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Phosphate Removal from Wastewater by Magnetic Amorphous Lanthanum Silicate Alginate Hydrogel Beads

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Abstract: It is of both fundamental and practical importance to develop effective adsorbents for removing phosphate from aqueous solutions continuously. In this study, magnetic amorphous lanthanum silicate alginate hydrogel beads (MALS-B) were prepared and used for phosphate removal. Mesoporous silica materials with highly ordered and hexagonal channel structures were synthesized from natural mineral rectorite (REC) at room temperature. On this basis, amorphous lanthanum silicate (ALS) was synthesized by the one-pot method using a silicon source from REC and a commercial lanthanum source. Further, MALS-B were synthesized from sodium alginate (SA) with ALS and Fe₃O₄ as the incorporated adsorbable and magnetic nanoparticles via a simple cross-linking method in CaCl₂ solution. The synthesized hydrogel beads were characterized by various techniques. ALS and Fe₃O₄ existed relatively independently in MALS-B, where ALS provided adsorption sites and Fe₃O₄ provided magnetism. They played a synergistic role in phosphate removal. The saturation magnetization value of MALS-B was 17.38 emu/g, enabling their facile separation from aqueous solutions after phosphate adsorption. MALS-B exhibited a preferable adsorption capacity of 40.14 mg P/g for phosphorus compared to other hydrogel beads based on adsorption experiments. More significantly, MALS-B exhibited excellent selectivity for phosphate in aqueous solutions with various interfering ions and possessed a high affinity to phosphate in a wide pH range. MALS-B showed the treatment volume of 480 BV when effluent phosphate concentration was below 0.5 mg/L in fixed-bed column adsorption. The adsorption mechanism was also revealed. Our work demonstrates that MALS-B can serve as a promising adsorbent for continuous phosphate adsorption.

Keywords: rectorite; amorphous lanthanum silicate; magnetism; hydrogel beads; continuous adsorption

1. Introduction

Phosphorus is an essential element of organisms, which maintains the normal physiological activities and functions of organisms. It plays a vital role in RNA, DNA, and cell metabolism [1,2]. Phosphate fertilizers are widely added to the soil to increase food production. However, the plants cannot absorb all phosphate of phosphate fertilizers. It is inevitable that unutilized phosphate is usually leached out from the soil and accumulates in the water body. Meanwhile, with the increasing frequency of human life and production activities, much industrial wastewater, agricultural wastewater, and domestic sewage containing phosphate are discharged into the water body [3]. When the P concentration in the water body exceeds 0.02 mg/L, eutrophication occurs in the water body [4]. Microorganisms, algae, and other aquatic plants in water bodies grow and reproduce rapidly.
As a result, the dissolved oxygen content of the water body is reduced, and the aquatic ecosystem is destroyed. Eutrophication of water bodies (lake and reservoir) has been considered to be a long-term environmental problem [5,6]. Therefore, it is urgent to remove excess phosphate from water bodies to meet increasingly stringent emission standards and to alleviate eutrophication of water bodies. Countries around the world have set strict discharge limits for total P (TP) in water, such as 0.05 mg/L recommended by EPA in the United States [7], 0.5 mg/L for Class 1 in China [8], 0.5–1.0 mg/L in Japan [9], and 1–2 mg/L in France [10].

Numerous treatment technologies have been used for phosphate removal from wastewater, such as chemical precipitation, biological treatment, ion exchange, membrane separation, crystallization, electrolysisis, and adsorption. Adsorption technology has attracted increasing attention to remove phosphate from wastewater [11,12]. In recent years, various lanthanum-based adsorbents have been used for phosphate removal due to the high affinity between lanthanum and phosphate [13]. Most lanthanum-based adsorbents are synthesized by loading lanthanum compounds on supports, such as clay minerals, carbon materials, high-molecular polymers, and iron oxides [14–19]. Moreover, in order to efficiently separate exhausted adsorbents from wastewater, magnetic adsorption materials have been synthesized for phosphate removal [20,21]. Most of these adsorbents exist in the form of powder. It is inevitable that powder adsorbents cause blockage in continuous column runs. Hydrogel beads have attracted increasing attention to embed powder adsorbents for wastewater treatment [22,23].

Highly ordered and hexagonal mesoporous silica materials can be considered the lanthanum supports due to the high specific surface area and channel structure. Rectorite (REC) contains a lot of silicon and has been used to synthesize mesoporous silicon by the hydrothermal method [24]. It is feasible to adsorb lanthanum with the channel structure of mesoporous silica to prepare adsorbents for phosphate removal. Sodium alginate (SA) is a natural anionic polysaccharide polymer, having the characteristics of wide sources, low cost, easy degradation, and good biocompatibility [25]. It can form a sodium alginate-based hydrogel network structure through ionic cross-linking with multivalent metal cations (Ca$^{2+}$) [26]. Powder adsorbents and magnetic particles can be mixed with SA to prepare hydrogel beads for easy separation after adsorption.

In this work, in order to solve the separation of exhausted adsorbents in batch experiments and the blockage of powder adsorbents in continuous column runs, the hydrogel embedding method was used to spheroidize powder adsorbents and magnetic particles. Briefly, amorphous lanthanum silicate (ALS) was synthesized through the one-pot method on the basis of facilely fabricating mesoporous silica materials. Highly ordered and hexagonal mesoporous silica materials provided rich channels for the adsorption of lanthanum. ALS and Fe$_3$O$_4$ could be embedded into the insoluble hydrogels due to abundant hydroxyl and carboxyl groups in the structure of SA. Magnetic amorphous lanthanum silicate alginate hydrogel beads (MALS-B) were synthesized by ionic cross-linking between SA and Ca$^{2+}$. ALS provided adsorption sites, and Fe$_3$O$_4$ made MALS-B easier to be separated after phosphate adsorption in batch experiments. The structure and morphology of magnetic and nonmagnetic hydrogel beads were characterized. Batch experiments and column experiments were conducted to evaluate the adsorption performance of synthesized hydrogel beads for phosphate. Meanwhile, the adsorption performance of magnetic and nonmagnetic hydrogel beads was carefully analyzed and compared. On this basis, the adsorption mechanisms of phosphate removal by MALS-B were proposed.

2. Materials and Methods

2.1. Materials

REC used in this study was obtained from Hubei, China. The chemical composition of REC was the same as reported in the literature with SiO$_2$ 40.35%, Al$_2$O$_3$ 33.77%, CaO 5.72%, TiO$_2$ 4.51%, Na$_2$O 1.47%, K$_2$O 0.84%, Fe$_2$O$_3$ 0.44%, SO$_3$ 0.36%, MgO 0.26%, SrO 0.13%, V$_2$O$_5$ 0.12%, ZrO$_2$ 0.11%, Cr$_2$O$_3$ 0.09%, MnO$_2$ 0.03%, ZnO 0.02%, and 11.79% loss.
on ignition [24]. Hydrochloric acid (HCl, ACS reagent grade), cetyltrimethylammonium bromide (CTAB, ACS reagent grade), lanthanum acetylacetonate (C$_{15}$H$_{21}$LaO$_{6}$xH$_{2}$O, ACS reagent grade), iron (III) chloride hexahydrate (FeCl$_3$·6H$_2$O, ACS reagent grade), iron (II) chloride tetrahydrate (FeCl$_2$·4H$_2$O, ACS reagent grade), potassium chloride (KCl, ACS reagent grade), potassium sulfate (K$_2$SO$_4$, ACS reagent grade), potassium carbonate (K$_2$CO$_3$), potassium bicarbonate (KHCO$_3$), potassium nitrate (KNO$_3$), and humic acid (HA) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, ACS reagent grade), 25% ammonia solution (NH$_3$·H$_2$O), and potassium dihydrogen phosphate (KH$_2$PO$_4$, ACS reagent grade) were purchased from Fisher Scientific. All chemicals in this study were used as received without further purification.

2.2. Synthesis of Powder Adsorbents
2.2.1. Synthesis of Mesoporous Silica Material

Suitable silicon sources from REC were prepared as described elsewhere [24]. A 0.5 g amount of CTAB was dissolved in deionized water, followed by adding 34 mL of anhydrous ethanol. After the mixture was stirred for 5 min, 40 mL of suitable silicon sources (6.65 g Si/L) from REC was added. Then, the mixed solution was stirred for 3 h after the pH value was adjusted to 9.0 with HCl solution. The mixed solution was filtered to obtain the as-synthesized samples, repeatedly washed with anhydrous ethanol and deionized water. After being dried at 35 °C, the as-synthesized samples were calcined at 550 °C in air for 6 h with a ramping rate of 2 °C/min in a furnace. The final white powder was mesoporous silica material.

2.2.2. Synthesis of ALS

The synthesis of ALS was similar to the synthesis of mesoporous silica material. The difference was that 0.5 g of lanthanum acetylacetonate was dissolved in 34 mL of anhydrous ethanol.

2.2.3. Synthesis of Magnetic Fe$_3$O$_4$

The synthesis of magnetic Fe$_3$O$_4$ nanoparticles followed a reported procedure [27]. Briefly, 1.64 g of iron (III) chloride hexahydrate and 0.58 g of iron (II) chloride tetrahydrate were dissolved in 50 mL of deionized water. After that, the mixture was heated to 50 °C, and the pH was adjusted to 10.0 with 25% ammonia solution, followed by increasing the temperature to 85 °C, then maintained for 1 h to finish the reaction. The obtained products were magnetically separated and washed by deionized water several times and then dried under vacuum to obtain magnetic Fe$_3$O$_4$ nanoparticles.

2.3. Synthesis of Hydrogel Bead Adsorbents

The synthesis of MALS-B is illustrated in Figure 1 and is briefly described below. A 0.5 g amount of ALS and 0.3 g of Fe$_3$O$_4$ were added to 5 mL of deionized water, followed by being fully sonicated until becoming uniform. Then, 5 mL of sodium alginate solution (8 wt%) was added. After that, the mixed solution was dropwise added to CaCl$_2$ solution (5 wt%) at a uniform speed through the syringe pump to form MALS-B. After being stirred and hardened for 16 h, MALS-B were washed with deionized water several times. Amorphous lanthanum silicate alginate hydrogel beads (ALS-B) were synthesized under the same conditions without adding Fe$_3$O$_4$. Mesoporous silica alginate hydrogel beads (MS-B) were synthesized under the same conditions as ALS-B with mesoporous silica replacing ALS.
Figure 1. Schematic illustration for the synthesis of MALS-B.

2.4. Characterization

XRD data were collected on a Bruker AXS D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) using Cu Kα radiation with a scan step of 2°/min. The morphologies of samples were observed by field-emission SEM (Tescan, MIRA3 LMU, Brno, Czech Republic) and TEM (JEOL JEM-2100F, Tokyo, Japan). The content of the La and Fe elements was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). Nitrogen gas adsorption–desorption isotherms were measured using an ASAP 2020 surface area analyzer (Micromeritics, Norcross, GA, USA). FTIR spectra were recorded on a Nicolet Nexus 670 infrared spectrometer (Thermo Company, Waltham, MA, USA) with a resolution of 2 cm⁻¹ using KBr pellets. The chemical compositions and surface states of the samples were analyzed by XPS on a Thermo Escalab 250Xi photoelectron spectrometer (Thermo Escalab, Thermo Scientific, Waltham, MA, USA) equipped with an Al Kα monochromated X-ray source.

2.5. Batch Experiments

A series of batch experiments were conducted to systematically evaluate the adsorption performances of the synthesized hydrogel beads. The phosphate solution used in this paper was orthophosphate solution, which was prepared by dissolving KH₂PO₄ into deionized water. Adsorption kinetics were analyzed as follows: 25 hydrogel beads were added to 50 mL of 25 mg P/L KH₂PO₄ solution with different adsorption time at initial pH 5.3. The pseudo-first-order and pseudo-second-order kinetic models provided in Supplementary Materials Text S1 were used to fit the adsorption kinetic data. Adsorption isotherms were performed as follows: 25 hydrogel beads were added to 50 mL of 25 mg P/L KH₂PO₄ solution with different initial concentrations varying from 10.0 to 90.0 mg/L at initial pH 5.3. Langmuir, Freundlich, and Langmuir–Freundlich models provided in Supplementary Materials Text S2 were used to fit the adsorption isotherm data. The effect of solution pH on phosphate adsorption was conducted by adjusting the pH of the solution from 2.0 to 12.0 with 25 hydrogel beads being added to 50 mL of 25 mg P/L KH₂PO₄ solution. The effect of various interfering ions such as Cl⁻, NO₃⁻, HCO₃⁻, SO₄²⁻, CO₃²⁻, and humic acid on the adsorption performances of hydrogel beads was investigated with 25 hydrogel beads being added to 50 mL of 25 mg P/L KH₂PO₄ solution at initial pH 5.3. To evaluate the regeneration of MALS-B, five consecutive phosphate adsorption–desorption cycles were conducted. Twenty-five hydrogel beads were added to 50 mL of 25 mg P/L KH₂PO₄ solution at initial pH 5.3 for each adsorption experiment. Afterwards, the exhausted MALS-B were regener-
ated using CaCl<sub>2</sub> solution (5 wt%). The collected MALS-B after regeneration were washed with DI water and then reused in the next adsorption experiment. The dosages of MALS-B, ALS-B, and MS-B for all batch experiments were 0.98, 0.77, and 0.77 g/L, respectively.

2.6. Column Experiments

To assess the adsorption performance of MALS-B for continuous phosphate removal from low concentration, fixed-bed column runs were conducted in acrylic columns (100 mm in length and 24 mm in inner diameter). The column was full of hydrogel beads, with gently tapping to make hydrogel beads compact. The influent was phosphate solution with a concentration of 2 mg/L. The column breakthrough point was set as 0.5 mg P/L, according to the discharge standard of China GB18918-2002 [28].

2.7. Analytical Methods

The P concentration in the filtrate was determined spectrophotometrically at a detecting wavelength of 700 nm on an ultraviolet–visible light (UV–vis) spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) based on the molybdenum blue method.

3. Results and Discussion

3.1. Characterization

The morphologies of ALS-B and MALS-B were captured by optical and SEM imaging (Figure 2). ALS-B and MALS-B had uniform spherical morphologies with an average diameter of about 3 mm in the wet state (Figure 2a,e). ALS-B and MALS-B were still spherical after freeze-dried, as observed from Figure 2b,f. ALS-B and MALS-B did not show a significant difference in their appearance. ALS-B and MALS-B both exhibited a rugged surface, and many compound particles were found on their surface. The compound particles on the surface of ALS-B were ALS (Figure 2c,d). The compound particles on the surface of MALS-B were ALS and Fe<sub>3</sub>O<sub>4</sub> (Figure 2g,h). These embedded compound particles did not affect the densification of hydrogel beads; on the contrary, increased the strength of hydrogel beads [29]. EDS elemental analysis results confirmed the existence of lanthanum in ALS-B and lanthanum and iron in MALS-B.

Figure 2. Optical and SEM images of (a–d) ALS-B; (e–h) MALS-B; EDS of (i) ALS-B and (j) MALS-B.

The morphology and element composition of MALS-B were characterized by TEM, HAADF-STEM, and corresponding elemental mapping distribution of MALS-B, as shown in Figure 3. It should be noted that MALS-B contained ALS and Fe<sub>3</sub>O<sub>4</sub>. The distribution of La and Si elements in MALS-B was the same, and the distribution of the Fe element was...
inconsistent with that of La and Si elements. These results clearly demonstrated that ALS and Fe$_3$O$_4$ existed independently in MALS-B. The Ca element appeared in the distribution position of Fe, La, and Si elements, which was attributed to the formation of hydrogel beads by dropping sodium alginate mixed with ALS and Fe$_3$O$_4$ into CaCl$_2$ solution.

XRD was conducted to understand the crystal structure of the synthesized hydrogel beads (Figure 4a). The observed diffraction peaks at 22.8° clearly demonstrated that the main component of MS-B was amorphous silica (Figure 4a) [30]. After adding lanthanum acetylacetonate, the main component of ALS-B changed from silica to ALS (JCPDS Card No. 48-0052), according to the displayed diffraction peaks. The diffraction peaks of Fe$_3$O$_4$ (JCPDS Card No. 65-3107) were found in the diffraction peaks of MALS-B, indicating that Fe$_3$O$_4$ was successfully embedded into MALS-B. Moreover, the magnetic performance of MALS-B was measured by a magnetic hysteresis loop plotted from −10 to 10 k Oe (Figure 4b). The saturation magnetization value was measured to be 17.38 emu/g. It should be noted that almost no hysteresis loops were found in the magnetization curve, suggesting the superparamagnetism of MALS-B [31]. MALS-B showed high magnetization values and superparamagnetic characteristics, which made it conducive to separate exhausted MALS-B from water. The saturation magnetization value of MALS-B after phosphate adsorption was measured to be 18.86 emu/g (Figure S5).

Figure 3. (a) TEM image of MALS-B; (b) HAADF-STEM image and corresponding elemental mapping distribution of MALS-B.

Figure 4. (a) XRD patterns of the synthesized hydrogel beads; (b) magnetic hysteresis curve of MALS-B.
3.2. Phosphate Adsorption by MALS-B
3.2.1. Adsorption Kinetics

In order to understand the adsorption kinetics of the synthesized hydrogel beads, the adsorption processes of MALS-B, ALS-B, and MS-B were investigated at the initial phosphorus concentration of 25 mg/L, as shown in Figure 5. The adsorption of phosphate by MALS-B and ALS-B had a piecewise characteristic. The adsorption capacity for phosphorus by MALS-B increased rapidly at the first 8 h, then increased slowly, and reached the adsorption equilibrium after 16 h. ALS-B displayed a parallel adsorption rate to MALS-B. The adsorption capacity for phosphorus by MS-B was much lower than that of MALS-B and ALS-B. This could be attributed to the fact that the adsorption behavior was mainly dominated by the lanthanum element. The phosphate adsorption kinetic data of MALS-B and ALS-B were fitted with pseudo-first-order and pseudo-second-order kinetic models, respectively. The results are shown in Figure 5 and Table S1. It could be seen from Table S1 that the correlation coefficient ($R^2$) of the pseudo-second-order kinetics of phosphate adsorption by MALS-B and ALS-B were 0.963 and 0.987, higher than the correlation coefficients ($R^2$) of pseudo-first-order models. This indicated that the pseudo-second-order kinetic model could better describe the adsorption processes of phosphate by MALS-B and ALS-B. In other words, the adsorption processes were dominated by chemical adsorption [32], which could be further demonstrated by XPS analysis.

![Figure 5](image-url)

**Figure 5.** Phosphate adsorption kinetics of the synthesized hydrogel beads with results fitted to the (a) pseudo-first-order and (b) pseudo-second-order models.

3.2.2. Adsorption Isotherms

Figure 6 compares the adsorption isotherms of phosphate removal by MALS-B, ALS-B, and MS-B at different initial phosphorus concentrations. The adsorption capacity of MALS-B, ALS-B, and MS-B for phosphorus increased with the increase of initial phosphorus concentration and finally reached equilibrium. At lower initial phosphorus concentration, the adsorption capacity of MALS-B, ALS-B, and MS-B increased sharply. When the initial phosphorus concentration continued to increase, the adsorption capacity increased slowly. The reason for this phenomenon may be that the number of active sites available on the surface of MALS-B, ALS-B, and MS-B decreased along with the ongoing adsorption processes. The maximum adsorption capacities of MALS-B, ALS-B, and MS-B were in the order of ALS-B > MALS-B > MS-B. MS-B showed the lowest adsorption capacity for phosphorus. The adsorption capacity of ALS-B for phosphorus increased significantly due to the addition of the lanthanum source. This was because that lanthanum increased the adsorption sites in the gel network, resulting in a higher affinity for phosphate [33]. Compared with ALS-B, the adsorption capacity of MALS-B for phosphorus decreased, but the content of lanthanum in MALS-B also reduced. Langmuir, Freundlich, and Langmuir–Freundlich models were used to fit the experimental data of adsorption isotherms of MALS-B, ALS-B, and MS-B. The Langmuir–Freundlich model fitted best (Figure 6 and Table S2), and the maximum adsorption capacities were in the following order: ALS-B (46.08 mg P/g) > MALS-B (40.14 mg P/g) > MS-B (3.87 mg P/g). MALS-B had obvious advantages over the
developed hydrogel beads adsorbents in recent years (Table 1). The content of lanthanum in ALS-B was 13.05 wt%, and the content of lanthanum and iron in MALS-B was 10.66 and 15.92 wt%, respectively. After conversion, the maximum adsorption capacity of unit La element in ALS-B and MALS-B were 353.10 and 376.55 mg P/La g, respectively. These results indicated that the addition of Fe$_3$O$_4$ to hydrogel beads did not only reduce the utilization of lanthanum, but also endowed hydrogel beads with magnetism, which was beneficial to the separation between exhausted adsorbents and water.

Table 1. Comparison of phosphorus adsorption capacity to other hydrogel beads.

| Adsorbents                                      | Concentration (mg/L) | pH  | Temperature (°C) | Adsorption Capacity (mg/g) | References |
|------------------------------------------------|-----------------------|-----|------------------|----------------------------|------------|
| Al-crosslinked PVA hydrogel beads               | 0–110                 | 6.0 | 30               | 26.0                       | [34]       |
| Al-inserted acid activated bentonite beads      | 6–183                 | 3.0 | 25               | 39.4                       | [35]       |
| MgFe$_2$O$_4$-BM-La(b)                          | 5–50                  | 5.3 | 25               | 26.83                      | [23]       |
| Zr-modified chitosan beads                      | 5–50                  | 4.0 | 25               | 60.6                       | [36]       |
| Fe-sericite beads                               | 3–61                  | 5.0 | 25               | 13.6                       | [37]       |
| NH-SA-ZrBT                                      | 5–200                 | 7.0 | 25               | 63.9                       | [22]       |
| SA-ZrBT                                         | 5–100                 | 7.0 | 25               | 37.5                       | [22]       |
| Fe$_3$O$_4$/PAM/SA-Zr beads                     | 0–100                 | 2.0 | 25               | 42.43                      | [38]       |
| ALS-B                                           | 0–70                  | 5.3 | 25               | 46.08                      | This work  |
| MALS-B                                          | 0–70                  | 5.3 | 25               | 40.14                      | This work  |

3.2.3. Effects of pH and Interfering Ions

The effect of pH value on the adsorption performance of MALS-B and the results are shown in Figure 7a. At pH 2.0, the adsorption capacity of MALS-B for phosphorus was about 4.4 mg/g. The value experienced a rapid increase to about 15.2 mg/g, with increasing pH to 4.0, and then leveled off with further increasing pH from 4.0 to 12.0. It should be noted that MALS-B remained appreciable adsorption capacity for phosphorus in a wide pH range from 4.0 to 12.0, which was overwhelmingly advantageous than other adsorbents, such as discarded lignocellulose biochar loaded with lanthanum and three-dimensional graphene/La(OH)$_3$-nanorod aerogel [39,40].
The result indicated that MALS-B had a continuous adsorption performance for phosphate removal from wastewater. Eutrophic water contains many ions and dissolved organics coexisting with phosphate; thus, the selectivity for phosphate over other anions (Cl\(^-\), SO\(_4\)\(^{2-}\), CO\(_3\)\(^{-}\), HCO\(_3\)\(^{-}\), NO\(_3\)\(^-\)) using MALS-B was investigated. Figure 7b displays a stable adsorption capacity of MALS-B for phosphorus in the presence of the interfering ions and dissolved organics with concentrations ranging from 10 to 50 mg/L, indicating that MALS-B exhibit excellent selectivity for phosphate and prospects of feasible application in practical wastewater. The result was highly consistent with the previous study on phosphate removal by La-based materials [41,42].

3.2.4. Fixed-Bed Column Adsorption

Batch experiments determine the adsorption capacity of MALS-B for phosphorus. It can be used as a reference for the quality of MALS-B. However, batch experiments were not continuous. Fixed-bed column adsorption is often used in engineering or practical applications to treat wastewater continuously [25]. Therefore, it is of great significance to explore the continuous adsorption performance of MALS-B. Analysis of the absorption breakthrough curve for phosphate adsorption by MALS-B was conducted (Figure 8). The influent phosphorus concentration was 2 mg P/L, and based on the preliminary experiment, the optimal empty bed contact time (EBTC) was set as 3.0 min, which was controlled by an adjustable peristaltic pump. Sewage was allowed to be discharged when the effluent phosphorus concentration was lower than 0.5 mg/L, according to the effluent discharge standard of China GB18918-2002 [2]. Hence, the column breakthrough point was set as 0.5 mg P/L. The total P in the effluent exceeded the column breakthrough point after 480 BV. The result indicated that MALS-B had a continuous adsorption performance for phosphate removal from wastewater.

![Figure 7](image-url)  
**Figure 7.** Effects of (a) different solution pH values and (b) interfering ions on phosphate adsorption by MALS-B.

![Figure 8](image-url)  
**Figure 8.** Breakthrough curve for phosphate adsorption by MALS-B.
3.3. Adsorption Mechanisms

The FTIR spectra of MALS-B before and after phosphate adsorption were investigated (Figure S6). After phosphate adsorption, a new peak at 613 cm\(^{-1}\) ascribed to the O-P-O bending vibration was observed, which demonstrated the formation of inner-sphere complexation between MALS-B and H\(_2\)PO\(_4\)\(^-\) or HPO\(_4\)\(^{2-}\) groups [43]. Therefore, complexation was an essential mechanism of phosphate removal by MALS-B. Lanthanum showed a strong affinity for phosphate, and the solubility of LaPO\(_4\) was low. As a result, it is easy to form LaPO\(_4\) precipitation between MALS-B and H\(_2\)PO\(_4\)\(^-\) or HPO\(_4\)\(^{2-}\) groups. Figure 9a shows the XRD pattern of MALS-B after phosphate adsorption. The observed diffraction peaks at 13.8°, 19.9°, 25.5°, 41.8°, and 48.4° clearly demonstrated that LaPO\(_4\) precipitations were formed [44]. It was further found that the P element appeared on the surface of MALS-B after phosphate adsorption by TEM image (Figure 9b,c). EDS elemental mapping analysis further confirmed that the adsorbed P element was highly correlated with the La element. Therefore, precipitation was also a mechanism of phosphate removal by MALS-B.

![Figure 9. (a) XRD pattern of MALS-B after phosphate adsorption; (b) TEM image of MALS-B after phosphate adsorption; (c) HAADF-STEM image and corresponding La, P elemental mapping distribution of MALS-B after phosphate adsorption.](image)

O 1s XPS spectra of MALS-B before and after phosphate adsorption are shown in Figure 10a,b. According to the binding energy of different oxygen species, the sum peak of O 1s can be divided into three overlapping peaks, corresponding to binding of oxygen to metal (M-O), binding of hydroxyl to metal (M-OH), and adsorbed water (H\(_2\)O) [45,46]. It could be seen from Figure 10a,b and Table S3 that the relative areas of the M-O peak, M-OH peak, and H\(_2\)O peak changed. The relative areas of the M-O peak, M-OH peak, and H\(_2\)O peak in MALS-B were 26.26%, 56.60%, and 17.15% and shifted to 30.76%, 49.55%, and 19.69% after phosphate adsorption, respectively. These results confirmed the critical role of hydroxyl groups on the surface of MALS-B. Hydroxyl groups were replaced by H\(_2\)PO\(_4\)\(^-\) or HPO\(_4\)\(^{2-}\) groups through ligand exchange in the adsorption process [47,48].

To further confirm the complexation mechanism, P 2p and La 3d XPS spectra of MALS-B before and after phosphate adsorption are presented in Figure 10c,d. In the P 2p XPS spectrum of MALS-B after phosphate adsorption, the P 2p peak was observed at 133.36 eV (Figure 10c), indicating that H\(_2\)PO\(_4\)\(^-\) or HPO\(_4\)\(^{2-}\) groups were successfully adsorbed by MALS-B. Compared with the standard KH\(_2\)PO\(_4\) sample, the binding energy corresponding to the P 2p absorption band in MALS-B after phosphate adsorption reduced 0.64 eV from 134.0 eV to 133.36 eV, demonstrating the formation of a complex between MALS-B and H\(_2\)PO\(_4\)\(^-\) or HPO\(_4\)\(^{2-}\) groups [49]. Moreover, the binding energy of La 3d\(_{5/2}\) and La 3d\(_{3/2}\) peaks shifted along the direction of high binding energy from 834.15, 837.62 eV and 850.96, 854.52 eV to 834.43, 837.79 eV and 851.29, and 854.67 eV before and after phosphate adsorption, indicating the occurrence of electron transfer from the valence band.
of the ligand atom to the 4f orbit of the La atom [50,51]. The inner-sphere complex of LaPO$_4$·xH$_2$O was formed between MALS-B and H$_2$PO$_4$ or HPO$_4^{2−}$ groups. Based on the adsorption performance and characterization analyses, the proposed mechanisms for phosphate removal by MALS-B are summarized in Figure 11.

![Proposed adsorption mechanisms for phosphate removal by MALS-B.](image)

**Figure 10.** XPS spectra of samples: (a) O 1s XPS spectrum of MALS-B; (b) O 1s XPS spectrum of MALS-B after phosphate adsorption; (c) P 2p XPS spectrum of MALS-B after phosphate adsorption and (d) La 3d XPS spectra of MALS-B before and after phosphate adsorption.

**Figure 11.** Proposed adsorption mechanisms for phosphate removal by MALS-B.

4. Conclusions

In summary, a novel spherical adsorbent was fabricated for phosphate removal. The preparation of MALS-B involved three consecutive steps: (1) the extraction of a silicon source from REC and the preparation of mesoporous silica materials; (2) the synthesis of
ALS and Fe$_3$O$_4$; (3) the synthesis of hydrogel beads by dropping sodium alginate mixed with ALS and Fe$_3$O$_4$ into CaCl$_2$ solution. Mesoporous silica materials had a specific surface area of 1499 m$^2$/g with a highly ordered and hexagonal channel structure, which could provide multiple contact sites for lanthanum to fabricate ALS. The average diameters of the synthesized ALS-B and MALS-B was 3 mm in the wet state, and ALS and Fe$_3$O$_4$ existed in independent forms in MALS-B. The preferable adsorption capacity of MALS-B for phosphorus was closely related to the affinity of ALS for phosphate. Due to the magnetism of Fe$_3$O$_4$, MALS-B after phosphate adsorption with a saturation magnetization value of 18.86 emu/g were easily separated from aqueous solutions. The phosphate adsorption kinetic data of MALS-B and ALS-B were better fitted with pseudo-second-order kinetic models, revealing that the adsorption processes of MALS-B and ALS-B for phosphate were dominated by chemical adsorption. Compared with Langmuir and Freundlich models, the experimental data of adsorption isotherms of MALS-B and ALS-B were best fitted to the Langmuir–Freundlich model. The maximum adsorption capacities of MALS-B and ALS-B were 40.14 and 46.08 mg P/g, respectively. Although the adsorption capacity of ALS-B was higher, the content of lanthanum in MALS-B was lower than that in ALS-B. MALS-B exhibited excellent selectivity for phosphate and had a wide range of pH applications. In the fixed-bed column adsorption experiment, MALS-B showed the treatment volume of 480 BV when the effluent phosphorus concentration was below 0.5 mg/L. Finally, the underlying mechanisms of phosphate removal by MALS-B involved precipitation, ligand exchange, and complexation according to the characterization results of MALS-B before and after phosphate adsorption. All the analyses confirmed that MALS-B could serve as a promising filling adsorbent candidate for continuous phosphate adsorption in practical application.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/min12020171/s1](https://www.mdpi.com/article/10.3390/min12020171/s1), Text S1: Kinetic models (pseudo-first-order and pseudo-second-order kinetic models); Text S2: Adsorption isotherms models (Langmuir, Freundlich, and Langmuir–Freundlich models); Text S3: Equation for calculating the adsorption capacity for phosphorus and removal efficiency of P; Table S1: Adsorption kinetic parameters for phosphorus adsorption by the synthesized hydrogel beads; Table S2: Adsorption isotherm parameters for phosphorus adsorption by the synthesized hydrogel beads; Table S3: The fitting parameters of O 1s peak of MALS-B before and after phosphate adsorption; Figure S1: SAXRD and WAXRD patterns of mesoporous silica materials; Figure S2: TEM images of mesoporous silica materials; Figure S3: N$_2$ adsorption–desorption isotherm curves and BJH pore size distributions of mesoporous silica materials; Figure S4: Regeneration of MALS-B under five consecutive adsorption–desorption cycles; Figure S5: Magnetic hysteresis curve of MALS-B after phosphate adsorption; Figure S6: FTIR spectra of MALS-B before and after phosphate adsorption.

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