



# Article Controllable Preparation of Superparamagnetic Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> Inorganic Polymer for Rapid Adsorption and Separation of Phosphate

Yao Lu<sup>1</sup>, Xuna Jin<sup>1</sup>, Xiang Li<sup>2</sup>, Minpeng Liu<sup>1</sup>, Baolei Liu<sup>2</sup>, Xiaodan Zeng<sup>3</sup>, Jie Chen<sup>3</sup>, Zhigang Liu<sup>3,\*</sup>, Shihua Yu<sup>1,\*</sup> and Yucheng Xu<sup>4</sup>

- <sup>1</sup> Jilin Institute of Chemical Technology, College of Chemical & Pharmaceutical Engineering, Jilin 132022, China
- <sup>2</sup> Jilin Institute of Chemical Technology, School of Petrochemical Technology, Jilin 132022, China
  <sup>3</sup> Jilin Institute of Chemical Technology, Centre of Analysis and Measurement, Jilin 132022, China
- <sup>3</sup> Jilin Institute of Chemical Technology, Centre of Analysis and Measurement, Jilin 132022, China
  <sup>4</sup> Pailway Transportation Department, Jilin Potrochemical Company, Jilin 132021, China
  - Railway Transportation Department, Jilin Petrochemical Company, Jilin 132021, China

\* Correspondence: lzg@jlict.edu.cn (Z.L.); ysh@jlict.edu.cn (S.Y.)

Abstract: Superparamagnetic Fe<sub>3</sub>O<sub>4</sub> particles have been synthesized by solvothermal method, and a layer of dense silica sol polymer is coated on the surface prepared by sol-gel technique; then La(OH)<sub>3</sub> covered the surface of silica sol polymer in an irregular shape by controlled in situ growth technology. These magnetic materials are characterized by TEM, FT-IR, XRD, SEM, EDS and VSM; the results show that La(OH)<sub>3</sub> nanoparticles have successfully modified on Fe<sub>3</sub>O<sub>4</sub> surface. The prepared Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> inorganic polymer has been used as adsorbent to remove phosphate efficiently. The effects of solution pH, adsorbent dosage and co-existing ions on phosphate removal are investigated. Moreover, the adsorption kinetic equation and isothermal model are used to describe the adsorption performance of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub>. It was observed that Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> exhibits a fast equilibrium time of 20 min, high phosphate removal rate (>95.7%), high sorption capacity of 63.72 mgP/g, excellent selectivity for phosphate in the presence of competing ions, under the conditions of phosphate concentration 30 mgP/L, pH = 7, adsorbent dose 0.6 g/L and room temperature. The phosphate adsorption process by Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> is best described by the pseudo-second-order equation and Langmuir isotherm model. Furthermore, the real samples and reusability experiment indicate that Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> could be regenerated after desorption, and 92.78% phosphate removing remained after five cycles. Therefore, La(OH)<sub>3</sub> nanoparticles deposited on the surface of monodisperse Fe<sub>3</sub>O<sub>4</sub> microspheres have been synthesized for the first time by a controlled in-situ growth method. Experiments have proved that Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> particles with fast separability, large adsorption capacity and easy reusability can be used as a promising material in the treatment of phosphate wastewater or organic pollutants containing phosphoric acid functional group.

Keywords: superparamagnetic; Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> inorganic polymer; phosphate adsorption

# 1. Introduction

Phosphorus (P) is one of the indispensable nutrient elements for the growth and reproduction of all organisms. However, the excessive discharge of phosphate not only causes the eutrophication of aquatic ecosystems but also aggravates the shortage of global phosphorus resources, making the global food crisis even worse. Therefore, it is urgent to develop an effective method to remove and recover excessive phosphate from wastewater for sustainable development [1].

Numerous treatment technologies, such as electrocoagulation [2], crystallization [3], biological treatment [4], chemical precipitation [5], membrane separation [6], ion exchange [7] and adsorption [8,9] have been developed to remove phosphate from wastewater. Among them, adsorption is considered as a promising technology for adsorbate effective removal and recovery. At present, a lot of functionalized adsorbents have been utilized for phosphate



**Citation:** Lu, Y.; Jin, X.; Li, X.; Liu, M.; Liu, B.; Zeng, X.; Chen, J.; Liu, Z.; Yu, S.; Xu, Y. Controllable Preparation of Superparamagnetic Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> Inorganic Polymer for Rapid Adsorption and Separation of Phosphate. *Polymers* **2023**, *15*, 248. https://doi.org/10.3390/ polym15010248

Academic Editor: Ignazio Blanco

Received: 2 December 2022 Revised: 29 December 2022 Accepted: 29 December 2022 Published: 3 January 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). elimination, including cation exchange resin [10], layered double hydroxides [11], fibrous adsorbent [12], hydrogel [13], metal organic frameworks [14], affinity membrane [15] and porous biochar [16]. Owing to the strong affinity between La and phosphate, La-based materials have attracted much attention. In particular, lanthanum (hydr)oxide offers both pore structures and large specific surface areas and provides a large number of coordination sites towards phosphate even at low concentration [17,18].

To enhance separation and re-dispersion performance of materials, Fe<sub>3</sub>O<sub>4</sub> is used as magnetic core to construct composites with the magnetic property and specific adsorption [19]. In recent years, it has been reported in some literatures that various magnetic particles have been used to remove phosphate, achieving good results [20–24]. However, these materials either have small specific surface area or have poor dispersion due to irregular shape and uneven size, which limits the contact with the adsorbate to some extent and reduces the removal efficiency of magnetic particles on phosphate.

In the early stage, we realized the controllable preparation of monodisperse and superparamagnetic Fe<sub>3</sub>O<sub>4</sub> magnetic beads with diameter of 50, 200, 400 nm [25–31]. In this paper, La(OH)<sub>3</sub> nanoparticles are grown in situ on the surface of the above functional magnetic beads and successfully prepared  $Fe_3O_4@La(OH)_3$  inorganic polymer. In the past,  $La(OH)_3/Fe_3O_4$  composite has been established to act as an adsorbent for phosphate, with large adsorption capacity, and can be separated by magnetic separation [32]. However,  $Fe_3O_4$  used in most literatures is prepared by coprecipitation method. In comparison to coprecipitation method,  $Fe_3O_4$  is prepared by solvent method in this study with the characteristic of monodisperse and fast magnetic response, and La(OH)3 can be directly modified on its surface. In addition, since  $Fe_3O_4$  has no dense protective layer, it is easy to be oxidized, and the corresponding magnetic response is weakened, so magnetic separation recycling cannot be achieved. We can improve the stability of  $Fe_3O_4$  by modifying its surface with a layer of dense silica and then with La(OH)<sub>3</sub>. A combination of the advantages described above with solid phase extraction spectrometry and the adsorption properties of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> for phosphate (adsorption performance optimization, kinetic, isotherm) is evaluated using batch experimental methods. Besides, actual sample testing and Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> composite reusability are also investigated in this study.

## 2. Materials and Methods

#### 2.1. Materials

Iron chloride hexahydrate, poly(ethylene glycol), ethylene glycol were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China); Sodium acetate (AR,  $\geq$ 99%), ascorbic acid (AR,  $\geq$ 99.7%), potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>, AR,  $\geq$ 99%), potassium antimony tartrate (AR,  $\geq$ 99%), ammonium molybdate (AR,  $\geq$ 99%), sulfate triacetyloxysilyl acetate (AR,  $\geq$ 99%), lanthanum nitrate hexahydrate (AR,  $\geq$ 99%) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China).

Accurately, a certain mass of  $KH_2PO_4$  was dissolved with water as phosphate stock solution, and the concentration was 1000 mgP/L. The adsorbed solution was prepared by diluting the stock solution with distilled water.

## 2.2. Preparation of Adsorbent

## 2.2.1. Synthesis of Fe<sub>3</sub>O<sub>4</sub> Particles

First, 60 mL ethylene glycol and 1.0 g polyethylene glycol were added into a 100 mL beaker and stirred in a 65 °C water bath until they were dissolved. Then 2.7 g of ferric chloride hexahydrate was dissolved in the above solution. After complete dissolution, 7.2 g of sodium acetate trihydrate was added and stirred for another 20 min. Finally, the solution was transferred to 100 mL polytetrafluoroethylene (PTFE) lined hydrothermal autoclave reactor and placed in a vacuum oven at 200 °C to react for 10 h. The black products were obtained and separated from the mixture by a magnet. Then they were washed with water and alcohol and dried in an oven at 60 °C.

## 2.2.2. Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Composite

The as-prepared  $Fe_3O_4$  particles (0.1 g), absolute ethanol (48 mL) and distilled water (12 mL) were dispersed in a 3-necked flask under ultrasonication for 10 min.  $NH_3 \cdot H_2O$  (2 mL) was added in the above solution and stirred mechanically for 20 min. A mixed solution of TEOS (1 mL) and absolute ethanol (1 mL) was slowly dropped into the 3-mouth flask and reacted at room temperature for 5 h. After complete reaction, the product was washed with water and alcohol; the final product was diluted with water to a concentration of 50 mg/mL.

## 2.2.3. Synthesis of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> Composites

The above prepared  $Fe_3O_4@SiO_2$  (10 mL), distilled water (40 mL) and NaOH solution (10 mL, 0.5 M) were added into a three-mouth flask and stirred for 60 min. Then,  $La(NO_3)_3$  (0.1 g) that dissolved it with 50 mL distilled water was slowly dropped into the above solution (30 min), and stirring continued for 4 h. Finally, the supernatant was poured out and washed with water for 5 times with the help of magnetic separation.

#### 2.3. Characterization of Adsorbent

Transmission electron microscopy (TEM) images were investigated using a JEOL JEM-2100F TEM (Tokyo, Japan). Fourier transform infrared spectra (FT-IR) were performed on a Spectrum One (PerkinElmer, Shelton, CT; USA) instrument to determine the functional groups of the absorbents. Scanning electron microscopic (SEM) image was obtained on a Hitachi S-4800 SEM (Tokyo, Japan), and the element mapping was analyzed on an Energy Dispersive X-Ray Spectroscopy (EDX) detector. The crystal structure of the particles was characterized by a D8FOCUS X-ray diffractometer (Bruker, Germany) with Cu K $\alpha$ radiation (k = 1.5406 Å). An UV-Vis T6 spectrometer (Beijing, China) was used to measure the concentration of phosphate. The pH values of solution were tested by Sartorius PB 220 pH meter (Gottingen, Germany).

## 2.4. Adsorption Experiments

The adsorption experiments were performed in triplicate, and the phosphate solutions used were prepared with standard phosphate solutions. The adsorption capability and removal efficiency of phosphate on  $Fe_3O_4@La(OH)_3$  was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

$$R_{e} = \frac{C_{0} - C_{e}}{C_{0}} \times 100\%$$
 (2)

where  $R_e$  (%) and  $q_e$  (mg/g) are the removal efficiency and adsorption capacity of phosphate, respectively.  $C_e$  and  $C_0$  (mgP/L) represented the equilibrium and initial phosphate concentrations, respectively. V (L) is the volume of phosphate solution, and M (g) is the weight of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub>.

The adsorption performance of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> composites for phosphate were investigated, by adding different doses of adsorbent (5–40) mg to a 3-mouth flask filled with phosphate solution (50 mL) and mechanically stirred at room temperature. When the adsorption experiment reached equilibrium, then magnetic separation, the residual phosphate concentration in the solution was tested. To study the change of pH, 30 mg Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> were dispersed in 50 mL of phosphate solution (30 mgP/L) at 25 °C. Solution pH change from 3.0 to 11.0 was adjusted with a 0.1 M HCl or 0.1 M NaOH solution. The influence of common coexisting anions on phosphate solutions at room temperature.

## 2.5. Adsorption Kinetics

To study the adsorption kinetics, 30 mg of adsorbent was dispersed in a 3-mouth flask containing 50 mL of phosphate with an initial concentration of 30 mgP/L and then stirred mechanically, and samples were taken with a pipette gun for certain time intervals at room temperature.

#### 2.6. Adsorption Isotherm

Sorption isotherm experiments were completed in an 18–38 °C water bath; 30 mg of  $Fe_3O_4/La(OH)_3$  were dispersed into phosphate solution (50 mL) with initial concentration ranging from 5 to 100 mgP/L, and the maximum adsorption amount was investigated.

## 2.7. Reusable Performance

The saturated adsorbent was magnetically separated and then dispersed in 1.0 M NaOH solution for phosphate desorption until the equilibrium state. The regenerated Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> was washed with deionized water and then reused in the succeeding cycle.

# 2.8. Real Samples

To demonstrate the applicability of  $Fe_3O_4@La(OH)_3$ , extra adsorption experiments were carried out in Tap water and Songhua River water, respectively. Water samples were filtered with microporous membrane, then spiked phosphate to 30 mg/L by standard solutions.

# 3. Results and Discussion

## 3.1. Preparation of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> Composite

The fabrication procedure for the Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> is shown in Figure 1. From the scheme, (i) super-paramagnetic Fe<sub>3</sub>O<sub>4</sub> particles are synthesized by solvothermal reaction as the magnetic core of composite, making it convenient to separate from the matrix by a magnet. (ii) The as-prepared Fe<sub>3</sub>O<sub>4</sub> particles are coating with silica by sol-gel method to increase its water solubility and monodispersity. (iii) Then the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> is covered with La(OH)<sub>3</sub> in an irregular shape via an in situ reduction reaction [32,33]. Meanwhile, TEM images of the magnetic particles obtained at each stage are also given in Figure 1, which proves the successful synthesis of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> composite and indicates that the surface of Fe<sub>3</sub>O<sub>4</sub> is modified by La(OH)<sub>3</sub> particle in the composite, compared to the relatively smooth surface of Fe<sub>3</sub>O<sub>4</sub>.



Figure 1. Schematic illustrations of the fabrication procedure for the Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub>.

# 3.2. Characterization of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> Composite

A suite of techniques, including FT-IR, XRD, VSM and SEM, are used to characterize the Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> composite. In the FT-IR spectra (Figure 2A), the relatively high intensity

of a band at 580 cm<sup>-1</sup> indicates the stretch of Fe–O [34]. In addition, the peaks at 795 cm<sup>-1</sup> and 472 cm<sup>-1</sup> could be assigned to the symmetrical stretching vibration of Si–O. The strong and broad absorption band near  $1090 \text{ cm}^{-1}$  is consistent with the characteristic absorption of Si–O–Si antisymmetric stretching vibration [35]. There is no obvious difference in absorption peaks between Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub>, mainly because the La–O and Si–O bond absorption peaks are overlapped [36]. The crystalline structures of magnetic particles are demonstrated by XRD as shown in Figure 2B. The positions of all diffraction peaks matched the JCPDS card (75–1610) for magnetite perfectly [37], which suggested that the introduction of  $SiO_2$  and  $La(OH)_3$  had no effect on the response of  $Fe_3O_4$  signals. In the meantime, the intensities of the main peaks have decreased marginally, which reveals that the SiO<sub>2</sub> layer is introduced and La(OH)<sub>3</sub> is successfully loaded. Figure 2C shows the magnetization curves of magnetic composite; it is discovered that the saturation magnetization of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> is decreased compared with that of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. That is because the shielding effect of  $La(OH)_3$  introduced on the surface of  $Fe_3O_4$ , and the reduction of the relative content of Fe<sub>3</sub>O<sub>4</sub> in the composite. Meanwhile, Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> still show good monodispersity, strong magnetism and rapid separation by using an external magnetic field (insert picture).



Figure 2. (A) FT-IR spectra, (B) XRD patterns and (C) VSM diagram of magnetic composites.

The microstructure and morphology of the magnetic particles are characterized using scanning electron microscopy (SEM). Figure 3A shows the magnetic cores have uniform size and rough surface. As is shown in Figure 3B, the surface of particles become smooth and flat due to the coating of nano layer, which further proves that the silica sol polymer is successfully prepared by sol-gel method. After the deposition of La(OH)<sub>3</sub> (Figure 3C), the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> particles are almost wrapped into the target material. Thus, the formation of

the composite resulted in the increase of size, and the average diameter of  $Fe_3O_4@La(OH)_3$ is about 420 nm (Figure 3B), compared with  $Fe_3O_4@SiO_2$  that has an average diameter of 370 nm (Figure 3A). Based on the SEM images, we can see magnetic composites are homogeneous, monodisperse and superparamagnetic particles. In addition, elemental analysis confirms the  $Fe_3O_4@La(OH)_3$  successfully prepared, as Fe, Si, O and La elements exist throughout the material matrix (Figure 3D). Then EDX elemental mapping of  $Fe_3O_4@La(OH)_3$  has been presented in Figure S1 (see Supplementary Materials), verifying the successful formation of a core-shell structure in the composite and the contents of Fe, Si and La are 90.15%, 5.99% and 3.85%, respectively.



Figure 3. SEM images of (A)  $Fe_3O_4$ , (B)  $Fe_3O_4@SiO_2$ , (C)  $Fe_3O_4@La(OH)_3$  and (D) elemental analysis of  $Fe_3O_4@La(OH)_3$ .

# 3.3. Optimization of Adsorption Experiment

# 3.3.1. Batch Factors Experiments

The adsorbent dosing levels on phosphate adsorption capacity and removal rate are tested to select the appropriate amount of magnetic lanthanum hydroxide. As presented in Figure 4A, phosphate adsorption capacity  $q_e$  decreased from 97.94 mg/g to 35.20 mg/g, with an increasing of the dosage from 5–40 mg. This result shows that less dosage is accompanied by less adsorption sites, resulting in saturation of adsorption sites and high adsorption capacity. With the increase of adsorbent dosage, the surface adsorption sites increase, while adsorption cannot reach saturation since the phosphate concentration is constant. Meanwhile, the phosphate removal rate gradually increased from 32.63% to 96.87% with the increase of dosage of 30 mg. Considering the sufficient adsorption and high removal efficiency, the adsorbent dosage of 30 mg is adopted in the subsequent experiment.

An experimental study on pH is carried out in the ranges of pH from 2 to 9. As can be seen from Figure 4B, phosphate adsorption on  $Fe_3O_4@La(OH)_3$  is greatly affected by the pH value of solution. As we know,  $H_2PO_4^-$  and  $HPO_4^{2-}$  are the dominant species of phosphate in the solution in the investigated pH range. At the same time, the surface charges of  $Fe_3O_4@La(OH)_3$  have been tested at different pH values by the zeta potential measurement

(Figure S2, see Supplementary Materials), and its isoelectric point is found to be 4.89. Thus, when pH < 4.89, the surface of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> particles became positively charged; the phosphate anions are favorable adsorbed because of the electrostatic attraction. Meanwhile, as the pH > 4.89, Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> is negatively charged; electrostatic repulsion leads to the decrease of phosphate adsorption capacity; and the phosphate removal decreased with the increase of pH [38,39]. For all that, a high phosphate removal rate (>95.7%) is maintained in the pH = 3–7 range.



Figure 4. The effect of (A) adsorbent dosage and (B) the solution pH on phosphate adsorption capacity.

#### 3.3.2. Influence of Interfering Ions

As the phosphate adsorption on Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> surfaces may interfere with common coexisting ions in environmental water, some interfering ions including  $SO_4^{2-}$ ,  $Cl^-$ ,  $CO_3^{2-}$ , Na<sup>+</sup> and K<sup>+</sup> on phosphate enrichment at pH 7.0 are investigated. As evidenced in Figure 5, these foreign ions do not cause significant interference, even when the concentration of the competing ions is at 10 times (300 mg/L) excess.



**Figure 5.** Adsorption capacity for phosphate in the presence of 30 mg/L phosphate and various concentrations of possible interference ions.

## 3.4. Adsorption Kinetics

The kinetic data obtained are analyzed by using pseudo-first-order rate (Equation (3)) and pseudo-second-order rate (Equation (4)), respectively [40]. A comparison of the



kinetic models for phosphate adsorption by  $Fe_3O_4@La(OH)_3$  using nonlinear regression is presented in Figure 6, and the relevant results are summarized in Table 1.

**Figure 6.** Kinetic curves for phosphate adsorption by  $Fe_3O_4@La(OH)_3$  (**A**) pseudo-first-order (**B**) pseudo-second-order model with initial phosphate concentration of 10 mg/L.

C <sub>0</sub> (mg/L)	q <sub>e,exp</sub> (mg/g)	Pseudo-First-Order			Pseudo-Second-Order		
		$k_1 \times 10^{-2}$	q <sub>e,cal</sub> (mg/g)	R <sup>2</sup>	$k_2 \times 10^{-3}$	q <sub>e,cal</sub> (mg/g)	<b>R</b> <sup>2</sup>
5	8.33	5.73	5.19	0.9236	3.09	8.64	0.9976
10	16.67	6.89	8.77	0.9015	1.68	17.29	0.9990
30	49.93	6.70	28.80	0.8681	0.32	53.16	0.9963
50	61.32	5.83	44.68	0.9146	0.25	65.44	0.9972
100	86.47	8.01	68.91	0.9429	0.13	94.43	0.9951

Table 1. Kinetic parameters for the adsorption of phosphate by Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub>.

Pseudo-first-order kinetic model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

Pseudo-second-order kinetic model:

$$\frac{\mathbf{t}}{\mathbf{q}_{\mathbf{t}}} = \frac{1}{\mathbf{k}_2 \mathbf{q}_{\mathbf{e}}^2} + \frac{\mathbf{t}}{\mathbf{q}_{\mathbf{e}}} \tag{4}$$

where  $q_t (mg/g)$  is phosphate adsorption (mg/g) at time t and  $q_e (mg/g)$  is the equilibrium adsorption;  $k_1 (min^{-1})$  and  $k_2 (g/(mg \cdot min))$  were the rate constants of pseudo-first-order and pseudo-second-order reaction, respectively.

As shown in Figure 6 and Table 1, the second-order kinetic model fit all the adsorption data well according to the relatively high correlation coefficients (r > 0.99). Moreover, the experimental date ( $q_{e,exp}$ ) is consistent with the calculated date ( $q_{e,cal}$ ) obtained from pseudo-second-order model. The results indicating that the rate limiting step might be due to chemical absorption, and its adsorption capacity is directly proportional to the number of surface active binding sites of magnetic materials.

#### 3.5. Adsorption Isotherms

Langmuir and Freundlich models are used to analyze the adsorption data [41]. The fitting equations are expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{C_e}{q_{max}}$$
(5)

$$\ln q_e = \frac{1}{n} \ln C_e - \ln k_F \tag{6}$$

where  $C_e (mg/L)$  is equilibrium concentration;  $q_{max} (mg/g)$  is the highest adsorption capacity; n is a parameter that represents the medium heterogeneity and adsorption intensity; and  $k_L (L/mg)$  and  $k_F ((mg/g)/(mg/L)^{1/n})$  are Langmuir and Freundlich constants, respectively. The fitting curves and correlation parameters are shown in Table 2.

**Table 2.** Freundlich and Langmuir constants and correlation coefficients for adsorption of phosphate onto Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub>.

<b>.</b>		Lan	Freundlich			
(K)	Q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	n	K <sub>F</sub> (mg/g)	R <sup>2</sup>
298	70.77	2.26	0.9994	1.22	0.027	0.9425
318	82.37	1.89	0.9966	1.93	0.026	0.9426
338	105.37	4.07	0.9990	4.34	0.017	0.9059

From the correlation coefficient ( $R^2$ ) of two models, it is discovered that the Langmuir model is more reasonable to interpret the isotherms of the adsorption process, suggesting that phosphates are absorbed in monolayer style, and the maximum absorption value of  $q_{max}$  predicted is 105.37 mg/g.

## 3.6. Removal of Phosphate in Actual Water and Its Reusability

The prepared Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> (30 mg) is added into 50 mL tap water and Songhua River water, respectively. None of the original samples are evaluated to contain phosphate as tested by solid phase extraction spectrometry and then two samples are spiked phosphate to 30 mg/L with standard solutions for subsequent extraction and detection. The results of actual water samples detection and composite particles reusability are shown in Figure 7. Figure 7A reveals that the adsorption rates of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> for phosphate in tap water and Songhua water are 96.17% and 95.46%, demonstrating the practical application of phosphate removal on Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> would be applicable. Also, the reusability of the adsorbent for phosphate is illustrated in Figure 7B; the phosphate removal rate could still reach 92.78% after five cycles of reuse [42]. The adsorption capacity of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> in our study is also contrasted with the materials reported in the literatures (Table S1, see Supplementary Materials); the comparison results show Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> particles exhibit significant advantages to realize rapid and efficient phosphate removal.



**Figure 7.** Reusability tests of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> for phosphate removing: five adsorption (**A**) and desorption (**B**) cycles in actual water samples.

# 3.7. Mechanism of Phosphate Removing by Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub>

To gain insight into the mechanisms of phosphate removing by the  $Fe_3O_4@La(OH)_3$  composite, the zeta potential measurements have been performed (Figure S2, see Supplementary Materials). Figure S2 shows that the isoelectric point  $(pH_{zpc})$  of  $Fe_3O_4@La(OH)_3$  particles is found to be about 4.89 before adsorption, while the value decreased to about 4.25 after adsorption.  $pH_{zpc}$  moves to a lower pH value due to the accumulation of negative charges within the shear plane, is typically considered as inner-sphere complexation phenomena caused by ligand exchange, which can be described in the following reactions [43–46]:

La-OH + 
$$H_2PO_4^- \leftrightarrow La-H_2PO_4 + OH^-$$
  
La=OH +  $HPO_4^{2-} \leftrightarrow La=HPO_4 + 2OH^-$   
La=OH +  $PO_4^{3-} \leftrightarrow La=PO_4 + 3OH^-$ 

The involvement of ligand exchange is further evidenced by the observed change of solution pH before and after adsorption. The initial pH of 30 mgP/L phosphate solution is 5.28, and the pH value gradually increased to 7.08 after adsorption for 1 h. The increase in pH value during sorption is attributed to the release of  $OH^-$  upon ligand phosphate removing. Based on the above analysis, the replacement of the surface hydroxyl groups by phosphate ions with the formation of inner-sphere complex played an important role in the removal of phosphate by  $Fe_3O_4@La(OH)_3$  particles.

## 4. Conclusions

In this study, hydrothermal methods and in-situ precipitation are adopted to prepare Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> inorganic polymer, which is confirmed based on the results of TEM, FT-IR, XRD, SEM and EDS. Batch experiments are used to investigate the ability of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> for phosphate removing from water. It is observed that Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> composites exhibit a fast equilibrium time of 20 min, high phosphate removal rate (>95.7%), high sorption capacity of 63.72 mgP/g, under the conditions of phosphate concentration 50 mgP/L, pH = 7, adsorbent dose 0.6 g/L and room temperature. Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> displayed excellent selectivity and anti-interference toward phosphate over other interfering ions including SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, Na<sup>+</sup> and K<sup>+</sup>, even if their concentration is 10 times higher than that of phosphate. In addition, the kinetic data and isotherm data are better described by pseudo-second-order equation and Langmuir model, respectively, indicating that monolayer chemisorption occurred during adsorption process. In summary, the Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> composites with the characteristics of superparamagnetic, fast adsorption efficiency, easy reusability, etc. will be a promising adsorbent for phosphate removal from wastewater or polluted surface water.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/polym15010248/s1, Figure S1: EDX elemental mapping of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub>. Figure S2: Zeta potential curves of Fe<sub>3</sub>O<sub>4</sub>@La(OH)<sub>3</sub> nanoparticles before (1) and after (2) the phosphate adsorption with the initial phosphate concentration of 30 mg/L. Table S1: Comparison of phosphate adsorption capacities with other reported adsorbents.

**Author Contributions:** Methodology and data curation, Y.L. and X.J.; software and validation, X.L., M.L. and B.L.; formal analysis, X.Z.; investigation, J.C.; resources, Z.L.; data curation and writing—original draft preparation, S.Y.; writing—review and editing, Z.L.; visualization, Y.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

**Data Availability Statement:** All data included in this study are available upon request by contact with the corresponding author.

Acknowledgments: We greatly appreciate the financial support from the projects of NSFC (No. 22106051), the program of Jilin department of science and technology (No. 20200901021SF, 20210509054RQ), Jilin province development and reform commission (2020C036-4), the education department of Jilin province (No. JJKH20200244KJ, No. JJKH20210229KJ).

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- 1. Rivera, R.; Chagnes, A.; Cathelineau, M.; Boiron, M.C. Conditioning of poultry manure ash for subsequent phosphorous separation and assessment for a process design. *Sustain. Mater. Technol.* **2022**, *31*, 377. [CrossRef]
- Hashim, K.S.; Al Khaddar, R.; Jasim, N.; Shaw, A.; Phipps, D.; Kot, P.; Pedrola, M.O.; Alattabi, A.W.; Abdulredha, M.; Alawsh, R. Electrocoagulation as a green technology for phosphate removal from river water. *Sep. Purif. Technol.* 2019, 210, 135–144. [CrossRef]
- 3. Li, B.; Boiarkina, I.; Yu, W.; Huang, H.M.; Munir, T.; Wang, G.Q.; Young, B.R. Phosphorous recovery through struvite crystallization: Challenges for future design. *Sci. Total. Environ.* **2019**, *648*, 1244–1256. [CrossRef] [PubMed]
- Ye, Y.; Ngo, H.H.; Guo, W.; Liu, Y.; Zhang, X.; Guo, J.; Ni, B.J.; Chang, S.W.; Nguyen, D.D. Insight into biological phosphate recovery from sewage. *Bioresour. Technol.* 2016, 218, 874–881. [CrossRef] [PubMed]
- Cichy, B.; Kuzdzal, E.; Krzton, H. Phosphorus recovery from acidic wastewater by hydroxyapatite precipitation. J. Environ. Manag. 2019, 232, 421–427. [CrossRef]
- 6. Xie, M.; Shon, H.K.; Gray, S.R.; Elimelech, M. Membrane-based processes for wastewater nutrient recovery: Technology, challenges, and future direction. *Water Res.* 2016, *89*, 210–221. [CrossRef]
- Chen, S.Y.; Shi, Z.; Song, Y.; Li, X.R.; Hu, Y.L. Phosphate removal from aqueous solution by Donnan dialysis with anion-exchange membrane. J. Cent. South Univ. 2014, 21, 1968–1973. [CrossRef]
- 8. Wang, H.; Zhu, J.; Fu, Q.; Hu, H. Adsorption of phosphate on pure and humic acid-coated ferrihydrite. *J. Soil Sediment* 2015, *15*, 1500–1509. [CrossRef]
- 9. Cheng, P.; Liu, Y.; Yang, L.; Wang, X.; Chi, Y.; Yuan, H.; Wang, S.; Ren, Y.X. Adsorption and recovery of phosphate from aqueous solution by katoite: Performance and mechanism. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *655*, 130285. [CrossRef]
- 10. Nur, T.; Johir, M.A.H.; Loganathan, P.; Nguyen, T.; Vigneswaran, S.; Kandasamy, J. Phosphate removal from water using an iron oxide impregnated strong base anion exchange resin. *J. Ind. Eng. Chem.* **2014**, *20*, 1301–1307. [CrossRef]
- Iftekhar, S.; Kucuk, M.E.; Srivastava, V.; Repo, E.; Sillanpaa, M. Application of zinc-aluminium layered double hydroxides for adsorptive removal of phosphate and sulfate: Equilibrium, kinetic and thermodynamic. *Chemosphere* 2018, 209, 470–479. [CrossRef] [PubMed]
- 12. Awual, M.R.; Jyo, A.; Ihara, T.; Seko, N.; Tamada, M.; Lim, K.T. Enhanced trace phosphate removal from water by zirconium(IV) loaded fibrous adsorbent. *Water Res.* **2011**, *45*, 4592–4600. [CrossRef] [PubMed]
- 13. Luo, D.; Wang, L.; Nan, H.; Cao, Y.; Wang, H.; Kumar, T.V.; Wang, C. Phosphorus adsorption by functionalized biochar: A review. *Environ. Chem. Lett.* **2022**, 2022, 1–28. [CrossRef]
- 14. Song, L.; Huo, J.; Wang, X.; Yang, F.; He, J.; Li, C. Phosphate adsorption by a Cu(II)-loaded polyethersulfone-type metal affinity membrane with the presence of coexistent ions. *Chem. Eng. J.* **2016**, *284*, 182–193. [CrossRef]
- Nehra, M.; Dilbaghi, N.; Singhal, N.K.; Hassan, A.A.; Kim, K.H.; Kumar, S. Metal organic frameworks MIL-100(Fe) as an efficient adsorptive material for phosphate management. *Environ. Res.* 2019, 169, 229–236. [CrossRef] [PubMed]
- Hui, B.; Zhang, Y.; Ye, L. Preparation of PVA hydrogel beads and adsorption mechanism for advanced phosphate removal. *Chem. Eng. J.* 2014, 235, 207–214. [CrossRef]

- Fang, L.; Wu, B.; Chan, J.K.M.; Lo, I.M.C. Lanthanum oxide nanorods for enhanced phosphate removal from sewage: A response surface methodology study. *Chemosphere* 2018, 192, 209–216. [CrossRef]
- Wu, Y.; Li, X.M.; Yang, Q.; Wang, D.B.; Xu, Q.X.; Yao, F.B.; Chen, F.; Tao, Z.L.T.; Huang, X.D. Hydrated lanthanum oxide-modified diatomite as highly efficient adsorbent for low-concentration phosphate removal from secondary effluents. *J. Environ. Manag.* 2019, 231, 370–379. [CrossRef]
- Lee, W.H.; Kim, J.O. Phosphate recovery from anaerobic digestion effluent using synthetic magnetite particles. J. Environ. Chem. Eng 2022, 10, 107103. [CrossRef]
- Liu, C.Y.; Wang, Y.L.; Li, X.L.; Li, J.Y.; Dong, S.X.; Hao, H.T.; Tong, Y.; Zhou, Y.Q. Highly efficient P uptake by Fe<sub>3</sub>O<sub>4</sub> loaded amorphous Zr-La (carbonate) oxides: Electrostatic attraction, inner-sphere complexation and oxygen vacancies acceleration effect. *J. Environ. Sci.* 2022, *120*, 18–29. [CrossRef]
- Chen, H.Y.; Zeng, H.B.; Yang, H.M. Phosphate removal from wastewater by magnetic amorphous lanthanum silicate alginate hydrogel beads. *Minerals* 2022, 12, 1–14. [CrossRef]
- Kong, X.M.; Bai, R.Y.; Wang, S.L.; Wu, B.; Zhang, R.Z.; Li, H.D. Recovery of phosphorus from aqueous solution by magnetic TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> composites. *Chem. Phys. Lett.* **2022**, *787*, 139234. [CrossRef]
- Xiong, H.X.; Peng, S.N.; Zhang, D. Phosphate adsorption removal by (La-doping) Mn-Al bimetal oxide composites. *Mater. Chem. Phys.* 2022, 285, 126195. [CrossRef]
- Zheng, W.S.; Sun, Y.; Gu, Y.P. Assembly of UiO-66 onto co-doped Fe<sub>3</sub>O<sub>4</sub> nanoparticles to activate peroxymonosulfate for efficient degradation of fenitrothion and simultaneous in-situ adsorption of released phosphate. *J. Hazard Mater.* 2022, 436, 129058. [CrossRef]
- 25. Liu, Z.G.; Gao, Y.; Jin, L.; Jin, H.; Xu, N.; Yu, X.Y.; Yu, S.H. Core-shell regeneration magnetic molecularly imprinted polymers-based SERS for sibutramine rapid detection. *ACS Sustain. Chem. Eng.* **2019**, *7*, 8168–8175. [CrossRef]
- 26. Yu, S.; Liu, Z.; Zhang, J.; Li, H.; Xu, N.; Yuan, X.X.; Wu, Y. An azo-coupling reaction-based surface enhanced resonance Raman scattering approach for ultrasensitive detection of salbutamol. *RSC Adv.* **2018**, *8*, 5536–5541. [CrossRef]
- Yu, S.H.; Liu, Z.G.; Li, H.W.; Zhang, J.P.; Yuan, X.X.; Jia, X.Y.; Wu, Y.Q. Combination of a graphene SERS substrate and magnetic solid phase micro-extraction used for the rapid detection of trace illegal additives. *Analyst* 2018, 143, 883–890. [CrossRef]
- 28. Yu, S.; Liu, Z.; Wang, W.; Jin, L.; Xu, W.; Wu, Y. Disperse magnetic solid phase microextraction and surface enhanced Raman scattering (Dis-MSPME-SERS) for the rapid detection of trace illegally chemicals. *Talanta* **2018**, *178*, 498–506. [CrossRef]
- Liu, Z.; Wang, Y.; Deng, R.; Yang, L.; Yu, S.; Xu, S.; Xu, W. Fe<sub>3</sub>O<sub>4</sub>@graphene oxide@Ag particles for surface magnet solid-phase extraction surface-enhanced Raman scattering (SMSPE-SERS): From sample pretreatment to detection all-in-one. ACS Appl Mater. Interfaces 2016, 8, 14160–14168. [CrossRef]
- 30. Liu, Z.; Wang, X.; Chen, J.; Gao, J.; Yu, S.; Wang, X. Three-template magnetic molecular imprinted polymer for the rapid separation and specific recognition of illegal cooking oil markers. *Microchem. J.* **2020**, *157*, 105052. [CrossRef]
- Liu, Z.; Yu, S.; Xu, S.; Zhao, B.; Xu, W. Ultrasensitive detection of capsaicin in oil for fast identification of illegal cooking oil by SERRS. Acs Omega 2017, 2, 8401–8406. [CrossRef]
- Wu, B.L.; Fang, L.P.; Fortner, J.D.; Guan, X.H.; Lo, I.M.C. Highly efficient and selective phosphate removal from wastewater by magnetically recoverable La(OH)<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposites. *Water Res.* 2017, *126*, 179–188. [CrossRef] [PubMed]
- 33. Xie, J.; Wang, Z.; Lu, S.Y.; Wu, D.Y.; Zhang, Z.J.; Kong, H.N. Removal and recovery of phosphate from water by lanthanum hydroxide materials. *Chem Eng.* **2014**, 254, 163–170. [CrossRef]
- Zhu, Y.L.; Zhang, D.F.; Chang, F.Q.; Zhu, J.; Wang, P.; Tan, F.; Li, X.H.; Li, L.; Hu, G.Z. CoFe<sub>2</sub>O<sub>4</sub>-CoFe microspheres for simultaneous electrochemical determination of trace lead(II) and cadmium(II) ions. *Surf. Interfaces* 2021, 25, 101266. [CrossRef]
- 35. Shojaei, B.; Miri, R.; Bazyari, A.; Thompson, L.T. Asphaltene adsorption on MgO, CaO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> nanoparticles synthesized via the pechini-type sol-gel method. *Fuel* **2022**, *321*, 124136. [CrossRef]
- Wang, L.; Wang, J.Y.; Yan, W.; He, C.; Shi, Y.J. MgFe<sub>2</sub>O<sub>4</sub>-biochar based lanthanum alginate beads for advanced phosphate removal. *Chem. Eng. J.* 2020, 387, 123305. [CrossRef]
- Zhang, Z.Y.; Fang, Y.R.; Zhuo, L.; Yuan, H.; Zhang, L.S. Reduced graphene oxide wrapped Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> yolk-shell nanostructures as a magnetic recyclable photocatalytic antibacterial agent. J. Alloy Compd. 2022, 904, 164001. [CrossRef]
- 38. Jais, F.M.; Ibrahim, S.; Yoon, Y.; Jang, M. Enhanced arsenate removal by lanthanum and nano-magnetite composite incorporated palm shell waste–based activated carbon. *Sep. Purif. Technol.* **2016**, *169*, 93–102. [CrossRef]
- Han, R.; Wang, F.; Zhao, C.F.; Zhang, M.X.; Cui, S.A.; Yang, J. Magnetic solid-phase extraction of pyrethroid and neonicotinoid insecticides separately in environmental water samples based on alkaline or acidic group-functionalized mesoporous silica. *Analyst* 2021, 147, 1995–2007. [CrossRef]
- 40. Jallouli, N.; Elghniji, K.; Hentati, O.; Ribeiro, A.R.; Silva, A.M.T.; Ksibi, M. UV and solar photo-degradation of naproxen: TiO<sub>2</sub> catalyst effect, reaction kinetics, products identification and toxicity assessment. *J. Hazard Mater.* **2016**, *304*, 329–336. [CrossRef]
- Wang, Y.; Wang, J.J.; Guan, M.; Kallem, P.; Qiu, H.D.; Chen, J. Bimetallic nitrogen-doped porous graphene for highly efficient magnetic solid phase extraction of 5-nitroimidazoles in environmental water. *Anal. Chim Acta* 2022, 1203, 339698. [CrossRef] [PubMed]
- 42. Han, Y.; Ma, Z.H.; Cong, H.N.; Wang, Q.Y.; Wang, X. Surface Chitosan-coated Fe<sub>3</sub>O<sub>4</sub> immobilized lignin for adsorbed phosphate radicals in solution. *Biochem. Eng. J.* **2022**, *187*, 108662. [CrossRef]

- 43. Ding, H.; Zhao, Y.L.; Duan, Q.L.; Wang, J.W.; Zhang, K.; Ding, G.Y.; Xie, X.M.; Ding, C.M. Efficient removal of phosphate from aqueous solution using novel magnetic nanocomposites with Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core and mesoporous CeO<sub>2</sub> shell. *J. Rare Earth* **2017**, *35*, 984–994. [CrossRef]
- 44. Yuan, L.; Qiu, Z.F.; Yuan, L.; Tariq, M.; Lu, Y.Q.; Yang, J.; Li, Z.; Lyu, S.G. Adsorption and mechanistic study for phosphate removal by magnetic Fe<sub>3</sub>O<sub>4</sub>-doped spent FCC catalysts adsorbent. *Chemosphere* **2019**, *219*, 183–190. [CrossRef] [PubMed]
- 45. Liu, T.; Chen, X.; Wang, X.; Zheng, S.R.; Yang, L.Y. Highly effective wastewater phosphorus removal by phosphorus accumulating organism combined with magnetic sorbent MFC@La(OH)<sub>3</sub>. *Chem. Eng. J.* **2018**, *335*, 443–449. [CrossRef]
- 46. Fang, W.K.; Wang, Z.; Xie, Q.; Liu, Y.; Wu, D.Y. Formation of Fe<sub>3</sub>O<sub>4</sub>@ZrO<sub>2</sub> nanocomposite and its performance as a magnetic adsorbent for phosphate uptake: Influences of end-point pH and stirring rate during synthesis process. *Chem Eng. Res. Des.* 2019, 145, 194–202. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.