption towards phosphates, therefore, the objection of the study is to attempt to reveal the sorption performance and mechanism of phosphate onto ZrP by a series of structure characterization and batch sorption runs. D-201, a widely used macroreticular polystyrene anion exchange resin and zirconium dioxide particles for phosphate removal were also employed as reference sorbents. Fourier-transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis were also performed to preliminarily elucidate its underlying sorption mechanism.

## 2. Materials and methods

### 2.1. Materials

All chemicals are of analytical grade from Tianjin Reagent Station (Tianjin, China), orthophosphate solution (1000 mg/L) is prepared by dissolving  $KH_2PO_4$  into the deionized water. D-201, a macroreticular polystyrene anion exchange resin (in Cl-type) with

total capacity of 3.20 meq/g was purchased from Zhengguang Resin Co. Ltd. (Zhejiang Province, China). It was obtained in spherical beads with particle size ranging from 0.6 to 1.0 mm. Prior to use, D-201 was subjected to flushing sequenced with 1% HCl, 1% NaOH and the deionized water to remove the residue impurities until neutral pH (6.8–7.2) and then vacuum desiccated at 343 K for 24 h until reaching the constant weight.

### 2.2. Fabrication of zirconium phosphate

ZrP particles are prepared by modification of the reference's methods [25,29,30]. In brief, 15 g  $ZrOCl_2$  was dissolved into 100-mL 2 M HCl solution at the ambient temperature. Then the above solution was gradually doped into a flask containing 350 ml 5 M  $H_3PO_4$  and the white precipitation (ZrP particles) was formed immediately as follows:



The white precipitation of ZrP particles was stirred for 24 h at 150 rpm 273 K and centrifuged to decant the aqueous portion. The obtained solid particles were subjected to washing by deionized water till pH = 4–5 and then the activation process were performed by immersing ZrP particles into 1% (w/w) NaOH for 24 h activation. Finally the activated ZrP particles were rinsed by deionized water till the neutral pH and vacuum desiccated at 323 K for 24 h for further study.

### 2.3. Batch sorption experiments

Batch sorption tests were carried out by traditional bottle-point methods, and the detailed experimental methods were performed by competing sorption, solution pH effects on adsorption, kinetic experiments, sorption isotherm tests, dose experiments and sorption-regeneration cycles.

#### 2.3.1. Competing sorption

To start the experiments, 0.05 g adsorbents (ZrP,  $ZrO_2$  and D201) were added into 50-ml solution containing known contents phosphate solution and  $SO_4^{2-}/NO_3^-/Cl^-$  were also introduced as coexistence ions. The bottles were then transferred into a G-25 model incubator shaker with thermostat and shaken under 200 rpm for 20 h, and then the solution was filtered and tested phosphate concentrations.

#### 2.3.2. Kinetic experiments

Sorption kinetics was determined by sampling 0.5 mL-solution at various times and the initial solution volume was 1000 mL containing a known concentration of phosphates and 0.5 g ZrP adsorbents, Kinetic data were calculated by detecting the sample contents at various times.

#### 2.3.3. Effects of solution pH

In this section, 0.025 g ZrP particles were introduced into glass bottles containing 50 ml phosphate solution with different pH values (1–14) and  $HNO_3$  (1%), NaOH (1%) solutions were used to adjust the solution pH throughout the experiments. The bottles were then transferred into incubator shaker at desired temperature for 20 h to ensure to reach sorption equilibrium. Finally, the solutions were subjected to filtering and the equilibrium solution pH and concentration were determined.

#### 2.3.4. Sorption-regeneration cycles

To evaluate the sorption stabilities, 0.5 g ZrP particles were subjected to running adsorption-desorption tests for 5 cycles and 5% NaOH solution was used as regenerant to strip of phosphate from

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