Facile synthesis of hydrous zirconia-impregnated chitosan beads as a filter medium for efficient removal of phosphate from water

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Research Article

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Abstract

The removal and recovery of phosphate from water using adsorption technology require that the adsorbent material is easily separable from treated water. Continuous efforts are still awaited to develop additional efficient phosphate adsorbents that are economical to fabricate. In this study, hydrous zirconia-impregnated chitosan beads (HZCB) containing different Zr/chitosan ratios were synthesized using a facile scheme. We found that HZCB with a Zr/amine molar ratio of ~ 1 (HZCB-1) possessed excellent stability and phosphate removal performance. This optimized material was characterized with XRD, SEM, FTIR, XPS, specific surface area and point of zero charge measurements. The maximum adsorption capacity was 42.02 mg/g (at pH ~ 6.7). The adsorption kinetics were best described by a pseudosecond-order model, and the rate constant of HZCB-1 was much lower than that of its powder but was similar to the commercial bead product Ferrolox. The removal of phosphate depended substantially upon pH and was enhanced by lowering the pH. Good selectivity of HZCB-1 for phosphate was observed, although the coexistence of sulfate produced a significant negative effect. Direct coordination of phosphate to Zr atoms by replacing hydroxyls was the dominant adsorption mechanism (~ 85%), while chitosan also contributed to phosphate removal (~ 15%). Adsorbed phosphate was successfully eluted by an NaOH solution, and the material obtained after desorption and regeneration was able to be repeatedly used. The results of column studies indicated that this material could be implemented in long-term application.

1. Introduction

Reductions in phosphorus concentrations in lakes and reservoirs have been regarded as a vital management measure to improve water quality and to restore healthy ecosystems by impeding the overgrowth of algae (Cooke et al., 2005; Lürling and Oosterhout, 2013; Schindler et al., 2016). Therefore, phosphorus must be removed from wastewater as much as possible before its discharge into the environment.

In addition, not only the removal of phosphorus from wastewater but also the recovery of removed phosphorus as a resource is widely recognized to be essential due to the scarcity and irreplaceability of phosphorus mines on land (Cordell et al., 2009, 2011). However, the use of traditional phosphorus removal technologies, i.e., chemical precipitation and biological methods, is either difficult or too costly to achieve sufficiently low phosphorus concentrations that will protect water bodies from eutrophication (Wu et al., 2020). In addition, because the removed phosphorus precipitates into sludge, phosphorus recovery is also difficult using these two technologies (De-Bashan and Bashan, 2004). On the other hand, adsorption technology might potentially achieve the dual effects of the removal and recovery of phosphorus from wastewater (Bacelo et al., 2020; Huang et al., 2019; Loganathan et al., 2014). However, the separation of the adsorbent from treated wastewater after adsorption must be easy to achieve these goals such that the desorption and recovery of adsorbed phosphorus, as well as the repeated use of the adsorbent are viable.
Adsorbents in their powder form, which is the major form of developed adsorbents, are not readily separable after being mixed with wastewater. As a result, adsorbents with high hydraulic conductivity that could be used in fixed-bed columns for flow-through applications have attracted increasing attention from researchers in recent years. For instance, Zr-containing materials have become popular phosphate adsorbents in the last two decades due to their excellent affinity for phosphate, although Fe-, Al-, Ca-, and Mg-based adsorbents have been investigated and practically applied for many years (Johir et al., 2016; Lin et al., 2018; Salehi and Hosseinifard, 2020; Shang et al., 2018). For practical applications, two types of Zr-containing adsorbents that may be packed in columns, including Zr-loaded ion exchange resins (Acelas et al., 2015; Awual et al., 2014, 2011; Biswas et al., 2008; Bui et al., 2021, 2018; Zhou et al., 2018; Zhu and Jyo, 2005) and Zr-containing hydrogel beads (Huang et al., 2019; Kumar and Viswanathan, 2017; Liu and Zhang, 2015; Luo et al., 2019; Shan et al., 2019; Wan et al., 2017; Zhang et al., 2021), have been developed.

Both anion (Acelas et al., 2015; Bui et al., 2021, 2018; Zhou et al., 2018) and cation exchange resin (Awual et al., 2014, 2011; Biswas et al., 2008; Zhu and Jyo, 2005) have been used to load zirconium on an ion exchange resin. However, ion exchange resins are mainly derived from petroleum-based raw materials, and they are thus already expensive commercial products, which may render the produced phosphate adsorbents less cost-effective.

An alternative to obtaining Zr-containing adsorbents with high hydraulic conductivity is the production of Zr-containing hydrogel beads using a polymer, preferably a biopolymer (Huang et al., 2019; Kumar and Viswanathan, 2017; Liu and Zhang, 2015; Luo et al., 2019; Shan et al., 2019; Wan et al., 2017; Zhang et al., 2021). Natural polysaccharides, such as chitosan (Liu and Zhang, 2015; Wan et al., 2017) and alginate (Huang et al., 2019; Kumar and Viswanathan, 2017; Luo et al., 2019; Shan et al., 2019; Zhang et al., 2021), have been shown to be successful. Polysaccharides are low-cost materials obtained from abundant natural resources and are environmentally friendly. However, because of the low mechanical strength and poor stability of biopolymers under acidic and/or alkaline conditions, a cross-linking process is generally employed to further modify the beads (Crini, 2005; Guibal, 2004; Wu et al., 2010). Additionally, an insoluble filling substance such as carbon materials (Crini, 2005; Jung et al., 2016) or aluminosilicate minerals (Jang and Lee, 2019; Xu et al., 2020) is usually added to produce composite beads with improved mechanical properties and stability. Notably, the use of multiple steps/materials may cause the preparation process to be complex, costly and less environmentally friendly. Furthermore, cross-linking by bonding with reactive functional groups such as amino and hydroxyl groups may decrease the adsorption performance of the obtained beads (Crini, 2005; Guibal, 2004; Wu et al., 2010).

Therefore, although Zr adsorbents with easy separability from water have been extensively investigated and encouraging results have been reported in recent years, each method has both merits and drawbacks. Continuous efforts from researchers are still awaited to investigate additional satisfactory adsorbent materials.
The aims of our present study were: i) to fabricate a novel hydrogel bead material composed of only hydrous zirconia and chitosan (HZCB) using a recipe free of both crosslinker and filling substances; ii) to investigate the performance of HZCB for phosphate removal by performing experiments of adsorption isotherms, the adsorption kinetics, the effect of pH, the effect of coexisting ions, the desorption and reusability of HZCB and the continuous adsorption in column systems. In addition, the phosphate adsorption mechanism by the HZCB was also studied.

2. Materials And Methods

2.1 Materials

Chitosan with a deacetylation degree of ≥ 95% and zirconium oxychloride octahydrate of analytical grade with a purity of > 99% were purchased from Aladdin Biochemical Technology Co., Ltd., Shanghai, China. All other reagents of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

HZCBs were prepared as described below. First, 200 ml of a 0.1 M ZrOCl₂ solution were obtained by dissolving ZrOCl₂•8H₂O in deionized (DI) water. Second, 3 g of chitosan were added to this ZrOCl₂ solution with magnetic stirring for 4 h. Third, this mixture solution was added dropwise into 400 ml of a 1 M NaOH solution with stirring at a dropping rate of 1 ml/min through a syringe pump and a needle with a nozzle diameter of ~ 2 mm. After all the mixed solutions were added, the formed hydrogel particles in NaOH solution were aged for 24 h and filtered through filter paper. The particles were subsequently rinsed with DI water three times and were finally dried at 45°C in an oven for 24 h to obtain dried beads. The ratio of the number of zirconium atoms to the number of amines in chitosan was ~ 1 (this product was thus denoted as HZCB-1), assuming that the number of amine groups (−NH₂) in chitosan was 6.21 mmol/g (Wu et al., 2010).

HZCBs with Zr concentrations of 0.025, 0.05, 0.075, and 0.2 M were also synthesized using the same method. Based on the ratio of the number of zirconium atoms to the number of amines in chitosan, the products were denoted as HZCB-0.25, HZCB-0.5, HZCB-0.75 and HZCB-2, respectively. In addition, HZCBs with Zr concentration of 0.05 M were prepared, but the pH of the mixed solution was adjusted to 2.0 and 1.0 via the addition of concentrated HCl. Therefore, seven HZCBs were obtained. An aliquot of the beads was crushed and ground to pass through an 80-mesh sieve to obtain powders for phosphate adsorption experiments to better understand the adsorption behaviour.

For comparison, hydrous zirconia without the addition of chitosan and chitosan without the addition of ZrOCl₂ were also obtained. The former was obtained in powder form using the same procedure described above, while the procedure was modified slightly to obtain chitosan beads, i.e., 6 g of chitosan were dissolved in 200 ml of 5% acetic acid instead of DI water. Finally, a commercial filtering material for phosphate removal from water/wastewater, Ferrolox®, was purchased from Kehaisi Scientific Technology Co., LTD., Beijing, China, to better understand the performance of HZCBs developed in this
study. Ferrolox is a granulated Fe(OH)$_3$ product manufactured by the German Water Treatment Solutions Co., LTD. and was reported to have good phosphate removal performance.

2.2 Physical properties of the synthesized products

Except for the measurements of the mass and diameter, all other experiments were performed in triplicate.

1) Mass and diameter of the hydrogel particles and HZCBs

The mass of wet hydrogel particles (the precursor of HZCBs) was measured after placing 100 granules of particles onto filter paper to carefully remove the surface water. These wet particles were then dried at 45°C for 24 h in an oven and weighed again to obtain the mass of HZCBs. Furthermore, the HZCBs were dried at 105°C for 24 h in an oven and then weighed again. The water content of HZCBs and their precursors was calculated as follows:

$$\alpha = \frac{m_0 - m_1}{m_0} \times 100\%$$

where $m_0$ is the mass of either HZCBs or wet hydrogel particles and $m_1$ is the mass of beads dried at 105°C.

The diameter of HZCBs and their precursors was measured using Vernier callipers with an accuracy of 0.01 mm.

The average value was calculated and reported.

2) Skeletal density

The skeletal density of HZCBs was measured with a pycnometer by weighing the sample ($w_1$), the pycnometer filled with DI water ($w_2$), and the pycnometer in which the sample was added and then filled with DI water ($w_3$). The density was calculated as follows:

$$\rho = \frac{w_1}{w_1 + w_2 - w_3} \times \rho_{water}$$

where $\rho_{water}$ is the density of DI water at the temperature measured during the experiments.

3) Stability under acidic conditions

HZCBs were formed in NaOH solution and thus were stable under alkaline conditions. Approximately 30 mg of HZCBs were weighed and placed in 50 ml centrifuge tubes to examine their stability under acidic conditions. Then, 40 ml of DI water were added, and the pH was adjusted to 4.0 and 6.0. After being shaken at 25°C at 120 rpm for 120 h, the content of the tube was filtered through a 20 mesh (pore size ~ 1 mm) gauze to remove DI water and any powder dissociated from HZCBs. The beads on the gauze were dried and weighed to calculate the percentage loss of mass.

2.3 Characterization of the materials
The surface morphology of the material was observed using a field emission scanning electron microscope (SEM, Sirion 200, FEI, USA). XPS spectra were obtained using an X-ray photoelectron spectrophotometer with monochromatic Al Kα X-ray radiation (AXIS Ultra DLD, Shimazu/Kratos, Japan). The FTIR spectra were determined using a Fourier transform infrared spectrometer (Nicolet 6700, Thermo Fisher Scientific, USA) with the KBr method. A D8 ADVANCE X-ray diffraction metre (BRUKER-AXS Company, Germany) was used to measure the crystalline structure of the materials under the conditions of 40 kV and 40 mA (Cu(II)-Kα filtered radiation) within the 2θ range of 5°–80°. The point of zero charge (pH_{PZC}) was determined using the pH drift method (Chen et al., 2022). The specific surface area and pore volume were measured using nitrogen adsorption-desorption experiments with the BET method (ASAP 2010 M+C, Micromeritics Inc., USA).

2.4 Batch adsorption experiments

The phosphate adsorption experiments were performed in batch mode. Phosphate stock solution (1.0 g/L) was prepared by dissolving 0.4390 g of KH$_2$PO$_4$ in 100 mL of DI water, and working solutions were prepared by dilution with DI water. All batch experiments were performed in triplicate, and the results are reported as elemental P concentrations.

Approximately 30 mg of material were accurately weighed and placed in 150 ml Erlenmeyer flasks. After adding 40 ml of phosphate solution at a concentration of 25 mg/L, the flasks were shaken in a temperature-controlled chamber at 25°C at 120 rpm for 96 h, which was confirmed to enable the establishment of adsorption equilibrium. Then, the water was filtered through a 0.45 µm membrane, and the phosphate concentration in the filtrate was quantified using the molybdenum blue colorimetric method (Chinese Environmental Protection Administration, 2002) with a UV-7504 spectrophotometer (Jingke Co., Ltd, China). The amount of adsorbed P at equilibrium ($q_e$) was calculated as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

where V is the volume of the solution (L), $C_0$ and $C_e$ are the concentrations of phosphate before and after adsorption (mg/L), respectively, and m is the dry mass of materials (g).

The adsorption isotherms were measured using phosphate solutions with initial concentrations ranging from 0-150 mg/L. The equilibrium pH was ~ 6.7. The adsorption kinetics were determined as a function of contact time ranging from 5 min to 120 h. The effect of pH on phosphate adsorption was examined by adjusting the pH of the adsorption system to different values with the addition of 0.1 M NaOH or HCl solutions. The equilibrium pH varied within the range of ~ 3 to ~ 10. The effect of competitive anions on phosphate adsorption was tested by performing experiments with phosphate solutions prepared using solutions of sodium chloride, sodium nitrate and sodium sulfate instead of DI water. Three concentrations of the competing ions, i.e., 100, 200 and 300 mg/L, were adopted. The desorbability of adsorbed phosphate was investigated using different concentrations of NaOH (0.05-2.0 M) as the
desorption reagent. The reusability of the materials was evaluated by desorbing the adsorbed phosphate with 0.5 M NaOH, which was shown to be a successful desorption solution, followed by regeneration of the adsorbent by neutralizing the pH of the adsorbent/water system to ~ 6.7 with the addition of a 0.1 M HCl solution. The time of both adsorption and desorption was 48 h. Adsorption-desorption-regeneration experiments were conducted for six cycles.

The commonly used Langmuir model and Freundlich model, which are provided below, were used to fit the isotherm data:

\[
q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}
\]

\[
q_e = K_F C_e^{1/n}
\]

where \(Q_m\) (mg/g) and \(K_L\) (L/mg) are the maximum adsorption capacity at the monolayer coverage and a constant representing the affinity for adsorption sites, respectively, while \(K_F\) ((mg/g)/(mg/L)^{1/n}) and \(n\) are constants related to adsorption strength and adsorption density, respectively.

In addition, four commonly used kinetic models, which are described below, were adopted to fit the adsorption kinetics data:

Pseudofirst-order model:

\[
\log \left( q_e - q_t \right) = \log q_e - \frac{k_1}{2.303} \times t
\]

Pseudosecond-order model:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

Elovich model:

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) - \frac{1}{\beta} \ln(t)
\]

Intraparticle diffusion model:
\[ q_t = \frac{k_1 t}{2} + C_i \]

where \( q_t \) is the adsorption amount of phosphate (mg/g) at time \( t \) (min), \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/(mg·min)) are the rate constants for the pseudofirst-order and pseudosecond-order models, respectively, \( \alpha \) and \( k_{id} \) are the initial adsorption rate (mg/g min) and the intraparticle diffusion rate constant, respectively, while \( \beta \) and \( C_i \) are constants specific to the two models, respectively.

### 2.5 Column experiments

Twenty grams of the HZCB-1 granules were added to each of the two plexiglass columns (length: 150 mm; inner diameter: 20 mm). The granules were packed below and above 10 mm thick quartz sand whose diameter was \( \sim \) 2 mm. Two columns were prepared to investigate the effect of pH on phosphate removal. Synthetic phosphate-containing wastewater with a phosphate concentration of 10 mg/L was prepared using tap water. The pH of this solution was adjusted to 5.0 and 7.0, and the pH-adjusted synthetic wastewater continuously flowed upwards at a volumetric flow rate of 1.0 ml/min using a syringe pump. The influents and effluents were collected at a specified time for the analysis of the phosphate concentration. The experiments were conducted during the period from April 21, 2021, to July 24, 2021, until the removal efficiency of phosphate decreased to less than 10%, which was presumed to be the limit of adsorption.

### 3. Results And Discussion

#### 3.1 Synthesis of HZCBs

In the process used to synthesize HZCBs, chitosan and zirconium salt were first dissolved in DI water and mixed well, generating a final pH ranging from 0.96 to 5.66 depending on the concentration of Zr (Table 1). Dissolution of zirconium salt generated hydrogen ions, while protonation of chitosan consumed hydrogen ions; hence, a higher Zr concentration caused a lower pH either before or after adding chitosan (Table 1). When the Zr concentration was equal to or less than 0.05 M, a colloidal solution formed due to the partial hydrolysis of zirconium, forming hydrous zirconium oxide (Fig. S1). On the other hand, a clear solution formed when the Zr concentration exceeded 0.075 M. The mixed solution underwent gelation by increasing the solution pH, i.e., by dropping it into an NaOH solution. Spherical hydrogel particles were formed when the Zr concentration exceeded 0.075 M (Fig. 1). However, spherical particles with a tail were generated at a Zr concentration of 0.05 M (Fig. 1). At the lowest Zr concentration of 0.025 M, a turbid NaOH solution was produced, although spherical hydrogel particles were generated, showing that part of the hydrolysed zirconium species was not incorporated into the particles. The size of the hydrogel particles increased with increasing Zr concentration. Upon drying the hydrogel particles, massive volumetric shrinkage occurred, leading to the formation of densely packed solid beads. In general, a larger, heavier and thus denser bead was produced at a higher Zr concentration (Table 1). The hydrogel particles contained 90.4–95.7% water, while the water content of HZCBs was 5.6–13.0%. In
addition, the white-coloured hydrogel particles turned into brown-coloured solid beads upon drying (Fig. 1).

| Item                        | Zr concentration (M) |
|-----------------------------|----------------------|
|                             | 0.025  | 0.05   | 0.075  | 0.1    | 0.2    | 0.05   | 0.05   |
| pH of the Zr solution       | 1.69   | 1.38   | 1.3    | 1.12   | 0.87   | 1.38   | 1.38   |
| pH of the mixed solution    | 5.66   | 4.02   | 2.12   | 1.66   | 0.96   | ~ 2.0  | ~ 1.0  |
| Diameter of hydrogel (mm)   | 3.46 ± 0.09 | N.D. a) | 3.22 ± 0.05 | 3.09 ± 0.04 | 3.06 ± 0.03 | N.D.   | N.D.   |
| Diameter of HZCB (mm)       | 0.85 ± 0.11 | N.D.   | 1.02 ± 0.03 | 1.05 ± 0.02 | 1.14 ± 0.02 | N.D.   | N.D.   |
| Mass of HZCB (mg)           | 0.822  | 1.178  | 1.080  | 1.314  | 1.931  | 0.994  | 0.998  |
| Density of HZCB (g/cm³)     | 1.58   | 1.78   | 1.95   | 2.08   | 2.30   | 1.80   | 1.82   |
| Mass loss at pH 6.0 (%)     | 0.1 ± 0.8 | 0.3 ± 0.6 | 0.1 ± 0.7 | 0.2 ± 0.2 | 0.1 ± 0.7 | 0.1 ± 1.6 | 0.6 ± 1.3 |
| Mass loss at pH 4.0 (%)     | 70.2 ± 5.3 | 82.5 ± 5.1 | 68.5 ± 2.6 | 1.5 ± 1.4 | 2.3 ± 1.6 | 74.3 ± 2.8 | 66.4 ± 1.1 |

a) Not determined due to the nonspherical shape.

The gelation of mixed solutions induced by increasing the pH to an alkaline level was presumed to be primarily due to the deprotonation of positively charged amine groups on chitosan, which led to the disappearance of electrostatic repulsion among chitosan molecules. On the other hand, the strong inter- and intramolecular hydrogen bonding between hydroxyl groups enabled the chitosan molecule to self-assemble, producing entangled or crosslinked polymeric networks that contribute to hydrogel formation (Crini, 2005; Guibal, 2004; Wu et al., 2010). In addition, the free electron doublet on nitrogen of deprotonated amine groups binds transition metal cations through chelation mechanisms (Crini, 2005; Wu et al., 2010). Both intramolecular chelation and intermolecular chelation with different configurations are possible, with one transition metal ion being bound by up to four amine groups (Wu et al., 2010). Zirconium is a typical transition metal with abundant vacant orbitals and might thus chelate to amine groups. However, under alkaline conditions, zirconium undergoes hydrolysis, and the hydrolysed monomers even further react to form polymers through a polycondensation process (Wang et al, 2016). With abundant hydroxyl groups on both hydrolysed Zr species and chitosan molecules, extensive hydrogen bonding between these molecules was expected, which might further consolidate the three-
dimensional network. The interactions in the gelled hydrogel particles and HZCBs are schematically shown in Fig. S2. Therefore, both chitosan and Zr were important for the establishment of stable beads.

However, although a further increase in Zr concentration to 0.3 M successfully resulted in the formation of spherical beads, the mixed solution containing a Zr concentration of 0.35 M did not solidify in NaOH solution to form hydrogel particles due to the low polymerization and entanglement rate arising from a low concentration of chitosan molecules. Therefore, the maximum ratio of the number of zirconium to the number of amines in chitosan to produce hybrid beads was ~3.

### 3.2 Stability and phosphate removal performance

Amine groups in HZCBs were protonated under acidic conditions, and protonation was thus detrimental to the stability of beads. Because chitosan had a pKa of 6.3, approximately half of the amine groups would be protonated at pH 6.0, while complete protonation would occur at pH 4.0. Although all the beads were stable at pH 6.0 with a mass loss lower than 1%, only HZCB-1 and HZCB-2 remained stable at pH 4.0, and massive destruction was observed for the other beads. This result clearly showed that the addition of Zr at a sufficiently high concentration enhanced the mechanical properties of the gel. Indeed, HZCB-1 was shown to be stable even at pH 3.0, as described later in Section 3.5.

The phosphate adsorption performance of HZCBs and their powders was determined, and the results are shown in Fig. 2. All HZCBs had a high adsorption capacity except HZCB-2, although it incorporated the highest Zr concentration. In addition, the difference in adsorption between the bead and its powder was closely related to the Zr concentration; the lower the Zr concentration was, the smaller the difference. This finding might be explained by the fact that the use of a low Zr concentration produced a bead with a low density, and this loosely organized 3D structure facilitated the diffusion of phosphate into the internal adsorption sites. HZCB-2 had the highest density due to the formation of a closely packed structure and thus the worst adsorption performance. Similarly, beads with an excessively high level of crosslinking have a low swelling capacity and a reduced accessibility of adsorption sites (Crini, 2005). In fact, the powder of HZCB-2 also had the lowest adsorption capacity, indicating that the small particles in powder form still had a limited ability for diffusion of phosphate and perhaps a finer powder would be needed to realize its adsorption potential.

The use of Zr exerted dual effects, providing not only a Zr source but also acidic conditions that enabled the protonation and dissolution of chitosan. The pH of the mixed solution with a Zr concentration of 0.05 M was artificially adjusted to ~2.0 and ~1.0 (approximately equal to the pH when the Zr concentration was 0.075 and 0.2 M, respectively) to further clarify the importance of each effect. Under these pH conditions, the mixed solution was clear, and ellipsoid hydrogel particles were formed without any tailing. However, the stability and the adsorption performance for phosphate were not improved to a substantial degree (Fig. 2, Table 1), showing that the supply of a Zr source using the Zr salt played the major role.

Considering the success of bead formation, its stability and its adsorption performance, the HZCB-1 beads would be the best choice as the adsorbent, and only this product was selected for further
characterization and adsorption studies.

3.3 Characterization

SEM images of HZCB-1 showed that this material had a spherical shape, but the surface was uneven and had irregular cracks (Fig. 3a, b). The XRD patterns of chitosan (the raw material), hydrous zirconia prepared without the addition of chitosan and HZCB-1 are presented in Fig. 3 (c), showing that both chitosan and hydrous zirconia have distinct peaks that reflect their crystalline structures. The characteristic peak at $2\theta = 20^\circ$ for chitosan is typical of the “tendon” allomorphic crystalline form of chitosan (Guibal, 2004). For hydrous zirconia, two strong peaks at $2\theta = 31.7^\circ$ and $45.5^\circ$ and four minor peaks at $2\theta = 27.3^\circ$, $56.6^\circ$, $66.3^\circ$ and $75.4^\circ$ were observed. However, only two weak and broad peaks emerged at the location where the strongest peaks for chitosan ($2\theta = 20^\circ$) and hydrous zirconia ($2\theta = 31.7^\circ$) were observed for HZCB-1, indicating that both chitosan and hydrous zirconia in HZCB-1 existed as amorphous phases. The dissolution under acidic conditions destroyed the crystallinity of the raw chitosan polymer, which was not restored by the subsequent gelling and drying processes. Meanwhile, the tight bonding of hydrous zirconia with chitosan also resulted in its poor crystallinity.

The FTIR spectra of the materials are presented in Fig. 3(d). Three peaks at 3370, 1624 and 1340 cm$^{-1}$ were detected for hydrous zirconia. The strong band at $\sim 3370^{-1}$ was assigned to the stretching vibration of O-H bonds arising from water molecules and hydroxyl groups, and the band at $1624^{-1}$ was attributed to water molecules, while the band at $1340^{-1}$ was due to the presence of hydroxyl groups. The occurrence of these peaks agreed well with previous studies (Cho et al., 2016; Johir et al., 2016) and was not surprising since hydrous zirconia contained abundant hydroxyl groups and water molecules on its surface. All these peaks also appeared on chitosan, which possessed hydroxyl groups and whose surface was hydrophilic. In addition, a number of other peaks occurred in the spectrum of chitosan, which were assigned to the functional groups of C–H, –NH$_2$, –NH, C = O, and C–O–C (Cho et al., 2016; Díaz-Flores et al., 2021; Liu and Zhang, 2015; Wan et al., 2017). The XPS survey scan (Fig. 3 (e)) showed that HZCB-1 had peaks from chitosan (the peaks of C1s and N1s), peaks from hydrous zirconia (the peaks of Zr 3s, Zr 3p and Zr 3d) and peaks from both chitosan and hydrous zirconia (the peaks of O1s and O2s), suggesting the formation of a three-dimensional network composed of chitosan and hydrous zirconia. The specific surface area and the BJH pore volume of HZCB-1 were measured to be 1.33 m$^2$/g and 0.001 ml/g, respectively. The low surface area of HZCB-1 without any pores was apparently due to the substantial shrinkage of hydrogel particles upon drying in air, leading to a densely packed solid product with no porous structure, although SEM images showed some cracks on the HZCB-1 surface.

The results of pH$_{pzc}$ determination are displayed in Fig. 3(f). Because the addition of a material to DI water whose pH was lower than pH$_{pzc}$ would increase the pH ($\Delta$pH $> 0$) and vice versa, the initial pH (pH$_i$) at which no pH change occurred ($\Delta$pH = pH$_f$ – pH$_i$ = 0) due to the addition of the material was regarded as the pH$_{pzc}$ (Chen et al., 2022). Accordingly, the pH$_{pzc}$ of HZCB-1 was estimated to be 8.1, indicating that
HZCB-1 would be positively charged within a wide pH range (i.e., pH ≤ 8.1), enabling the effective adsorption of phosphate.

3.4 Adsorption kinetics

The adsorption of phosphate on HZCB-1, the powder of HZCB-1 and Ferrolox was investigated as a function of adsorption time within the range of 0–120 h, and the results are presented in Fig. 4. The adsorption evidently proceeded rapidly at the initial stage for each material, but then the increase in adsorption slowed and finally plateaued. The rapid adsorption rate at the initial stage might be ascribed to the high concentration gradient of phosphate between water and the adsorbent surface and to the large number of available adsorption sites on the adsorbent surface. However, as the concentration gradient of phosphate and the number of unoccupied adsorption sites decreased, the adsorption rate decreased, and adsorption equilibrium was attained when all adsorption sites were saturated with phosphate. In our present study, the time required to reach adsorption equilibrium was judged by a statistical analysis, i.e., the adsorption process was regarded as terminated when no statistically significant increase in the amount of adsorption occurred at a longer adsorption time (Duncan's multiple range tests, \( p > 0.05 \)). The results indicated that the HZCB-1 powder established adsorption equilibrium within 36 h, while 96 h was needed for the two granulated materials to complete the adsorption process. Therefore, the adsorption rate of HZCB-1 developed in our laboratory was similar to the commercial product of Ferrolox. The lower adsorption rate of the two granulated materials suggested that their large particle size caused steric hindrance and restricted the diffusion of phosphate to approach the interior adsorption sites.

However, the final amount of phosphate adsorbed by HZCB-1 and its powder product was approximately the same, signifying that the adsorption sites in HZCB-1 had accessibility as good as that of its powder. This result apparently contradicted the low surface area and lack of porosity of HZCB-1 caused by the collapse of the structure of the hydrogel particle and the formation of a densely compacted three-dimensional network, as mentioned in the previous section. However, dried polysaccharide-based hybrid beads generally swell when placed in water again (Crini, 2005; Guibal, 2004; Wu et al., 2010). In this case, the specific BET surface area and porosity of HZCB-1 determined in nitrogen gas after drying at 150°C in this study did not reflect the real reactive areas in solution. We observed that the diameter of HZCB-1 was expanded by 15% on average (from 1.05 mm to 1.21 mm) after swelling in water, and thus, the volume of the beads should increase by 53% (from 0.6 mm\(^3\) to 0.93 mm\(^3\)), creating a much porous structure for phosphate adsorption after the dried beads were immersed in water. As a result, although the kinetics on beads were slower than those on powders, the final amount of phosphate that was adsorbed at equilibrium was essentially the same.

The kinetic data were fitted to four commonly used adsorption kinetic models to better analyse the phosphate adsorption process. The fitting results are listed in Table S1, in which the correlation coefficient \( R^2 \) showed that the pseudosecond-order model described the behaviour of adsorption kinetics best, but the Elovich and intraparticle diffusion models also fit the data reasonably well, while the
pseudofirst-order model had the worst fitting results. Good fitting to the pseudosecond-order model may indicate that phosphate adsorption on the materials was essentially dominated by a chemisorption step that controlled the overall adsorption rate (Chen et al., 2022; Díaz-Flores et al., 2021; Luo et al., 2019; Salehi and Hosseinifard, 2020; Shan et al., 2019). From the rate constants of $K_2$ of the pseudosecond-order model and $\alpha$ of the Elovich model, the HZCB-1 powder clearly had a distinctly higher adsorption rate, while the adsorption rates of the two granulated products were rather similar. However, the rate constant of the intraparticle diffusion model did not differ substantially for different materials. Based on these results, the HZCB-1 powder that was crushed to pass through an 80-mesh sieve and thus had a diameter smaller than 0.18 mm was still composed of grain particles whose phosphate adsorption was also governed by intraparticle diffusion process after the fast film diffusion process at the initial stage, similar to the granulated materials.

### 3.5 Effect of pH

As shown in Fig. 5, phosphate adsorption by HZCB-1 was substantially affected by the solution pH and decreased with increasing pH. For instance, when the pH was less than ~ 4.5, the amount of adsorbed phosphate exceeded ~ 39 mg/g, leading to nearly complete removal of phosphate (i.e., the removal efficiency was greater than 95%). However, the adsorption amount and removal efficiency decreased to less than ~ 4 mg/g and 10%, respectively, when the pH exceeded ~ 8.0. Actually, the adsorption of phosphate by HZCB-1 was nearly completely blocked when the pH surpassed ~ 9.0.

The effect of pH on phosphate adsorption by HZCB-1 might be explained by multiple factors. First, the surface charge of HZCB-1 varied substantially according to the pH of the system. As described in Section 3.3, HZCB-1 had a $pH_{zpc}$ of 8.1, and thus, the surface of the adsorbent was either be positively charged at pH < 8.1 or negatively charged at pH > 8.1. Furthermore, the surface charge would reach an increasingly positive value through the protonation of the hydroxyls of zirconia under more acidic conditions. In addition, protonation of amine groups on chitosan was also expected under acidic conditions, leading to an increase in the adsorption of negatively charged phosphate ions (Eltaweil et al., 2021). Second, phosphate might undergo progressive protonation ($PO_4^{3-} \rightarrow HPO_4^{2-} \rightarrow H_2PO_4^- \rightarrow H_3PO_4$) at decreasing pH (Fig. 5). Therefore, more negatively charged phosphate species would form with increasing pH, which then impeded adsorption. Under the pH conditions commonly observed for natural water and wastewater, $H_2PO_4^-$ and $HPO_4^{2-}$ should be the dominant phosphate species, and the former has a higher affinity for metal ions than the latter (Del Nero et al., 2010). Third, in addition to phosphate (adsorbate), $OH^-$ ions would occur in water under alkaline conditions, and hence, their competition with phosphate for adsorption sites might further reduce the performance of phosphate adsorption.

### 3.6 Effect of competing ions

In real water/wastewater, phosphate anions are never present alone, and the evaluation of the effects of other anions on phosphate capture is important to elucidate the performance of an adsorbent. In this study, three anions, i.e., chloride, nitrate and sulfate ions, which are commonly present in natural water and wastewater, were chosen to evaluate their competitive effect on phosphate adsorption, and the
results are presented in Fig. 6. By comparing the amount of phosphate adsorbed on HZCB-1 in the presence or absence of competing ions, both chloride and nitrate exhibited no significant interference on the uptake of phosphate at all concentrations studied ($p > 0.05$). However, even at the lowest concentration, sulfate significantly hindered phosphate adsorption ($p < 0.05$).

However, the presence of sulfate reduced the adsorption of phosphate by only 13.5%, even at the highest concentration, indicating that HZCB-1 had good selectivity for phosphate, whose removal from water would not be substantially altered by the presence of coexisting anions. The preferential adsorption of phosphate over sulfate might be explained by the greater electron pair donating ability of the former than the latter (Wu et al., 2020). Our results were consistent with previous studies showing that other zirconium-containing materials have good selectivity for phosphate (Guan et al., 2020; Shan et al., 2019; Shang et al., 2018; Wang et al., 2017, 2016).

### 3.7 Adsorption isotherms

The adsorption isotherms, i.e., the amount of adsorbed phosphate as a function of the equilibrium concentration, of the materials are displayed in Fig. 7. The isotherm data were fitted to the Langmuir model and the Freundlich model to better understand the phosphate adsorption capacity of each material, and the fitting results are listed in Table S2. The isotherm data fit better to the Langmuir model for HZCB-1 and hydrous zirconia, while the Freundlich model described the isotherm data better for chitosan and Ferrolox. However, as shown in Fig. 7 (the Langmuir fitting curves) and Table S2, the Langmuir model still produced a reasonably good fit to the data for chitosan and Ferrolox. Therefore, the maximum adsorption capacity of phosphate at monolayer coverage was calculated for all the materials using this model. The maximum adsorption capacity followed the order of HZCB-1 $\approx$ hydrous zirconia $\approx$ Ferrolox $>\$ chitosan. As discussed in the Introduction, different, easily separable Zr-containing adsorbents have been investigated for practical applications in phosphate removal. Therefore, the adsorption capacity of HZCB-1 was compared with those materials (Table 2). The adsorption capacity of HZCB-1 was greater than or comparable to those materials. However, although the summarized data provided information to understand roughly the adsorption potential of phosphate by each material, it should be noted that the comparison was not exact since the experimental conditions differed from each other.
Table 2
Comparison of the phosphate adsorption capacity of different easily separated Zr-containing adsorbents.

| Material                                           | pH  | Temp | $Q_m$ (mg/g) | Ref.                  |
|---------------------------------------------------|-----|------|--------------|-----------------------|
| Zr/chitosan beads                                 | 6.7 | 25   | 42.02        | This study            |
| Zr/anion exchange resin                           | 5.5 | 25   | 26.1         | Bui et al.            |
| Zr/anion exchange resin                           | NA  | 22   | 91.74        | Acelas et al.         |
| Zr/acidic cation exchanger                        | 7.0, 3.0 | 30 | 43.0, 70.0   | Biswas et al.         |
| Zr(VI)/chitosan beads with a clinker              | 4.0 | 15   | 60.6         | Liu and Zhang         |
| Zr/Fe$_3$O$_4$/chitosan/PVA beads                 | 6.5 | 22   | 50.8         | Wan et al.            |
| Zr/alginate/bentonite beads                       | NA  | 30–50| 30.27–30.33  | Kumar et al.          |
| Zr/GO/alginate beads                              | NA  | 25   | 189.06       | Shan et al.           |
| Zr/Fe$_3$O$_4$/alginate/PAM                       | 2.0 | 25–45| 52.40-58.73  | Luo et al.            |
| Zr/alginate/Sr beads                              | 7.0 | room | 52.5         | Huang et al.          |
| Fe–Mg–Zr/alginate beads                           | 6.7 | 25   | 21.61        | Zhang et al.          |

a) Temperature; b) data not available.

3.8 Adsorption mechanism

Theoretically, both hydrous zirconia and chitosan might provide binding sites for phosphate. In the adsorption of phosphate by metal (hydr)oxide, the formation of both outer-sphere complexes via electrostatic attraction and inner-sphere complexes via covalent bonding is possible. In HZCB-1, formation of the former with protonated chitosan is also likely (Eltaweil et al., 2021). Interestingly, the adsorption of HZCB-1 was even higher than that of hydrous zirconia prepared alone under the same conditions (Fig. 7, Table S2). This result might be explained by the fact that hydrous zirconia existed as an amorphous phase in HZCB-1, in contrast to the crystalline structure of separately prepared zirconia, and an amorphous state potentially results in more available functional groups on its surface (Bacelo et al., 2020; Chen et al., 2022; Wang et al., 2017, 2016).

The negligible competitive effect of chloride and nitrate (Fig. 6) indicated that electrostatic forces played only a minimal role and that the major driving force for phosphate uptake should be covalent bonding with zirconium atoms. Unlike chloride and nitrate, which bound solely via the formation of outer-sphere complexes, sulfate additionally establishes inner-sphere complexes with metal (hydr)oxides (Wu et al., 2020). Thus, the result that sulfate exerted a greater inhibitory effect on phosphate removal than chloride and nitrate is not surprising.
At the low concentration range of the adsorption isotherms, the much greater affinity of hydrous zirconia or HZCB-1 for phosphate than chitosan was particularly evident (Fig. 7). The contribution of chitosan to the adsorption of HZCB-1 was estimated to be ~15%, based on the percentage of chitosan content in HZCB-1 (49.3%) and the $Q_m$ values of chitosan and HZCB-1 for phosphate (Table S2). Therefore, 85% of the adsorption capacity of HZCB-1 was attributed to amorphous hydrous zirconia.

FTIR and XPS spectroscopy studies of adsorption were performed to better understand the underlying mechanism of phosphate adsorption by HZCB-1. Unfortunately, no obvious change was observed in the FTIR spectra before and after phosphate adsorption within the region of 750–1250 cm$^{-1}$, where characteristic bands should be detected with P binding (Bui et al., 2018; Guan et al., 2020; Shan et al., 2019). This lack of change was probably due to overlap with the densely appearing bands from chitosan (Fig. 3d). On the other hand, two peaks that were assigned to P 2s and P 2p emerged in the XPS spectrum following the adsorption of phosphate (Fig. 3e and Fig. 8a). Because no changes were observed in the location and intensity of peaks in the XPS spectra due to both N 2s and C 1s (Fig. 8b, c) before and after phosphate adsorption, we postulated that phosphate was mainly not bound to the functional groups on chitosan, including the amine and hydroxyl groups. Meanwhile, the peaks due to Zr 3d$_{5/2}$ and Zr 3d$_{3/2}$ shifted to higher binding energies following phosphate adsorption, from 182.08 to 182.32 eV and from 184.49 to 184.61 eV, respectively (Fig. 8d). Therefore, the chemical environment of Zr atoms was altered by phosphate adsorption, which was caused by the replacement of hydroxyls with phosphate (Guan et al., 2020; Lin et al., 2021; Luo et al., 2019; Shan et al., 2019; Shang et al., 2018). Therefore, the mechanism of phosphate adsorption by HZCB-1 was ligand exchange between phosphate and hydroxyls via direct coordination of phosphate, a Lewis base that donates electrons, to zirconium atoms that have vacant orbitals and might thus accept electrons. However, although chitosan was not involved in phosphate adsorption to a substantial degree, it played an essential role in HZCB to enable the formation of stable granules and to facilitate the formation of amorphous hydrous zirconia with a high adsorption performance.

3.9 Desorption and reusability

The desorbability of phosphate adsorbed on an adsorbent is of crucial importance not only to enable the recovery of the pollutant but also to regenerate the material for repeated applications and thus to render the adsorption technology cost-effective in the industry. The desorption performance of phosphate once adsorbed on HZCB-1 was examined using NaOH solutions at different concentrations. As shown in Fig. 9, the desorption efficiency increased substantially with increasing NaOH concentrations within the range from 0.05 M to 0.5 M. At an NaOH concentration of 0.05 M, approximately half of the adsorbed phosphate was desorbed, while the desorption efficiency exceeded 95% when the NaOH concentration was increased to 0.5 M. However, a significant increase in desorption efficiency was not observed upon further increasing the NaOH concentration ($p > 0.05$).

Phosphate adsorption by the material after the desorption of phosphate using a 0.5 M NaOH solution was repeated to test the reusability of the material for phosphate adsorption, and the adsorption-
desorption-regeneration experiments were performed for six cycles. The desorption efficiency for each cycle was >93%, and overall, it did not change significantly among the six cycles (Fig. 9). The amount of phosphate adsorbed by HZCB-1 after each cycle of desorption also did not decrease significantly compared with the original material ($p > 0.05$), indicating that HZCB-1 was restored to close to its original status for efficient reuse with an undiminished phosphate uptake ability (Fig. 9). At the same time, the material remained intact without any obvious physical changes or damage. The loss of the mass of the material was only 5.1% after the six cycles of operation, suggesting that the stability of our material is sufficiently satisfactory for reuse.

### 3.10 Column studies

Continuous column experiments were conducted with 20 g of HZCB-1, which generated a bed height of 7 cm and a porosity of 58.9%, to assess the practical applicability of our material for phosphate removal. Tap water, which was employed to prepare the synthetic wastewater, contained $\text{SO}_4^{2-}$ (10.1 mg/L), $\text{Cl}^-$ (6.0 mg/L), $\text{NO}_3^-$ (1.1 mg/L) and $\text{SiO}_4^{2-}$ (5.8 mg/L) as major anions. At an operating flow rate of 1 ml/min, the empty bed contact time (EBCT) was 20 min, while the time that the water flow was in contact with the filter bed was 11 min.

As shown in Fig. 10, fixed-bed columns were able to treat ~6500 bed volumes of water before adsorption failure. The treatment performance was substantially affected by the initial pH of the synthetic wastewater. At pH 5.0, the column treated with 500 bed volumes of synthetic wastewater exhibited a phosphate removal efficiency >90%, while the removal efficiency was less than 90% at pH 7.0, even at the first sampling time (bed volume of 10). The amount of phosphate captured by HZCB-1 in the column was estimated to be 32.03 mg/g at pH 5.0 and 17.46 mg/g at pH 7.0 using the integral of reduced phosphate concentration versus bed volume. This behaviour was sufficiently explained by the improvement in phosphate adsorption at a lower pH (Fig. 5). However, recently, we observed that the competitive effects of coexisting anions on the adsorption sites of hydrous zirconia were hampered under acidic conditions compared with alkaline conditions (Guan et al., 2020; Wang et al., 2017). Therefore, the impeded competition from coexisting anions may also contribute to the better performance at pH 5.0 compared with that at pH 7.0. Our results indicated that this material could be used for long-term applications, and its performance might be improved by operating at a lower initial pH.

### 4. Conclusions

A novel hydrogel bead material composed of only zirconium and chitosan (HZCB) was fabricated using a recipe free of both crosslinker and filling substance, characterized and investigated for phosphate removal. By carefully choosing a suitable Zr/chitosan ratio (i.e., zirconium/amine molar ratio of 1:1), the developed material (HZCB-1) had both good phosphate adsorption performance and good mechanical and chemical stability to be used in column systems. HZCB-1 was shown to have a higher adsorption capacity (42.02 mg/g versus 25.58 mg/g) and a similar adsorption rate when compared with Ferrolox, a commercial filtering material for phosphate removal. The adsorption capacity of HZCB-1 was also greater
than or comparable with other easily separable Zr-containing materials reported in the literature. The material selectively adsorbed phosphate in the presence of competitive anions. The adsorption mechanism was proposed to be the direct coordination of phosphate to Zr atoms by replacing hydroxyls. The adsorbed P was satisfactorily stripped using an NaOH solution, and P-free HZCB-1 was reused for P harvesting. Finally, the performance of HZCB-1 for long-term application was validated by performing column studies. In conclusion, HZCB-1 is a promising material for recovering P from water to conserve nonrenewable P resources and reduce the external P loading into natural waters.

**Declarations**

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**Competing Interests**

“The authors have no relevant financial or non-financial interests to disclose.”

**Author Contributions**

Zhiyong Zhang: Conceptualization, Investigation, Writing-original draft

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Deyi Wu: Supervision, Writing-reviewing and editing

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**Figures**

![Figure 1](image1)

**Figure 1**

Pictures of hydrogel particles (upper row) and HZCBs (lower row). HZCBs from left to right: HZCB-0.25, HZCB-0.5, HZCB-0.75, HZCB-1, and HZCB-2.
Figure 2

Comparison of the adsorption performance of the seven HZCBs and their powders.
Figure 3

SEM images of HZCB-1 beads (a and b); XRD patterns of chitosan (CS), hydrous zirconia (HZ) and HZCB-1 (c); FTIR spectra of chitosan (CS), hydrous zirconia (HZ), and HZCB-1 before and after phosphate adsorption (d); full scan XPS spectra of HZCB-1 before and after phosphate adsorption (e); and the relationship of $\Delta pH$ ($pH_f - pH_i$) to $pH_i$ after adding HZCB-1 in water (f).
Figure 4

Phosphate adsorption by HZCB-1, the HZCB-1 powder and Ferrolox as a function of adsorption time. Some error bars located inside the symbols.
Figure 5

The effect of pH on phosphate adsorption by HZCB-1 (black solid line with circle symbols) and the distribution of phosphate species as a function of pH (coloured dotted lines without symbols).
Figure 6

The effect of coexisting anions on phosphate adsorption by HZCB-1. The same letters on the columns indicate a statistically insignificant difference (Student-Newman–Keuls multiple-range tests, $p > 0.05$).
Figure 7

Adsorption isotherms of phosphate on HZCB-1, chitosan (CS) and hydrous zirconia (HZ) (left panel), as well as Ferrolox (right panel). The lines were drawn using the data predicted from the Langmuir model. Some error bars are located inside the symbols.
Figure 8

High-resolution XPS spectra of the P 2p (a), N 1s (b), C 1s (c) and Zr 3d (d) regions in HZCB-1 before and after the adsorption of phosphate.
Figure 9

Desorption efficiency of phosphate adsorbed on HZBC-1 by different concentrations of NaOH solutions (left panel); desorption efficiency of phosphate adsorbed on HZBC-1 by 0.5 M NaOH and the amount of phosphate adsorbed after the desorption of phosphate and the regeneration of HZBC-1 during the six cycle experiments (right panel).
Figure 10

Residual phosphate concentration in effluent versus treated number of bed volumes as affected by the initial pH during the column experiments.

Supplementary Files

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