Low-Cost Efficient Magnetic Adsorbent for Phosphorus Removal from Water

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ABSTRACT: Adsorption using magnetic adsorbents makes the phosphorus removal from water simple and efficient. However, most of the reported magnetic adsorbents use chemically synthesized nanoparticles as magnetic cores, which are expensive and environmentally unfriendly. Replacing the nanomagnetic cores by cheap and green magnetic materials is essential for the wide application of this technique. In this paper, coal-fly-ash magnetic spheres (MSs) were processed to produce a cheap and eco-friendly magnetic core. A magnetic adsorbent, ZrO2 coated ball-milled MS (BMS@ZrO2), was prepared through a simple chemical precipitation method. Careful structural investigations indicate that a multipore structural amorphous ZrO2 layer has grown on the MS core. The specific surface area of BMS@ZrO2 is 48 times larger than that of the MS core. The highest phosphorus adsorption is tested as 16.47 mg g−1 at pH = 2. The BMS@ZrO2 adsorbent has a saturation magnetization as high as 33.56 emu g−1, enabling efficient magnetic separation. Zeta potential measurements and X-ray photoelectron spectroscopy analysis reveal that the phosphorus adsorption of BMS@ZrO2 is triggered by the electrostatic attraction and the ligand exchange mechanism. The BMS@ZrO2 adsorbent could be reused several times after proper chemical treatment.

1. INTRODUCTION

Excessive phosphorus content is one of the main causes of eutrophication, which leads to short- and long-term environmental problems in various confined water bodies.1,2 On the other hand, phosphorus is an important industrial raw material, so it is important to recycle the phosphorus resource. Removing phosphorus from water remains an urgent task for environmental protection and phosphorus recycling. Many technologies have been explored to remove phosphorus from water.3,4 Chemical precipitation and biological phosphorus removal are the two most common methods for phosphate removal. Application of the chemical precipitation method is hindered by high cost, low efficiency, sludge handling problems, and possible secondary pollution. Meanwhile, the biological phosphorus removal method requires a large operation area and complex processes. Furthermore, the removal efficiency for trace concentrations of phosphorus is low in both methods. In contrast, adsorption is an economical and efficient approach for phosphorus removal, particularly from low concentrations in water.5 In addition, the adsorbed phosphorus can be easily retrieved. As a result, the adsorption method has attracted significant interest in the past two decades. As the key factor in adsorption, various P adsorbents have been fabricated and studied, including aluminum-based compounds,6 iron-based compounds,7 calcium-based compounds,8 lanthanum-based compounds,9,10 layered double hydroxides or oxides,11 ion exchange resins,12 mesoporous silicates,13 surface-modified natural minerals,14 and industrial solid wastes.15 Recently, zirconium-based compounds, such as mesoporous ZrO2, have been reported as being capable of removing phosphate ions from wastewater.16 Considering its tremendous affinity to phosphate ions, excellent biocompatibility, and high chemical inertness toward acids and alkalis, ZrO2 could serve as an efficient P adsorbent.17,18

The other prominent difficulty for adsorption technology is the low solid–liquid separation efficiency due to the tiny diameter and high suspendability of the adsorbents. To address this problem, the magnetic separation technique was introduced. Various magnetic adsorbents have been explored and used in P adsorption.19 Most of these magnetic adsorbents have been core–shell-structured, however, and used magnetic nanoparticles, e.g., nanomagnetite, as a core. Given that nanomagnetic cores need to be chemically synthesized, the application of these magnetic adsorbents has been limited by their high cost, agglomeration, and significant environmental impact. In addition, possible oxidation of the Fe2+ in nanosized magnetite requires a hypercritical preservation condition. Finding green and cheap magnetic cores is necessary for the wide application of magnetic adsorbents.
Coal fly ash (CFA) is a bulk industrial waste product with tremendous output and widespread distribution, especially in developing countries where coal acts as major energy source. Coal-fly-ash magnetic spheres (MSs) are one of the major components of CFA, with a percentage of 2–23 wt %, depending on the mining environment.\textsuperscript{20} MS has strong magnetism, so it can be separated easily from CFA by magnetic separation. Since MS is a recycled resource extracted from industrial waste, it is cheap, in ample supply, and eco-friendly.\textsuperscript{21,22} MS particles are mainly porous ceramic balls with typical diameters of 1–100 μm and average densities of 3.1–3.9 g cm\textsuperscript{-3}.\textsuperscript{23} Considering all the above features, MS is regarded as one of the most promising candidates for magnetic adsorbent cores, although raw MS cannot be used directly since the original diameter of MS is too large for water-treatment application. MS also contains some nonmagnetic impurities, which reduce the magnetism. Therefore, careful processing is required before magnetic core application.

In this study, MS was processed by ball milling and multilevel magnetic separation to prepare ball-milled MS magnetic cores (BMS). Then, BMS@ZrO\textsubscript{2} magnetic P adsorbent was fabricated by a simple chemical precipitation method. The obtained samples were characterized in terms of morphology, composition, structure, magnetism, and specific surface area. The P adsorption performance of BMS@ZrO\textsubscript{2} under different operation conditions was carefully investigated. The adsorption mechanism is discussed in detail.

### 2. RESULTS AND DISCUSSION

#### 2.1. Characterizations of BMS@ZrO\textsubscript{2}

The diameters of the BMS particles decreased to less than 5 μm after ball milling, with a D\textsubscript{50} of 1.41 μm, as indicated in the particle diameter distribution curve (Figure S1). The composition, morphology, magnetism, and surface properties also changed dramatically.\textsuperscript{24} The scanning electron microscopy (SEM) images (Figure 1a,c) show that the BMS particles have a relatively smooth surface. In contrast, the surface of BMS@ZrO\textsubscript{2} is rough with bumps and pores on the surface, showing that the BMS core has been well covered by the grown complex. As shown in the energy-dispersive spectroscopy (EDS) spectra (Figure 1b), there are Fe, O, Al, Si, and Ca peaks in the BMS EDS spectrum, but the Cu peak is owing to the copper sample holder used in the SEM observations and the unmarked peak is from the sputtering platinum. The presence of the distinct zirconium peak in the BMS@ZrO\textsubscript{2} EDS spectrum (Figure 1d) suggests that the coating material is a zirconium compound. The element contents of the BMS and BMS@ZrO\textsubscript{2} are listed in Table 1. The presence of ZrO\textsubscript{2} was further proven by the X-ray diffraction (XRD) spectra (Figure 2a) and X-ray photoelectron spectroscopy (XPS) analysis.

#### 2.2. Phosphorus Adsorption

##### 2.2.1. Equilibrium P Adsorption Capacity

BMS powder and prepared BMS@ZrO\textsubscript{2} adsorbents were used to treat two types of P-containing water, with concentrations of 10 and 20 mg L\textsuperscript{-1}. As presented in Figure 4a, the equilibrium adsorption capacity of BMS@ZrO\textsubscript{2} (16.47 mg g\textsuperscript{-1}) was much higher than that of the BMS (2.42 mg g\textsuperscript{-1}). BMS@ZrO\textsubscript{2} exhibited better affinity toward the phosphorus ions due to the ZrO\textsubscript{2} coating and its higher specific surface area. This was in good agreement with the BET result. According to the adsorption curves, the detailed P adsorption could be divided into two stages. Stage I occurred in the first 15 min followed by the long Stage II. In Stage I, P adsorption was very fast. A 12.54 mg P g\textsuperscript{-1} adsorption was reached at the end of 15 min. In contrast, P adsorption in Stage II was much slower, and the adsorption rate decreased gradually with the adsorption time. The adsorption process extended to approximately 3 h until the saturation adsorption was reached. The P adsorption capacity of BMS@ZrO\textsubscript{2} was slightly lower than that of some reported amorphous nano-ZrO\textsubscript{2} but higher than that of other zirconium adsorbents, as summarized in

![Figure 1](image-url)
Table 2. BET Surface Properties of BMS and BMS@ZrO$_2$

| Samples       | BET surface area (m$^2$ g$^{-1}$) | Total pore volume (cm$^3$ g$^{-1}$) | Average pore diameter (nm) |
|---------------|-----------------------------------|-------------------------------------|----------------------------|
| BMS           | 3.15                              | 0.01                                | 15.63                      |
| BMS@ZrO$_2$  | 146.57                            | 0.11                                | 3.55                       |

Table 3. Comparison of P Adsorption Capacities for Reported Metal Oxide Adsorbents

| Adsorbents                      | pH adsorption capacity (mg g$^{-1}$) | ref. |
|--------------------------------|--------------------------------------|------|
| mesoporous ZrO$_2$             | 6.70–6.90                            | 29   |
| amorphous nano-ZrO$_2$         | 6.20                                 | 30   |
| NaLa(CO$_3$)$_2$/Fe$_3$O$_4$    | 4–11                                 | 31   |
| Zr-La-shaddock peels           | 3                                    | 32   |
| calcium silicate hydrate       | 8.50                                 | 33   |
| crosslinked-chitosan-Fe(III)   | 3                                    | 34   |
| La-modified rice husk biochar  | 3–10                                 | 35   |
| ACF-LaOH                       | 2                                    | 36   |
| La-zeolite                     | 3–7                                  | 37   |
| graphene/La(OH)$_3$            | 4                                    | 38   |
| Fe-Zr binary oxide             | 4                                    | 39   |
| Zr-loaded fibers               | 2–6.95                               | 40   |
| Ca-zeolite                     | 4–9                                  | 41   |
| BMS@ZrO$_2$                    | 2–3                                  | present study |

Table 3. Most of these ZrO$_2$ based adsorbents also worked best under acidic conditions as BMS@ZrO$_2$. Some other magnetic adsorbents, e.g., NaLa(CO$_3$)$_2$/Fe$_3$O$_4$, have even higher P adsorption. However, the core–shell structural BMS@ZrO$_2$ has a large BMS core. If considering that the mass ratio of magnetic core in the material is more than 60%, the specific adsorption performance of ZrO$_2$ should be much higher. In addition to the adsorption performance, the BMS@ZrO$_2$ sample has other advantages. First, its magnetic core
comes from a ready-made material, CMS. As a result, the synthetic process is simple and of low cost and produces less chemical waste liquid and other pollutants. Second, the CMS is originated from industrial waste coal fly ash; thus, the consumption of CMS has positive environmental effects. Third, the diameter of BMS@ZrO2 is in micron size and has strong magnetism; thus, it has a higher magnetic separation efficiency and is easier to operate in practical applications. Considering the low cost and efficient magnetic separation, high dosage addition can be used in actual P adsorption application.

The P adsorption capacities of BMS@ZrO2 at different pH values are shown in Figure 4b. It is found that the solution pH value has a significant effect on P adsorption.42 P adsorption was high under low pH conditions. The highest adsorption of 16.47 mg g⁻¹ was obtained at pH = 2. P adsorption declined sharply with increasing pH for pH > 3. In an alkaline environment, P adsorption became very weak. At pH = 10, the absorption capacity was only 1.82 mg g⁻¹.

2.2.2. Adsorption Mechanism. To study the P adsorption mechanism of BMS@ZrO2, pseudo-first-order and pseudo-second-order kinetic models were used to fit the time-dependent experimental data, and the Freundlich and Langmuir models were chosen to fit the P adsorption isotherm equilibrium. As discussed in Sections 1 and 2 in the Supporting Information and illustrated in Figures S2 and S3 and Tables S1 and S2, the adsorption isotherm and kinetic fittings were better described by the Langmuir and pseudo-second-order models, indicating that the nature of the P adsorption was monolayer chemical adsorption. It is well known that surface hydroxyl groups play an important role in the adsorption process.42 According to the FTIR investigation (Figure S4), there are a large number of hydroxyl and deformed hydroxyl groups on the surface of BMS@ZrO2. The properties of the surface hydroxyl groups changed with the chemical environment. When the solution pH was lower than the point of zero charge (PZC) of the material, the surface hydroxyl groups were protonated and positively charged. Otherwise, the surface hydroxyl groups were negatively charged. The zeta potential results for BMS@ZrO2 are presented in Figure 4b. It shows that the PZC of BMS@ZrO2 is at pH = 6.76 and that the highest zeta potential are observed when the solution pH = 2. The BMS@ZrO2 surface was positively charged at pH < 6.76 and negatively charged below pH > 6.76. In the P adsorption process, the pH value ranged from 2 to 10, where the dominant phosphate species were negatively charged H₂PO₄⁻ and HPO₄²⁻ anions.43 Therefore, the phosphate anions tended to be adsorbed on the BMS@ZrO2 surface by electrostatic attraction when pH < 6.76. The specific reaction processes are expressed by eqs 1–3. Under lower pH conditions, the zeta potential of BMS@ZrO2 was more positive, and thus the adsorption of phosphate anions was stronger.42 This was in good agreement with the P adsorption results.
The surface properties of BMS@ZrO₂ before and after P adsorption were characterized by XPS. As shown in Figure 5a, there is a new peak at approximately 133.84 eV in the XPS curve of the P-adsorbed BMS@ZrO₂. This peak corresponds to the phosphate group, indicating the adsorption of phosphate anions on the BMS@ZrO₂ surface. The Zr 3d spectra of BMS@ZrO₂, before and after P adsorption, are shown in Figure 5b. An obvious binding energy change in the 3d electrons can be observed. The Zr 3d₅/₂ binding energies of the original and P adsorbed BMS@ZrO₂ are 182.22 and 182.82 eV, respectively, while the corresponding Zr 3d₃/₂ binding energies are 184.44 and 185.28 eV, respectively. The increase in binding energy indicates the chemical bonding between the zirconium oxide and the phosphate groups. Since the P ion has a higher electronegativity than the H ion, the Zr ion loses electron density after P adsorption, leading to the increase in the Zr 3d₅/₂ and 3d₃/₂ binding energies. An obvious increase in the solution pH was observed with the P adsorption when pH < 8.9, as shown in Figure 6a. As discussed above, the P adsorption is dominated by the monolayer chemical adsorption and is closely related to the surface hydroxyl groups. Therefore, we could assume that the ligand exchange mechanism played an important role in the P adsorption of BMS@ZrO₂. In this mechanism, an exchange between hydroxyl groups and phosphate ions occurred in the adsorption process, and the pH increased for the sustained release of OH⁻ ions. The ligand exchange mechanism could be expressed as follows:

\[
\text{Zr} + \text{OH} + \text{H}_2\text{PO}_4^- \rightarrow \text{Zr(OH)}_2\text{PO}_4^- + \text{OH}^-
\]

\[
2\text{Zr} + \text{OH} + \text{HPO}_4^{2-} \rightarrow \text{Zr}_2\text{(HPO}_4^- + 2\text{OH}^-
\]

Interestingly, the solution pH decreased slightly with the P adsorption under high-pH conditions. This pH decrease could be attributed to the deprotonation of the surface hydroxyl groups from the release of H⁺. According to the ligand exchange mechanism, OH⁻ was released into the solution during the P adsorption process. Under strong alkaline conditions, however, the P adsorption was very slow, so the release of OH⁻ became very weak. The OH⁻ production was even slower than the H⁺ release. This finding was further proven by an adsorption experiment comparing the pH changes in the solutions containing P and without P, as shown in Figure 6b. Above all, a mechanism combining electrostatic attraction with ligand exchange is likely to dominate the P adsorption process of BMS@ZrO₂. Electrostatic attraction and ligand exchange work simultaneously but depend on the solution pH. The whole P adsorption mechanism is presented in Figure 7. From the discussion above, it is found that the phosphorus adsorption of BMS@ZrO₂ is a two-stage complex process and the adsorption mechanism is different from most of the previous reports.

2.2.3. Desorption of P and Reuse of BMS@ZrO₂. Phosphate ions adsorbed on BMS@ZrO₂ could be separated magnetically and desorbed in NaOH solution. The desorbed phosphorus had a relatively high concentration, and thus, it could be retrieved easily for recycling. The used BMS@ZrO₂ could be reused as a P adsorbent after proper chemical treatment, as described in Section 3. The P adsorption of the recycled BMS@ZrO₂ is demonstrated in Figure 8. The P adsorption capacity decreased slowly with increasing cycle time. After four cycles, the P adsorption remained at over 60% of the original adsorption capacity.

3. METHODS

3.1. Materials and Reagents. The CFA used in this study was obtained from Luohe power plant in Huainan, China. Zirconyl chloride (ZrOCl₂·8H₂O), anhydrous potassium dihydrogen orthophosphate (KH₂PO₄), ascorbic acid (C₆H₈O₆), ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O), antimony potassium tartrate (KSbC₄H₄O₇·1/2H₂O), concentrated hydrochloric acid (HCl, 32–38%), and sodium hydroxide (NaOH, 98%) were all purchased from Shanghai Nanopart Company (Shanghai, China). All the reagents were of analytical reagent grade.
The P-containing waste water was prepared by dissolving KH₂PO₄ in an appropriate amount of deionized water. The pH of the solution was adjusted by 0.1 M NaOH and/or HCl.

3.2. Preparation of BMS. The preparation of BMS particles included multilevel magnetic separation of CFA and the ball-milling treatment of MS. Briefly, crude MS was obtained by using a magnetic separation tube to process 100 mesh CFA under the strong magnetic field of 300 mT followed by weak magnetic separation (100 mT) to obtain the refined MS. The refined MS was ball-milled for 10 h at a rotation speed of 400 rpm followed by weak magnetic separation (100 mT) to obtain the BMS.

The BMS@ZrO₂ magnetic adsorbent was synthesized via a chemical precipitation method. A certain amount of BMS particles was dispersed into 100 mL of 0.05 M ZrOCl₂·8H₂O solution and sonicated for 10 min. Then, 6 M NaOH solution was added dropwise until the pH value reached 8.5. A stirring rate of 400 rpm was maintained throughout the titration process. The suspension was stirred continuously for 6 h. Subsequently, the precipitates were collected by an external field and washed with deionized water and ethanol. Finally, the product was dried at 60 °C in a vacuum drier for 24 h and sealed for later P adsorption experiments. The synthesis of BMS@ZrO₂ is schematically illustrated in Figure 9.

3.3. Characterization and Measurements. The prepared adsorbents were characterized by various techniques as follows. The distribution of MS particle diameters before and after ball milling was measured by a SALD-7101 LDPAZ (Japan). The crystalline structure was characterized using a Bruker D8-Focus X-ray diffractometer by applying monochromated Cu Kα radiation (λ = 0.15418 nm) in the 2θ range of 20–80 ° at 2° min⁻¹. The morphology and elemental composition were analyzed by a JSM-7001F SEM (JEOL, Japan) equipped with and EDS (Oxford, Britain) operating at 20 kV. XPS (ESCALAB 250Xi, Thermo Fisher Scientific, USA) was used to measure the chemical composition and the binding energy of Zr 3d before and after P adsorption. A VSM (Lake Shore 7400, USA) was used to measure the room-temperature magnetism of the magnetic adsorbents. BET surface areas and pore size distributions were determined through N₂ adsorption/desorption over a Micromeritics ASAP 2010 system (Micromeritics, USA) at 77 K. A ZetaProbe 7020 Zeta-Potential meter was used to analyze the zeta potential. A FTIR (Thermo Scientific Nicolet iS50, USA) was used to analyze functional groups on the adsorbents in the region of 4000–400 cm⁻¹.

3.4. P Adsorption Experiment. All P adsorption experiments were performed at room temperature in 250 mL glass beakers. A 150 mL home-made phosphate solution was used in each experiment, with a fixed dose of BMS@ZrO₂ at 0.5 g L⁻¹. The mixture was stirred electrically at 200 rpm for a certain time. After the adsorption, 10 mL of supernatant solution was extracted, centrifuged, and subjected to residual phosphate concentration analysis. The concentration of phosphate was determined using ultraviolet–visible (UV–Vis) spectrometry. The phosphate adsorption capacity was calculated according to the following equation:

\[ q_e = \frac{V(C_0 - C_e)}{m} \]  

where \( q_e \) is the equilibrium adsorption capacity (mg g⁻¹), \( C_0 \) is the initial phosphate concentration (mg L⁻¹), \( C_e \) is the equilibrium phosphate concentration (mg L⁻¹), \( V \) is the volume of phosphate solution (L), and \( m \) is the mass of the adsorbent (g).

Two initial phosphate concentrations of 10 and 20 mg L⁻¹ were used in the P adsorption experiments. The initial solution pH was adjusted from 2 to 10, and the adsorption time was 0–3 h. Pseudo-first-order and pseudo-second-order kinetic models were used to fit the time-dependent experimental data. The effect of the solution pH on P adsorption was studied using the 20 mg L⁻¹ concentration phosphate solution. The adsorption time was 3 h. The effects of coexisting anions on phosphate adsorption were evaluated by adding NaNO₃, Na₂SO₄, and Na₂CO₃ at concentrations of 0, 0.05, 0.1, 0.15, and 0.20 M; the initial solution pH was 2, and the adsorption time was 3 h. For the equilibrium adsorption isotherm study, the initial phosphate concentration ranged from 1 to 20 mg L⁻¹, and the adsorption time was 3 h. The adsorption equilibrium was investigated through Freundlich and Langmuir model isotherm adsorption fitting.

P desorption experiments under alkaline conditions were performed in five consecutive cycles to test the reusability of BMS@ZrO₂. In each cycle, the BMS@ZrO₂ adsorbent after adsorption was treated in 0.2 M NaOH solution under mechanical stirring at 500 rpm for 12 h. The adsorbent was then separated magnetically and washed thoroughly with deionized water until neutral pH was achieved. The regenerated adsorbent was dried at 60 °C for 12 h in a vacuum drier. In the re-adsorption experiments, the initial phosphate concentration was 20 mg L⁻¹, the pH was 2, and the adsorption time was 3 h.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03657.

Adsorption kinetic model and fitting, adsorption isotherm model and fitting, FTIR investigation, partial element content in BMS and BMS@ZrO2, and particle diameter distributions of MS before and after ball milling (PDF).

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Notes
The authors declare no competing financial interest.

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