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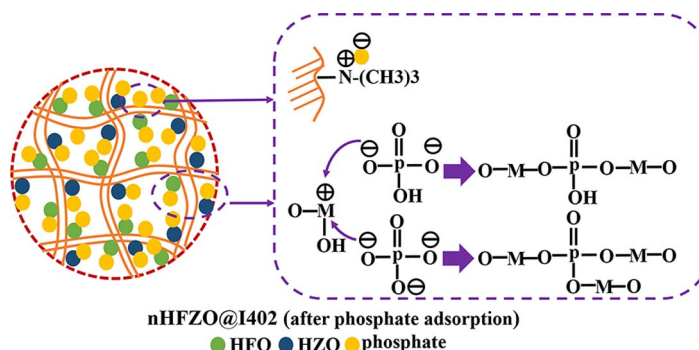
## Enhanced phosphate removal using nanostructured hydrated ferric-zirconium binary oxide confined in a polymeric anion exchanger

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## HIGHLIGHTS

- Nano hydrated Fe–Zr binary oxide was simply loaded into polymeric anion exchanger.
- High phosphate removal efficiency was achieved by nHFZO@I402 over a wide pH range.
- nHFZO@I402 showed specific affinity to phosphate regardless of coexisting anions.
- Selective sorption mechanism was probed and discussed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Phosphate removal is an important measure required to control eutrophication of water bodies as it inhibits excessive algal growth. Currently available phosphate removal methods have various limitations and function poorly under wide pH ranges. This study successfully prepared and characterized a novel nanocomposite adsorbent, nHFZO@I402, which has high capacity and specific affinity towards phosphate. The nHFZO@I402 constituted of nanostructured hydrated ferric oxide and hydrated zirconium oxide loaded on the surface and inside the pores of a polymeric anion exchanger. Batch experiments were conducted to investigate the effects of varied conditions on phosphate adsorption. The results demonstrated that nHFZO@I402 achieved high phosphate removal efficiencies over a wide pH range (4–11), which indicates higher adaptability towards varying environmental conditions. In addition, nHFZO@I402 exhibited enhanced phosphate adsorption capacity regardless of coexisting anions (chloride, nitrate, sulfate, and carbonate) at different concentrations. Kinetic analysis suggested that the adsorption process best-fitted with the pseudo-second-order kinetic model, suggesting chemical sorption mechanism. Furthermore, the underlying mechanism of phosphate adsorption by nHFZO@I402 was assessed through XPS analysis. Phosphate removal was effected by the replacement of hydroxyl groups by phosphate species and interaction between ammonium groups and phosphate. In general, these results indicated that nHFZO@I402 is a highly efficient adsorbent for phosphate removal with excellent adaptability to varying and undesirable environmental conditions.

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## 1. Introduction

Excessive release of phosphate compounds has contributed adversely to eutrophication in many lakes and surface waters globally. High levels of phosphate (above 0.02 mg P/L) can interrupt the nutritive balance and accelerate undesirable eutrophication. Therefore, efficient removal of phosphate from wastewater is essential to control eutrophication before the wastewater is discharged into receiving waterways. Numerous technologies including biological process, chemical precipitation, electrochemical process, and adsorption have been proposed to capture excess phosphate from contaminated waters [1–3]. However, these processes have various limitations, which restrict their effectiveness in meeting increasingly stringent regulations. For example, the phosphate removal efficiency of biological process is highly variable due to the difficulty in maintaining ideal anaerobic or aerobic states [4]. Currently, adsorption is considered as an adequate and attractive technique due to its stable uptake of phosphate from wastewater and desirable low residual concentration.

Recently, different kinds of adsorbents have been developed for removing phosphate, such as fly ash [5], red mud [6], blast furnace slag [7], activated carbon [8,9], and others [10,11]. However, they have some limitations. Some adsorbents recorded optimum adsorption performance under acidic conditions [12], while municipal wastewater is generally neutral in pH [13]. Thus, external chemicals have to be added to increase the acidity to facilitate better adsorption efficiency of the adsorbents. Moreover, wastewater pH has to be restored back to neutral to meet the emission standards after adsorption, which significantly increases the operation costs. Additionally, anions such as chloride, nitrate, sulfate, and carbonate coexist with phosphate in the wastewater and are likely to hinder phosphate uptake through competitive adsorption [14]. Therefore, a novel adsorbent that offers superior adsorption capacity and high selectivity for phosphate under a wide pH range needs to be developed.

Multiple researches have been conducted to improve phosphate adsorption performance through proper modifications on the adsorbents. For example, various metal hydroxides have been applied to different adsorbents to improve their adsorption efficiency [15,16]. Among these metal hydroxides, hydrated ferric oxide (HFO) and hydrated zirconium oxide (HZO) are low-cost and environmentally friendly substances, demonstrating chemical stability over a wide pH range. Moreover, HFO and HZO particles are rich in hydroxyl groups and exhibit preferable phosphate capture through specific adsorption by Lewis acid-base interactions [17–20]. Additionally, anion exchangers are better alternatives compared to other activated carbon materials for metal oxides immobilization [21]. The ammonium groups present in the anion exchanger host enhance the capture of phosphate through electrostatic interaction. These features indicate that an anion exchanger modified by HFO and HZO can serve as an efficient phosphate adsorbent.

In this study, a novel nanocomposite adsorbent, nHFZO@IRA402, was developed by immobilizing HFO and HZO nanoparticles on an IRA402 anion exchanger. The basic morphology and physicochemical properties of the adsorbent were characterized and effects of pH, adsorbent dosage, and coexisting anions were examined. Additionally, the underlying phosphate adsorption mechanism was investigated under varying environmental conditions to assess the roles of HFO and HZO on the phosphate removal.

## 2. Materials and methods

### 2.1. Materials

All chemicals utilized in this study were reagent grade and did not require further purification. Zirconium oxychloride ( $ZrOCl_2 \cdot 8H_2O$ ), metals basis, 99.9%) and anhydrous iron (III) chloride were acquired from Shanghai Macklin Biochemical Co. Ltd., China and Sinopharm

Chemical Reagent Co. Ltd., China, respectively. Phosphate stock solution containing 100 mg P/L orthophosphate was prepared by dissolving  $NaH_2PO_4$  (Aladdin Biochemical Technology Co. Ltd., Shanghai, China) in de-ionized (DI) water. IRA402, a strongly basic anion exchanger of chloride type and styrene/divinylbenzene copolymer matrix, was acquired from Aladdin Biochemical Technology Co. Ltd., Shanghai, China. The IRA402 exchanger was in the form of spherical beads ranging from 0.6 mm to 0.8 mm in diameter with rich ammonium groups covalently binding the matrix, which can exert Donnan membrane effect on ionic species. Prior to use, the IRA402 was washed five times with DI to remove possible residue impurities and dried in a vacuum oven at 323 K for 24 h.

### 2.2. Preparation of adsorbent

Separate solutions of ferric chloride (0.1 M) and zirconium (0.1 M) were prepared in hydrochloric acid (0.1 M). Equal volumes of the solutions were mixed together. Subsequently, 30 g of the preprocessed IRA402 was added to 200 mL of the mixed solution and was subject to mechanical stirring (0.5 h, 300 rpm). Next, Fe (III) and Zr (IV)-loaded IRA402 beads were introduced into sodium hydroxide (1.0 M) and continuously stirred till the pH reached 8.0, when hydrated iron oxide (HFO) and hydrated zirconium oxide (HZO) were precipitated on the surface of IRA402. Finally, the resultant HFO and HZO-loaded IRA402 beads (nHFZO@IRA402) were filtered, washed with deoxygenated water, and dried in vacuum (323 K, 24 h) for subsequent use.

### 2.3. Adsorbent characterization

#### 2.3.1. Transmission electron microscope (TEM)

The morphology of HFO and HZO nanoparticles dispersed on the surface and inside the pores of nHFZO@IRA402 was observed using TEM. TEM images were recorded using a Tecnai G2 F20 S-Twin (FEI Co., USA) instrument operated at 200 kV and resolution of 0.24 nm. The diameters of the nanoparticles and structural parameters of the nHFZO@IRA402 samples were measured using Nano Measurer 1.2 software. Elemental composition was analyzed using energy-dispersive X-ray spectroscopy (EDS) and an X-Max 80T detector (Oxford Instruments Ltd., UK).

#### 2.3.2. X-ray diffraction (XRD)

XRD patterns were generated using D8 ADVANCE powder diffractometer (Bruker AXS Inc., Germany) employing  $Cu K\alpha$  radiation (40 kV, 40 mA) at wavelength of 0.154 nm to identify the crystalline components of nHFZO@IRA402. All XRD patterns were obtained over  $2\theta$  range of  $10^\circ$ – $90^\circ$  with scan speed of  $0.2^\circ/\text{min}$ . The resulting diffractograms were analyzed using MDI Jade 6.0 software.

#### 2.3.3. Fourier transform infrared spectroscopy (FT-IR)

FT-IR (Nicolet 5700 FTIR Spectrometer) was used to qualify the chemical bonds between the functional groups of nHFZO@IRA402. The samples were subjected to wave numbers in the range of  $500$ – $4000\text{ cm}^{-1}$  at a resolution of  $4\text{ cm}^{-1}$ .

#### 2.3.4. X-ray photoelectron spectroscopy (XPS)

XPS characterizations were executed using Kratos AXIS 165 electron spectrometer equipped with an Al  $K\alpha$  X-ray monochromator. High-resolution measurements in oxygen 1s, ferrum 2p, zirconium 3d, and phosphorus 2p regions were conducted at pass energy of 200 eV. XPS peak 4.0 was used for fitting XPS spectral peaks.

### 2.4. Batch adsorption experiments under varied operation conditions

Batch-wise experiments for phosphate were carried out to examine the adsorption behavior of phosphate on nHFZO@IRA402. Firstly, pH-dependent adsorption behaviors in the pH range of 3–11 were studied

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