

Article

Removal of Phosphorus by Ferric Ion-Rich Solutions Prepared Using Various Fe(III)-Containing Minerals

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Abstract: Various biological, chemical, and physical technologies have been studied to effectively remove total phosphorus (T-P) from wastewater. Among them, some mineral suspensions and cations in the aqueous phase have shown great potential for promoting phosphorus removal via chemical precipitation. Herein, we investigated the efficiency of T-P removal using various chemical-based cations (Fe^{2+} , Fe^{3+} , Mg^{2+} , and Al^{3+}); ferric ions (Fe^{3+}) showed the highest T-P-removal efficiency (33.1%), regardless of the type of anion (Cl^- , NO_3^- , and SO_4^{2-}). To prepare natural Fe^{3+} -rich solutions, three different Fe(III)-rich minerals (hematite, lepidocrocite, and magnetite) were treated with various HCl concentrations to maximize the dissolved Fe^{3+} amounts. Lepidocrocite in 2 N HCl showed the most effective Fe^{3+} -leaching ability (L-Fe dissolved solution). Almost no significant difference in Fe^{3+} leaching was observed between HCl and H_2SO_4 , whereas lepidocrocite-2 N H_2SO_4 showed the highest T-P-removal ability (91.5%), with the formation of amorphous Fe(III)-P precipitates. The L-Fe dissolved solution exhibited a higher T-P-removal efficiency than polyammonium chloride under real wastewater conditions. Our results can provide fundamental knowledge about the effect of cations on T-P removal in wastewater treatment and the feasibility of using the Fe^{3+} leaching solution prepared from Fe(III)-containing minerals for efficient T-P removal via chemical precipitation.

Keywords: Fe(III)-rich minerals; lepidocrocite; Fe^{3+} dissolved solution; T-P removal; chemical precipitation



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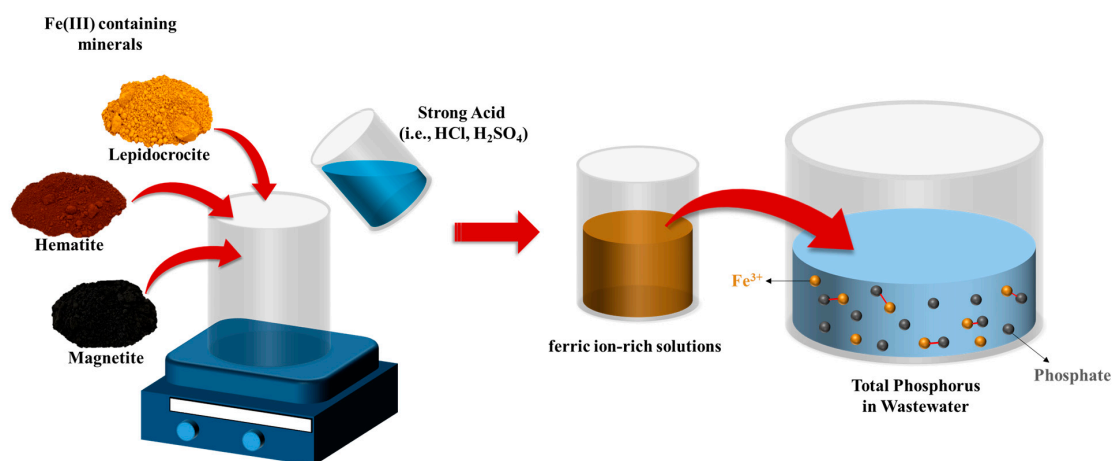
1. Introduction

The total amount of phosphorus (T-P) in inorganic and organic phosphorus compounds in water is an essential element usually generated from various anthropogenic sources such as detergents, fertilizers, animal feedlots, meat, and livestock wastewater [1–4]. Economic development and population growth driven by rapid industrialization have increased the demand for phosphorus as an agricultural fertilizer to stimulate the growth of plants and chemical manufacturing processes [5,6]. However, it is a substance that causes serious environmental problems [7]. When wastewater containing a large amount of phosphorus is discharged into rivers, lakes, or the sea, it greatly affects the surrounding ecosystem owing to the excessive accumulation of nutrients in water bodies [8]. Eutrophication and algal blooms may occur by accelerating the growth of algae and organisms, endangering the existence of aquatic plants and animals due to the lack of oxygen. Therefore, regulations to reduce phosphorus emissions have increased worldwide, resulting in reinforced emission limits for wastewater treatment facilities [9].

In general, three methods for phosphorus removal are typically used worldwide: biological (biomass growth, bacterial polyphosphate accumulation), physical (settling, filtration), and chemical (precipitation) treatments [10–16]. Each wastewater treatment method has its own advantages and disadvantages. The biological process is simple, inexpensive, and well-accepted by the public [17]. However, they usually require large areas, generate large amounts of sludge, and are slow and inconsistent in maintaining low phosphorus concentrations [17,18]. Although physical methods, such as membranes

with reverse osmosis, are known to be able to remove almost all of the contaminants in wastewater, these systems require high pressure, which in turn requires a reliable and demanding energy source [19]. In contrast, chemical-based phosphorus removal is associated with high sludge production and disposal challenges but is extremely durable, technologically simple, and economically advantageous [8]. Physicochemical treatment using metal ions is a representative removal technique, and some studies have shown the potential use of metal-containing minerals (Ca, Fe, Mg, and Al) [16,20,21]. However, the direct application of metal-containing minerals has some drawbacks, such as the massive production of unreacted mineral sludge and waste [22]. Therefore, a novel approach should be developed to overcome the disadvantages of the direct use of metal-containing minerals and achieve effective phosphorus precipitation in wastewater treatment plants (WWTP).

In the present study, we first investigated T-P removal by various chemical-based cations (Fe^{2+} , Fe^{3+} , Mg^{2+} , and Al^{3+}) to determine the most efficient cation for the chemical precipitation of T-P. Further, the effect of the number of anions on T-P removal was evaluated using various Fe^{3+} solutions prepared using different Fe(III) chemicals. To prepare natural Fe^{3+} -dissolved solutions, three different Fe(III)-containing minerals—hematite ($\alpha\text{-Fe}_2\text{O}_3$), lepidocrocite ($\gamma\text{-FeOOH}$), and magnetite (Fe_3O_4)—were used for Fe(III) extraction at different HCl concentrations and applied for T-P removal (Scheme 1). Finally, various parametric studies and surface analyses, such as X-ray diffraction (XRD), scanning electron microscope-energy dispersive spectrometry (SEM-EDS), and Fourier-transform infrared spectroscopy (FTIR), were conducted to investigate the T-P precipitation mechanism.



Scheme 1. Experimental concept of this study.

2. Materials and Methods

2.1. Chemicals and Minerals

Sodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$; 98.0%; Samchun Pure Chemical Co., LTD., Seoul, Korea), hydrochloric acid (HCl; 35%; Daejung Chemical & Metal Co., LTD., Seoul, Korea), Iron(II) chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; 98%; Sigma Aldrich, Saint Louis, MO, USA), Iron(III) chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; 97%; Sigma Aldrich, USA), iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; $\geq 98\%$; Sigma Aldrich, USA), iron(II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; $\geq 99\%$; Sigma Aldrich, USA), magnesium chloride (MgCl_2 ; Sigma Aldrich, USA), aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$; $>99\%$; Sigma Aldrich, USA), and sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$; Sigma Aldrich, USA) were used to conduct the experiments. Hematite ($\alpha\text{-Fe}_2\text{O}_3$), lepidocrocite ($\gamma\text{-FeOOH}$), and magnetite (Fe_3O_4) were obtained from the Bayferrox LANXESS Corp. In this study, deionized water (DIW; 18.3 M Ω) obtained from an ultrapure filtration system (HUMAN POWER I+ water purification system) was used to prepare all solutions.

2.2. T-P Removal via Chemical Induction Using Cation Solutions

A batch experiment was performed using a glass beaker to characterize the removal of T-P via chemical induction using cation solutions. The PO_4^{3-} -P solution (100 mg·L $^{-1}$)

was prepared in a 200 mL beaker. T-P-removal experiments were initiated by adding cation solutions (Fe^{2+} , Fe^{3+} , Mg^{2+} , and Al^{3+} , 10 mL, 1 mM) and different Fe^{2+} (FeCl_2 and FeSO_4) and Fe^{3+} anions (FeCl_3 and $\text{Fe}(\text{NO}_3)_3$).

2.3. T-P Removal by Solutions Containing Dissolved Fe^{3+} That Were Prepared Using Fe(III)-Containing Minerals

To determine the appropriate concentration of Fe minerals and strong acids, a batch experiment was conducted with $10 \text{ g}\cdot\text{L}^{-1}$ of Fe(III)-containing minerals, and the kinetics of Fe dissolution were monitored. Other experiments were conducted with Fe(III)-containing minerals ($20 \text{ g}\cdot\text{L}^{-1}$) to confirm the amount of Fe dissolution after mixing for 24 h at different HCl concentrations.

Batch kinetic experiments were conducted to investigate the maximum amount of Fe dissolution with different contents of lepidocrocite ($20\text{--}200 \text{ g}\cdot\text{L}^{-1}$) in 2 N HCl, and $40 \text{ g}\cdot\text{L}^{-1}$ was selected as the optimal mineral content to investigate the T-P removal by lepidocrocite-Fe(III) dissolved solution (L-Fe dissolved solution) prepared with different strong acids (HCl and H_2SO_4) and concentrations (1, 2, and 4 N). An identical amount of Fe^{3+} ($3 \text{ mg}\cdot\text{L}^{-1}$) was transferred to a beaker containing $10 \text{ mg}\cdot\text{L}^{-1}$ of PO_4^{3-} -P for the T-P-removal experiments.

For practical application, the T-P-removal efficiencies of different amounts of initial Fe^{3+} (1, 2, and $5 \text{ mg}\cdot\text{L}^{-1}$) in L-Fe dissolved solutions were compared with those of a commercial polyammonium chloride (PAC) ($1, 2, 5 \text{ mg}\cdot\text{L}^{-1}$). An exact amount of artificial PO_4^{3-} -P solution was spiked into a beaker containing approximately $1 \text{ mg}\cdot\text{L}^{-1}$ T-P of secondary treated real wastewater (Initial pH = 7.4) obtained from a WWTP in Bucheon, South Korea. The prepared initial concentration of T-P was $10 \text{ mg}\cdot\text{L}^{-1}$, as the other laboratory experiments described above.

2.4. Analytical Methods

The concentration of T-P in aqueous solution was measured using a spectrophotometer (DR 3900, HACH) after filtering the suspension through a $0.2 \mu\text{m}$ membrane filter (Whatman). The molybdovanadate method with acid persulfate digestion (method 10127) was used in this study. The Fe concentration of the suspension was measured using a UV-Vis spectrometer (GENESYS 10S, Thermo Scientific, Waltham, MA, USA). The concentration of Fe was quantified by measuring the peak of absorbance (562 nm) using the ferrozine method [23].

Changes in the functional groups on the surface of the precipitates after T-P removal were monitored using an FTIR spectrometer (NICOLET iS10, Thermo) with a Smart OMNI-Transmission Accessory. The IR spectra ($4000\text{--}400 \text{ cm}^{-1}$) were recorded at a resolution of 4 cm^{-1} by averaging 50 scans. The mixture of powders (mass ratio of KBr to sample was 50:1) was transferred to a 7-mm pellet die, and the KBr pellet was analyzed after fabrication with a pellet press.

To identify the structural characteristics of the precipitates, XRD (Rigaku Smartlab, Tokyo, Japan) was performed. The morphology and local elemental composition of the precipitates were identified by SEM-EDS analysis using an EM-30AXN instrument (Coxem, Daejeon, Korea).

3. Results and Discussion

3.1. Removal of T-P via Chemical Induction Using Cation Solutions

Figure 1a shows the amount of T-P ($100 \text{ mg}\cdot\text{L}^{-1}$) removed by different cation solutions. A comparative experiment was performed to identify the most effective cation for T-P removal. The Fe^{3+} solution showed the highest removal efficiency (33.1%), followed by Mg^{2+} (7.3%), Fe^{2+} (6.2%), and Al^{3+} (4.1%), indicating the great potential of the Fe^{3+} solution for T-P removal. The difference in the T-P-removal effects could be explained by the different moles of Fe^{2+} and Fe^{3+} required for T-P removal (Equations (1) and (2)). The

general mechanism of the reaction of Fe^{2+} and Fe^{3+} with PO_4^{3-} follows the following chemical equations:

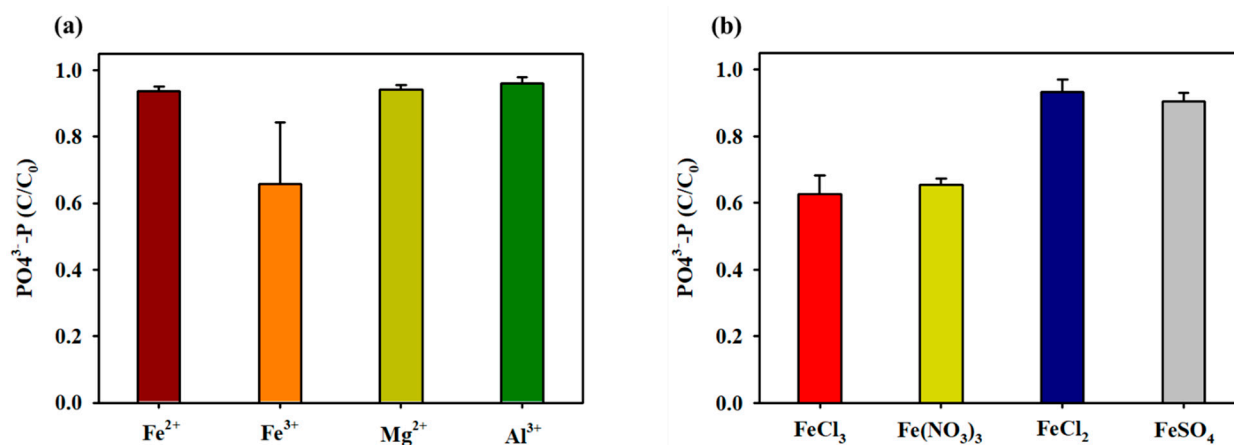
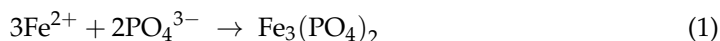


Figure 1. Removal of T-P by (a) different cation solutions and (b) Fe solutions with different anions. Experimental conditions: [cations] = 1 mM, $[\text{PO}_4^{3-}\text{-P}]_0 = 100 \text{ mg}\cdot\text{L}^{-1}$.

The anion effect of the Fe^{2+} and Fe^{3+} solutions was further investigated to identify the potential loss of T-P by the anion during the reaction (Figure 1b). FeCl_2 and FeSO_4 (both Fe^{2+} chemicals) showed only 6.8% and 9.5% T-P removal, whereas almost 37.4% and 34.4% T-P removal was obtained by FeCl_3 and $\text{Fe}(\text{NO}_3)_3$ (both Fe^{3+} chemicals), respectively. As a result, we concluded that the effect of the Fe charge amount was greater than that of the counter anion in the T-P removal by Fe-dissolved solutions when various anions were used.

3.2. Monitoring Fe(III) Dissolution

To investigate the Fe dissolution of Fe-containing minerals ($10 \text{ g}\cdot\text{L}^{-1}$) in 2 N HCl, we monitored the concentrations of Fe(II), Fe(III), and total Fe during the 1-h reaction (Figure 2a–c). The dissolved Fe concentrations in lepidocrocite and magnetite suspensions increased continuously and reached an equilibrium state, except in the case of hematite, which showed an almost negligible amount of Fe dissolution owing to its high strength and crystallinity compared to the other minerals [24]. In the case of magnetite, total Fe concentrations of $5472.5 \text{ mg}\cdot\text{L}^{-1}$ and $5919.9 \text{ mg}\cdot\text{L}^{-1}$ were observed at 24 and 51 h, respectively. In addition, 3699.3 and $4490.8 \text{ mg}\cdot\text{L}^{-1}$ of dissolved Fe^{3+} were obtained at each time because magnetite has a mixed Fe oxidation state ($\text{Fe(II):Fe(III)} = 1:2$). On the other hand, lepidocrocite showed a similar amount of total Fe ($6050.1 \text{ mg}\cdot\text{L}^{-1}$ at 51 h) to that of magnetite, but a higher Fe^{3+} amount ($5538.4 \text{ mg}\cdot\text{L}^{-1}$ at 51 h) than that of magnetite. Although lepidocrocite is an Fe(III) oxyhydroxide, we observed a small amount of dissolved Fe^{2+} in 2 N HCl, probably due to the presence of some Fe(II) impurities during mineral synthesis.

Figure 2d,e show a comparison of Fe dissolution at different HCl concentrations (2–8 N) for lepidocrocite and magnetite ($20 \text{ g}\cdot\text{L}^{-1}$). For lepidocrocite, we observed a slight increase in Fe dissolution (both total Fe and Fe^{3+} ions) with different HCl concentrations because lepidocrocite tends to be easily dissolved in a wide range of acidic solutions. For magnetite, a significant increase in Fe dissolution was observed as the HCl concentration increased. Interestingly, the gap between the total Fe and Fe^{3+} in the magnetite-HCl suspension grew continuously closer because the dissolved Fe^{2+} can be oxidized to Fe^{3+} in a strong acid [25]. As a result, the amount of Fe^{3+} dissolved in 2 N HCl was $10,213.6 \text{ mg}\cdot\text{L}^{-1}$ for lepidocrocite, which was similar to that of magnetite in 6 M ($10,295.5 \text{ mg}\cdot\text{L}^{-1}$). Because there was no significant difference in the amount of Fe dissolution after 24 h in the experiments, subsequent experiments were conducted with a solution obtained by dissolving lepidocrocite (L-Fe dissolved solution) for 24 h.

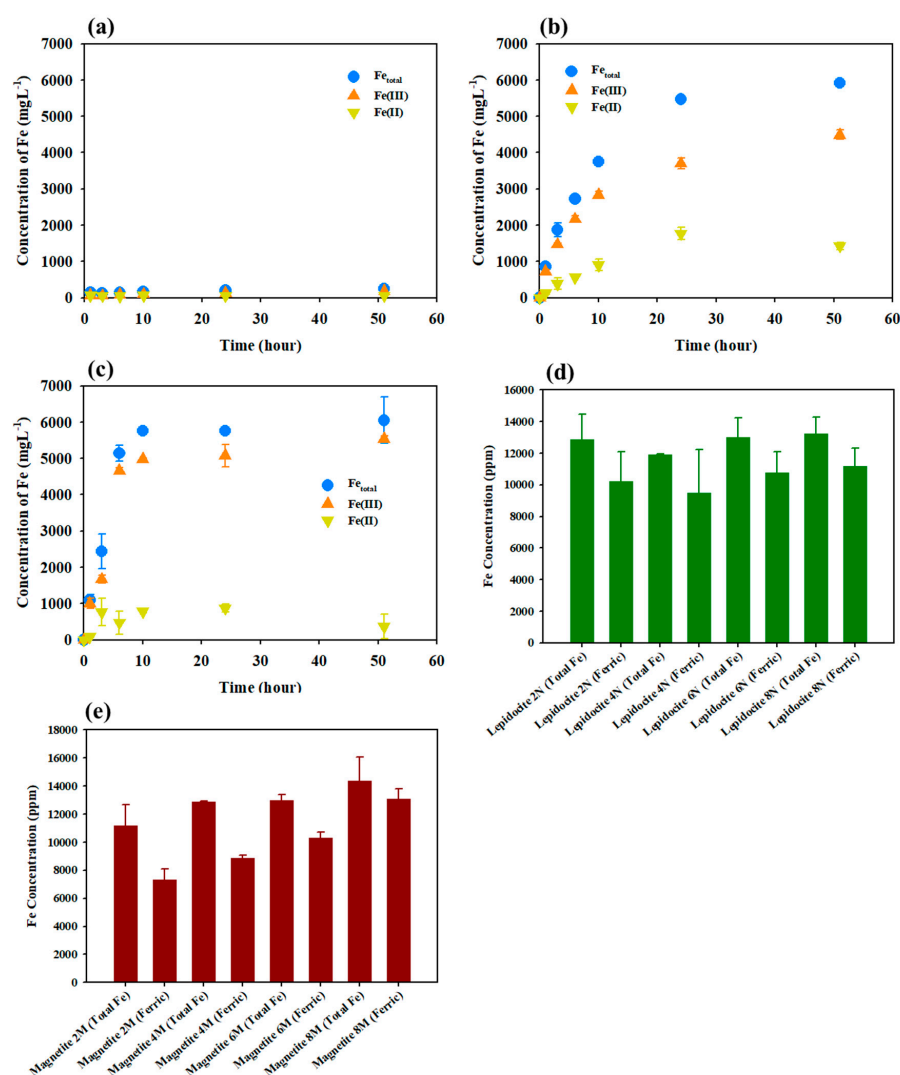


Figure 2. Kinetics of Fe dissolution in suspensions of Fe(III)-containing minerals (2 N HCl); (a) hematite, (b) magnetite, (c) lepidocrocite, (d) dissolved Fe amount for lepidocrocite, and (e) magnetite in different HCl concentrations. Experimental conditions: (a–c) $[\text{minerals}]_0 = 10 \text{ g} \cdot \text{L}^{-1}$, (d,e) $[\text{minerals}]_0 = 20 \text{ g} \cdot \text{L}^{-1}$.

3.3. Removal of T-P by L-Fe Dissolved Solution

Figure 3a shows the equilibrium amount of Fe^{3+} dissolved in the lepidocrocite suspension at different initial contents. In the case of a small amount of lepidocrocite ($<40 \text{ g} \cdot \text{L}^{-1}$), the dissolved Fe^{3+} amount rapidly increased as the lepidocrocite content increased but reached the maximum concentration after almost $100 \text{ g} \cdot \text{L}^{-1}$. Thus, the initial lepidocrocite concentration was fixed at $40 \text{ g} \cdot \text{L}^{-1}$ for further studies. We also conducted additional experiments to investigate the amount of Fe dissolved at various normal concentrations of HCl and H_2SO_4 (Figure 3b,c). The dissolved amount of Fe continued to increase as the acid concentration increased to 2 N. Specifically, the total dissolved Fe in 2 N HCl was $24,951.7 \text{ mg} \cdot \text{L}^{-1}$, which was slightly higher than that of 2 N H_2SO_4 ($23,089.7 \text{ mg} \cdot \text{L}^{-1}$). With regard to Fe^{3+} , 2 N HCl and 2 N H_2SO_4 showed dissolved Fe contents of $22,988.5 \text{ mg} \cdot \text{L}^{-1}$ and $21,018.4 \text{ mg} \cdot \text{L}^{-1}$ with a negligible amount of Fe^{2+} ($1963.2 \text{ mg} \cdot \text{L}^{-1}$ and $1071.3 \text{ mg} \cdot \text{L}^{-1}$), respectively. These results indicate that higher amounts of total Fe and Fe^{3+} were obtained using the suspension prepared using HCl at a normal concentration of 2 N.

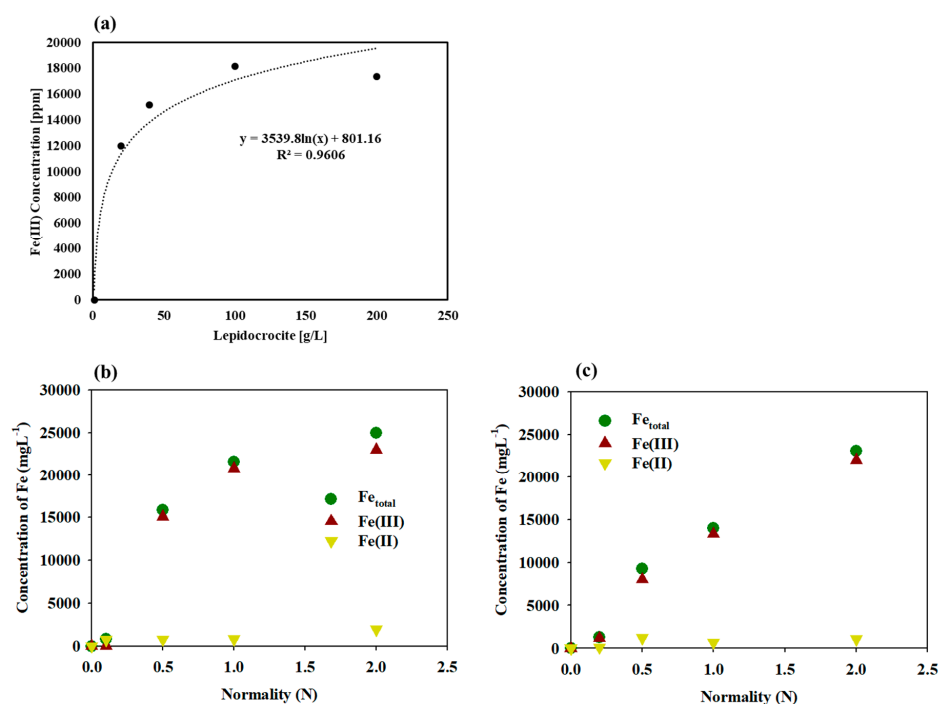


Figure 3. Concentrations of Fe ions under different variables; (a) Fe^{3+} dissolution at different amounts of lepidocrocite (2 N HCl), (b) at different normality of HCl, and (c) H_2SO_4 . Experimental conditions: (b,c) $[\text{minerals}]_0 = 40 \text{ g} \cdot \text{L}^{-1}$.

To determine the removal capacity of the L-Fe dissolved solution prepared in different acids, batch experiments were performed using the same amount of Fe^{3+} dissolved solutions prepared at different acid concentrations. All the L-Fe dissolved solutions prepared at different HCl concentrations showed almost identical removal efficiencies (1 N = 37.6%, 2 N = 37.0%, and 4 N = 37.2%) (Figure 4a). We also observed that pH was not significantly reduced in 1 and 2 N HCl-prepared solutions due to the injection of a small volume of Fe dissolved stock solution, while 4 N showed a slight decrease in pH from 7.2 to 6.53. The results also indicated that pH variation may not have significantly influenced T-P removal in this study. Figure 4b shows the cases of T-P removal by H_2SO_4 -prepared solutions. L-Fe dissolved in 2 N H_2SO_4 showed the highest removal efficiency (51.8%), followed by solutions dissolved in 4 N (40.9%) and 1 N (33.8%). Similar to the HCl experiments, almost no change in the pH was observed in any of the H_2SO_4 experiments. The results confirmed that the L-Fe dissolved solution prepared with 2 N H_2SO_4 was the most effective for the removal of T-P. This might be because anions compete with phosphate for adsorption and inhibit the adsorption of phosphorus by ferric iron ions [26]. Although the anion inhibition effects of SO_4^{2-} and Cl^- were not significantly different, we suspected that the inhibition effect of anions could be reduced owing to the half molarity of anions in the H_2SO_4 solution compared to that of the HCl solution.

Figure 4c shows the pH effect on T-P removal, showing that alkaline pHs higher than 9 can remove T-P via OH-precipitation. However, there was no significant T-P removal and pH variation at initial pH 7, indicating the neglect removal of T-P by OH-precipitation and pH effect in this study, respectively. To further validate the practical application in the WWTP, we obtained real wastewater (secondary treated wastewater) and used it to compare the removal efficiency of T-P between the L-Fe dissolved solution and PAC (Figure 5). In general, the T-P-removal efficiency continuously increased as the metal ion content increased. The T-P-removal efficacy and metal ion contents were highly correlated for both cases, with R^2 values of 0.99 and 0.97, respectively. Interestingly, the L-Fe dissolved solution showed a slope of 18.7 (Figure 5a), whereas PAC showed a slope of

12.1 (Figure 5b), indicating that the L-Fe dissolved solution had a higher efficiency for T-P removal in practical applications.

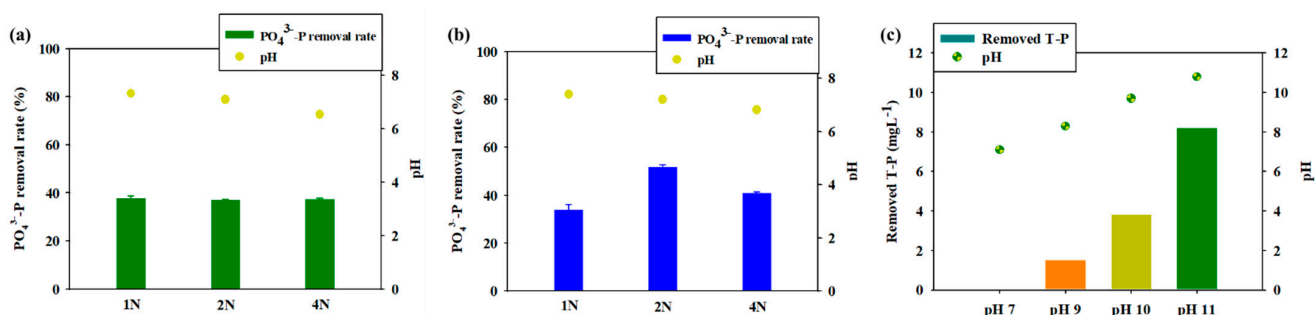


Figure 4. T-P-removal efficiency using L-Fe dissolved solution with different normality; (a) L-Fe dissolved solutions with HCl mixing, (b) L-Fe dissolved solutions with H₂SO₄ mixing. Experimental conditions: $[\text{PO}_4^{3-}\text{-P}]_0 = 10 \text{ mg}\cdot\text{L}^{-1}$, $[\text{Fe}^{3+} \text{ solution}]_0 = 3 \text{ mg}\cdot\text{L}^{-1}$. (c) T-P removal efficiency and variation of final pH in different pH solutions.

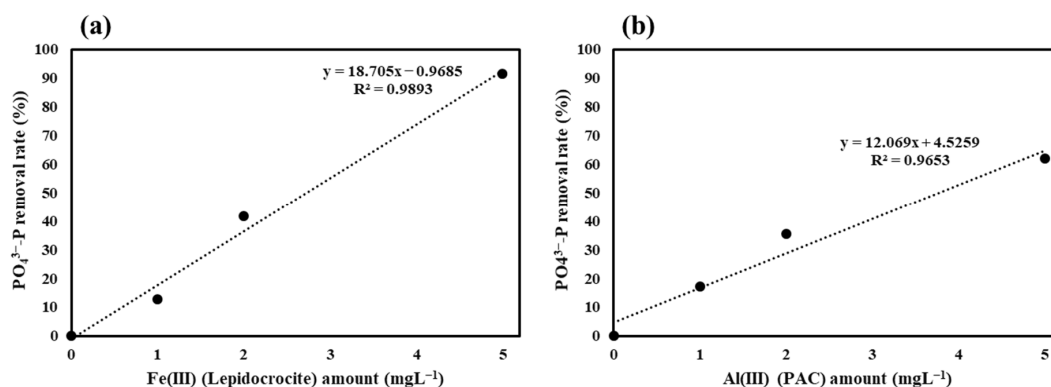


Figure 5. Removal efficiency of T-P by (a) L-Fe dissolved solutions prepared in 2 N H₂SO₄ (b) and PAC.

The matrix effect in wastewater on T-P removal may be negligible because no significant difference in T-P removal was observed between the experimental data obtained from real wastewater and DI water. For comparison with other studies, the most frequently used ferric-type coagulant, i.e., ferric chloride, was compared at the same ratio of Fe:P (0.9). Almost complete T-P removal (100%) was observed in this study, whereas other ferric chloride-based experiments showed lower removal efficiency (~80%) [27,28], indicating the applicability of the L-Fe dissolved solution.

3.4. Analysis of the Precipitates

Figure 6 shows the FTIR spectra of pure lepidocrocite and P-Fe precipitates using the L-Fe solution prepared with different acids. The broad absorption near 3100 cm^{-1} was assigned to the typical O-H stretching vibration band of oxyhydroxides of pure lepidocrocite (Figure 6a) [29]. The bands around 1160 , 1020 , and 750 cm^{-1} that appeared in the pure lepidocrocite sample are attributed to their characteristic vibrations [30,31]. The absorption band near 1650 cm^{-1} is ascribed to the vibrations of the H-O-H group, indicating the presence of physisorbed water on the surface due to weathering over time, whereas the broad band around 3410 cm^{-1} is assigned to the OH group, which is associated with Fe [32,33]. The asymmetric stretching vibration of the PO_4^{3-} group was detected at approximately 1060 cm^{-1} in Figure 6b,c, which is caused by the chemical bond between the T-P and L-Fe dissolved solutions [34]. No significant differences were observed in the FTIR results of the HCl and H₂SO₄ prepared samples, except that the HCl sample revealed a peak at 669 cm^{-1} , indicating low absorption of C-Cl (Figure 6b) [35].

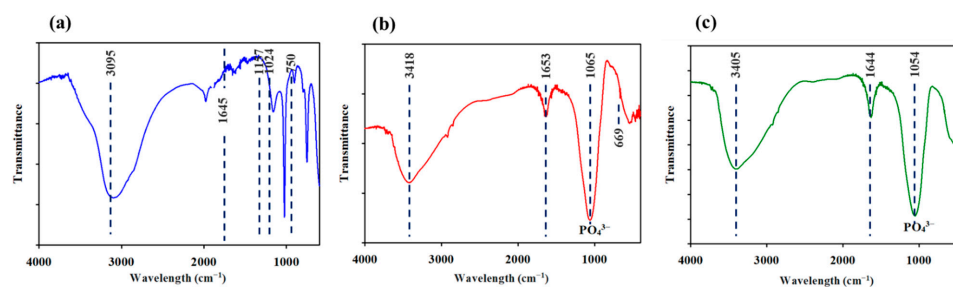


Figure 6. FTIR spectra from different materials; (a) pure lepidocrocite, P-Fe precipitates after using L-Fe dissolved solution with (b) HCl and (c) H_2SO_4 .

To investigate the physical characteristics of the precipitates after T-P removal using the L-Fe dissolved solution with H_2SO_4 , additional XRD and SEM-EDS analyses were performed (Figure 7). Compared to pure lepidocrocite, which showed an almost homogenous particle size and the absence of P (Figure 7a), the precipitate obtained after using the L-Fe dissolved solution with H_2SO_4 (Figure 7b) showed the formation of different-sized particles and a significant decrease in Fe content with an increase in phosphorus and sulfur contents. The initial Fe content of lepidocrocite (55.8%) decreased to 24.6%, and the contents of P and S increased from 0% to 11.7% and 2.8%, respectively, after T-P removal (Table 1). This result confirms the formation of Fe(III)-P precipitates and the rest of the ferric sulfate solution used in the present study. An additional XRD analysis was conducted to investigate the mineral phase of the precipitate (Figure 7c), but no clear crystalline peaks were observed, indicating the formation of amorphous Fe(III)-P precipitates, such as FePO_4 [36].

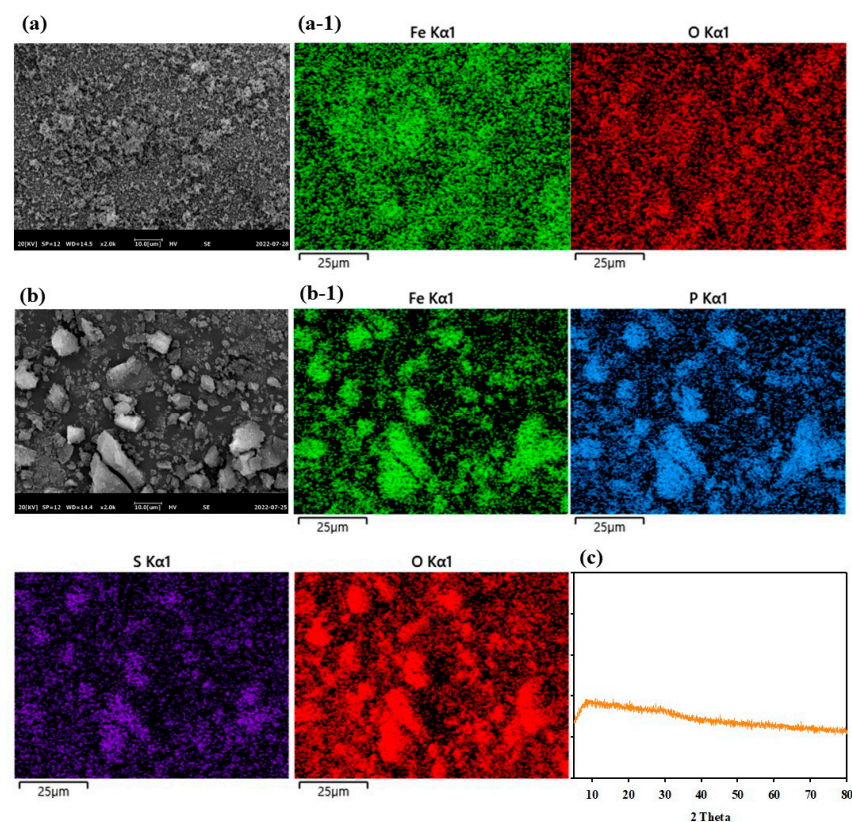


Figure 7. SEM-EDS analysis of (a) pure lepidocrocite, (b) the precipitates after T-P removal by L-Fe dissolved solution with H_2SO_4 , and (c) XRD results of precipitates after T-P removal by lepidocrocite- H_2SO_4 solution. EDS electron mapping for different conditions (a-1,b-1).

Table 1. EDS results of precipitates before and after reaction.

	Fe (wt%)	O (wt%)	P (wt%)	S (wt%)
Before reaction	55.8	43.3	0	0
After reaction	24.6	60.2	11.7	2.8

4. Conclusions

In this study, Fe^{3+} showed the highest T-P-removal efficiency compared to Fe^{2+} , Mg^{2+} , and Al^{3+} , and the number of anions did not show a significant effect when Fe^{2+} and Fe^{3+} solutions were used for T-P removal. Among the three different Fe(III)-containing minerals, lepidocrocite dissolved in 2 N H_2SO_4 for 24 h showed the highest T-P-removal efficiency, owing to its relatively soft crystalline characteristics, resulting in high Fe^{3+} dissolution in a strong acid. Interestingly, the T-P-removal efficiency under real wastewater conditions revealed that the L-Fe solution surpassed the efficiency of PAC at the same Fe^{3+} and Al^{3+} content. Because we did not observe any significant pH drop after applying the L-Fe dissolved solution and obtained a high T-P-removal efficiency without additional unreacted chemical/mineral sludge, the results highlight the potential use of mineral-dissolved Fe^{3+} solution for effective T-P removal in WWTP via cost-effective and eco-friendly methods without additional sludge production.

Author Contributions: Writing—Original draft preparation, investigation, data curation, J.J.; investigation, data curation, M.C.; investigation, writing, A.K.R.P.; investigation, visualization, J.L.; supervision, project administration, funding acquisition, writing—review and editing, S.B. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in the study is available on request from the corresponding author.

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Conflicts of Interest: The author declares that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Kroiss, H.; Rechberger, H.; Egle, L. Phosphorus in water quality and waste management. *Integr. Waste Manag.* **2011**, *2*, 18482. [\[CrossRef\]](#)
2. Holtan, H.; Kamp-Nielsen, L.; Stuanes, A.O. Phosphorus in soil, water and sediment: An overview. *Phosphorus Freshw. Ecosyst.* **1988**, *34*, 19–34. [\[CrossRef\]](#)
3. Bouwman, L.; Goldewijk, K.K.; Van Der Hoek, K.W.; Beusen, A.H.W.; van Vuuren, D.P.; Willems, J.; Rufino, M.C.; Stehfest, E. Exploring global changes in nitrogen and phosphorus cycles in agriculture induced by livestock production over the 1900–2050 period. *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 20882–20887. [\[CrossRef\]](#)
4. Jarvie, H.P.; Neal, C.; Withers, P.J. Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? *Sci. Total Environ.* **2006**, *360*, 246–253. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Shin, J.; Kwak, J.; Kim, S.; Son, C.; Lee, Y.-G.; Kim, J.; Bae, S.; Park, Y.; Lee, S.-H.; Chon, K. Highly selective recovery of phosphate ions using a novel carbonaceous adsorbent synthesized via co-pyrolysis of spent coffee grounds and steel slags: A potential phosphatic fertilizer. *Chem. Eng. J.* **2023**, *451*, 138978. [\[CrossRef\]](#)
6. Wang, H.; Xiao, K.; Yang, J.; Yu, Z.; Yu, W.; Xu, Q.; Wu, Q.; Liang, S.; Hu, J.; Hou, H.; et al. Phosphorus recovery from the liquid phase of anaerobic digestate using biochar derived from iron-rich sludge: A potential phosphorus fertilizer. *Water Res.* **2020**, *174*, 115629. [\[CrossRef\]](#)
7. Correll, D.L. The role of phosphorus in the eutrophication of receiving waters: A review. *J. Environ. Qual.* **1998**, *27*, 261–266. [\[CrossRef\]](#)
8. Mkilima, T.; Bazarbayeva, T.; Assel, K.; Nurmukhanbetova, N.N.; Ostretsova, I.B.; Khamitova, A.S.; Makhanova, S.; Sergazina, S. Pore size in the removal of phosphorus and nitrogen from poultry slaughterhouse wastewater using polymeric nanofiltration membranes. *Water* **2022**, *14*, 2929. [\[CrossRef\]](#)

9. Bashar, R.; Gungor, K.; Karthikeyan, K.; Barak, P. Cost effectiveness of phosphorus removal processes in municipal wastewater treatment. *Chemosphere* **2018**, *197*, 280–290. [\[CrossRef\]](#)
10. Peng, Y.; He, S.; Wu, F. Biochemical processes mediated by iron-based materials in water treatment: Enhancing nitrogen and phosphorus removal in low C/N ratio wastewater. *Sci. Total Environ.* **2021**, *775*, 145137. [\[CrossRef\]](#)
11. Jia, Y.; Zeng, W.; Fan, Z.; Meng, Q.; Liu, H.; Peng, Y. An effective titanium salt dosing strategy for phosphorus removal from wastewater: Synergistic enhancement of chemical and biological treatment. *Sci. Total Environ.* **2022**, *842*, 156960. [\[CrossRef\]](#)
12. Nguyen, T.A.H.; Ngo, H.H.; Guo, W.S.; Nguyen, T.T.; Vu, N.D.; Soda, S.; Nguyen, T.H.H.; Nguyen, M.K.; Tran, T.V.H.; Dang, T.T.; et al. White hard clam (*Meretrix lyrata*) shells as novel filter media to augment the phosphorus removal from wastewater. *Sci. Total Environ.* **2020**, *741*, 140483. [\[CrossRef\]](#)
13. Wang, H.; Dai, J.; Chen, H.; Wang, F.; Zhu, Y.; Liu, J.; Zhou, B.; Yuan, R. Adsorption of phosphate by Mg/Fe-doped wheat straw biochars optimized using response surface methodology: Mechanisms and application in domestic sewage. *Environ. Eng. Res.* **2022**, *28*, 210602. [\[CrossRef\]](#)
14. Naz, A.; Masood, H.; Ehsan, S.; Tahir, T. Removal of acid black 1 by acacia concinna; adsorption kinetics, isotherm and thermodynamic study. *Membr. Water Treat.* **2020**, *11*, 407–416. [\[CrossRef\]](#)
15. Nielsen, P.H.; McIlroy, S.J.; Albertsen, M.; Nierychlo, M. Re-evaluating the microbiology of the enhanced biological phosphorus removal process. *Curr. Opin. Biotechnol.* **2019**, *57*, 111–118. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Bellier, N.; Chazarenc, F.; Comeau, Y. Phosphorus removal from wastewater by mineral apatite. *Water Res.* **2006**, *40*, 2965–2971. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Crini, G.; Lichtfouse, E. Advantages and disadvantages of techniques used for wastewater treatment. *Environ. Chem. Lett.* **2019**, *17*, 145–155. [\[CrossRef\]](#)
18. Pratt, C.; Parsons, S.A.; Soares, A.; Martin, B.D. Biologically and chemically mediated adsorption and precipitation of phosphorus from wastewater. *Curr. Opin. Biotechnol.* **2012**, *23*, 890–896. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Kyllönen, H.; Heikkinen, J.; Ceras, J.; Fernandez, C.; Porc, O.; Grönroos, A. Membrane-based conceptual design of reuse water production from candy factory wastewater. *Water Sci. Technol.* **2021**, *84*, 1389–1402. [\[CrossRef\]](#)
20. Yin, Z.; Chen, Q.; Zhao, C.; Fu, Y.; Li, J.; Feng, Y.; Li, L. A new approach to removing and recovering phosphorus from livestock wastewater using dolomite. *Chemosphere* **2020**, *255*, 127005. [\[CrossRef\]](#)
21. Li, R.; Kelly, C.; Keegan, R.; Xiao, L.; Morrison, L.; Zhan, X. Phosphorus removal from wastewater using natural pyrrhotite. *Colloids Surfaces A Physicochem. Eng. Asp.* **2013**, *427*, 13–18. [\[CrossRef\]](#)
22. Paul, E.; Laval, M.L.; Sperandio, M. Excess sludge production and costs due to phosphorus removal. *Environ. Technol.* **2001**, *22*, 1363–1371. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Jung, J.; Kim, J.; Yoon, S.; Reddy, P.A.K.; Hwang, Y.; Bae, S. The role of Fe dissolution in olivine-hydroxylamine-induced Fenton reaction for enhanced oxidative degradation of organic pollutant. *Chemosphere* **2022**, *306*, 135557. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Bae, S.; Lee, W. Enhanced reductive degradation of carbon tetrachloride by biogenic vivianite and Fe(II). *Geochim. Et Cosmochim. Acta* **2012**, *85*, 170–186. [\[CrossRef\]](#)
25. Yoon, S.; Bae, S. Novel synthesis of nanoscale zerovalent iron from coal fly ash and its application in oxidative degradation of methyl orange by fenton reaction. *J. Hazard. Mater.* **2018**, *365*, 751–758. [\[CrossRef\]](#)
26. Wu, H.-F.; Wang, J.-P.; Duan, E.-G.; Hu, W.-H.; Dong, Y.-B.; Zhang, G.-Q. Phosphorus removal by adsorbent based on poly-aluminum chloride sludge. *Water Sci. Eng.* **2020**, *13*, 193–201. [\[CrossRef\]](#)
27. Caravelli, A.H.; Contreras, E.M.; Zaritzky, N.E. Phosphorous removal in batch systems using ferric chloride in the presence of activated sludges. *J. Hazard. Mater.* **2010**, *177*, 199–208. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Zhou, Y.; Xing, X.-H.; Liu, Z.; Cui, L.; Yu, A.; Feng, Q.; Yang, H. Enhanced coagulation of ferric chloride aided by tannic acid for phosphorus removal from wastewater. *Chemosphere* **2008**, *72*, 290–298. [\[CrossRef\]](#)
29. Cui, H.; Ren, W.; Lin, P.; Liu, Y. Structure control synthesis of iron oxide polymorph nanoparticles through an epoxide precipitation route. *J. Exp. Nanosci.* **2012**, *8*, 869–875. [\[CrossRef\]](#)
30. Moreno, E.M.; Zayat, M.; Morales, M.P.; Serna, C.J.; Roig, A.; Levy, D. Preparation of narrow size distribution superparamagnetic γ -Fe₂O₃ nanoparticles in a sol-gel transparent SiO₂ matrix. *Langmuir* **2002**, *18*, 4972–4978. [\[CrossRef\]](#)
31. Burstein, G.T. The iron oxides: Structure, properties, reactions, occurrence and uses. *Corros. Sci.* **1997**, *39*, 1499–1500. [\[CrossRef\]](#)
32. Yousefi, T.; Davarkhah, R.; Golikand, A.N.; Mashhadizadeh, M.H.; Abhari, A. Facile cathodic electrosynthesis and characterization of iron oxide nano-particles. *Prog. Nat. Sci.* **2013**, *23*, 51–54. [\[CrossRef\]](#)
33. Hou, J.; Luo, J.; Song, S.; Li, Y.; Li, Q. The remarkable effect of the coexisting arsenite and arsenate species ratios on arsenic removal by manganese oxide. *Chem. Eng. J.* **2017**, *315*, 159–166. [\[CrossRef\]](#)
34. Liu, Y.; Li, Z.; You, Y.; Zheng, X.; Wen, J. Synthesis of different structured FePO₄ for the enhanced conversion of methyl cellulose to 5-hydroxymethylfurfural. *RSC Adv.* **2017**, *7*, 51281–51289. [\[CrossRef\]](#)
35. Lee, K.E.; Teng, T.T.; Morad, N.; Poh, B.T.; Mahalingam, M. Flocculation activity of novel ferric chloride–polyacrylamide (FeCl₃-PAM) hybrid polymer. *Desalination* **2011**, *266*, 108–113. [\[CrossRef\]](#)
36. Liu, Y.; Zhou, Y.; Zhang, J.; Zhang, S.; Xu, S. The transformation from amorphous iron phosphate to sodium iron phosphate in sodium-ion batteries. *Phys. Chem. Chem. Phys.* **2015**, *17*, 22144–22151. [\[CrossRef\]](#)