

Article

Iron- and Calcium-Based Mineral Media for Phosphorus Removal from Synthetic Phosphate Solutions: Implications for Agricultural Runoff Interception

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Abstract

Agricultural phosphorus losses create a need for simple and sustainable reactive media suitable for decentralized interception. This study compared unmodified pyrite, iron filings, and limestone for phosphorus removal from low-concentration synthetic phosphate solutions using dosage, apparent thermodynamic, nonlinear isotherm, kinetic, pH, SEM, and binary-mixture analyses. Based on the tested dosage range, 60 g/L was selected for pyrite and 40 g/L for iron filings and limestone. Pyrite showed an exothermic apparent response ($\Delta H^\circ = -8.12$ kJ/mol), whereas limestone and iron filings were endothermic ($\Delta H^\circ = 11.75$ and 19.99 kJ/mol). Nonlinear Freundlich fitting provided a slightly better description than Langmuir fitting, with R^2 values of 0.9867, 0.9821, and 0.9648 for pyrite, limestone, and iron filings, respectively. Linearized pseudo-second-order fitting characterized the short-term phosphorus-removal kinetics of pyrite and limestone, while iron filings exhibited non-monotonic behavior. The 1:1 iron filings–limestone mixture maintained phosphorus removal above 99% across 10–100 g/L, with the highest removal at 40 g/L. The pH and SEM observations supported material-specific reaction environments and surface transformations. These batch-scale results identify unmodified Fe- and Ca-based media as candidates for further evaluation in sustainable agricultural phosphorus management under real runoff and continuous-flow conditions.

Keywords: agricultural runoff interception; phosphorus removal; sustainable phosphorus management; pyrite; iron- and calcium-based mineral media; binary mineral mixtures



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1. Introduction

Phosphorus is crucial to crop production and food security, but the inefficient use of phosphorus directly leads to a decline in agricultural productivity and a deterioration in water quality. Increased fertilizer input and intensive cultivation have led to the accumulation of residual phosphorus in agricultural soil [1,2]. Crop harvest can only remove part of the phosphorus, and the rest of the phosphorus may be released through erosion, surface runoff and subsurface drainage [3–5], and then transported to the surface water systems [4–6]. Excessive phosphorus will promote eutrophication and loss of biodiversity, thus undermining water quality and aquatic ecosystem functions [4,5]. Therefore, reducing phosphorus loss in farmland is not only important for pollution control, but

also for the sustainable management of nutrient resources, agricultural production and freshwater ecosystems.

Because the loss of agricultural phosphorus is affected by both source areas and transport pathways, to effectively reduce the loss of phosphorus, it is necessary to combine source control measures with field interception measures [7–9]. In a dispersed agricultural environment, the treatment system must adapt to phosphorus concentration fluctuations, flow changes, short contact time, seasonal changes and limited operation and maintenance. Reactive-media interception can be integrated into drainage ditches, ecological interception areas, field filters and constructed wetlands [10–12]. Such systems provide a relatively simple method to intercept dissolved phosphorus before it enters the downstream water body. Their actual performance depends on the cost of materials, hydraulic stability, phosphorus load, contact time, and the ability to maintain the removal effect under changes in flow and inlet concentration [10–13]. Accordingly, simple field-interception technologies can contribute to more sustainable management of agricultural nutrient losses by reducing phosphorus transfer from farmland to downstream aquatic ecosystems.

For these applications, the reactive medium should be inexpensive, easy to obtain, hydraulically stable, and able to maintain phosphorus-removal performance under different operating conditions. Modified biochar and engineered metal-based composites can remove phosphate through electrostatic interactions, ligand exchange, surface complexation and mineral precipitation [14–19]. However, compared with the direct use of mineral media, material synthesis and chemical modification may increase the cost and operational complexity of large-scale application. Therefore, unmodified iron-containing and calcium-containing materials may provide a simpler alternative. Accordingly, the direct use of widely available, unmodified mineral media may provide a simpler pathway toward a more sustainable phosphorus-interception system. Pyrite (FeS_2) can gradually produce an active iron phase through oxidation and dissolution [20–22], while iron filings (Fe^0) can form Fe(II)/Fe(III) corrosion products with high affinity for phosphorus [23–25]. Limestone (CaCO_3) can release Ca^{2+} and provide surface sites for calcium-phosphate complexation, nucleation and precipitation [26–28]. These pathways may be complementary: iron-containing materials can promote rapid surface complexation and Fe-P fixation, while limestone can support Ca-P precipitation and buffer the acidity produced by iron oxidation.

Previous studies have investigated modified biochars, engineered Fe/Ca adsorbents, calcium-phosphate recovery processes, and Ca-loaded reactive media [14–19,29–31]. Pyrite has also been used in constructed wetlands [20–22], including electrolysis-assisted systems [32], steel-slag-coupled systems [33], and microbial fuel-cell configurations [34]. Biochar–pyrite and microelectrolysis systems have also been developed to provide multiple nutrient-removal pathways [35,36], while recirculating and carbon-limited wetland systems further demonstrate the potential of pyrite for phosphorus retention [37,38]. However, direct comparisons of unmodified pyrite, iron filings, and limestone under the same low-phosphorus conditions remain limited. In addition, relatively little information is available on the performance of simple binary mixtures of these unmodified mineral media. This study therefore provides a direct comparative screening of three unmodified Fe- and Ca-based mineral media, including their dosage, apparent thermodynamic, equilibrium, kinetic, and surface-morphology responses. A fixed 1:1 mass ratio was also used to screen three binary combinations for potential complementary phosphorus-removal behavior.

Based on these considerations, the objectives were to: (1) compare phosphorus removal by pyrite, iron filings, and limestone in low-concentration synthetic phosphate solutions; (2) characterize their dosage, temperature, equilibrium, and kinetic responses; (3) examine surface morphology before and after reaction; and (4) screen binary mineral mixtures at a fixed 1:1 mass ratio and compare their phosphorus-removal performance with the

corresponding individual materials. Through this comparative screening, the study aims to provide a mechanistic basis for selecting simple reactive media for sustainable agricultural phosphorus management.

2. Materials and Methods

2.1. Materials

Pyrite particles (1–3 mm) purchased from Hunan Province, China, iron filings (1–2 mm) purchased from Henan Province, China, and limestone particles (2–5 mm) purchased from Jiangsu Province, China, were used without chemical modification. Before use, all materials were washed with distilled water until the wash water approached neutral pH and then dried at 60 °C in an electrothermal blowing drying oven (Model GZX-9140MBE; Shanghai Boxun Industry & Commerce Co., Ltd. Medical Equipment Factory, Shanghai, China).

In conventional agricultural systems, total phosphorus in farmland drainage and runoff commonly ranges from 0.03 to 5.89 mg/L [4,5,7]. A synthetic phosphate solution was prepared from potassium dihydrogen phosphate (KH_2PO_4 , analytical reagent grade; Sinopharm Chemical Reagent Co., Ltd. (SCRC), Shanghai, China) at phosphorus concentrations of 0.5–5 mg/L. This range was selected to approximate the low phosphorus concentrations reported for agricultural runoff.

All batch experiments were independently performed in triplicate ($n = 3$) under identical experimental conditions. Directly measured experimental results are presented as mean $\pm$ standard deviation (SD). Data analysis and plotting were performed using OriginPro 2024b (OriginLab Corporation, Northampton, MA, USA).

2.2. Experimental Methods

2.2.1. Single-Material Dosage Experiments

For each mineral, samples of 0.5, 1, 2, 3, or 5 g were placed in separate centrifuge tubes. Each tube was filled with 50 mL of synthetic phosphate solution containing 2 mg/L phosphorus. The suspensions were shaken in a THZ-82 constant-temperature shaker (Changzhou Guohua Electric Appliance Co., Ltd., Changzhou, China) for 8 h at 20 °C and 180 r/min. The suspensions were then filtered, and residual phosphate was measured by the molybdenum-antimony spectrophotometric method using a 752N UV-Vis spectrophotometer (Shanghai INESA (Group) Co., Ltd., Shanghai, China). Phosphorus removal efficiency and apparent adsorption capacities were calculated from the following equations:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%, \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m}, \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m}. \quad (3)$$

In these equations, η is the phosphorus removal efficiency (%). C_0 , C_t , and C_e are the initial, time t , and equilibrium phosphorus concentrations (mg/L), respectively. V is the solution volume (L), and m is the mineral mass (g). The terms q_t and q_e denote the apparent phosphorus adsorption capacities at time t and at equilibrium (mg/g), respectively. Because q_t and q_e were calculated from changes in dissolved phosphorus concentration, they represent apparent aqueous-phase phosphorus uptake rather than directly measured phosphorus in the solid phase.

pH measurements were conducted under representative batch conditions using five treatments: a mineral-free control, 60 g/L pyrite, 40 g/L limestone, 40 g/L iron filings, and

a 1:1 iron filings–limestone mixture at a total dosage of 40 g/L. Each treatment contained 50 mL of synthetic phosphate solution with an initial phosphorus concentration of 2 mg/L and was shaken at 20 °C and 180 r/min. Initial pH was measured immediately after mineral addition and before shaking, and final pH was measured after 8 h.

2.2.2. Adsorption Thermodynamic Experiments

Adsorption experiments for thermodynamic analysis were conducted at 298, 303, and 308 K with an initial phosphorus concentration of 2 mg/L. Pyrite was dosed at 60 g/L, while limestone and iron filings were each dosed at 40 g/L. All other experimental conditions were as described in Section 2.2.1. The equilibrium phosphorus concentration (C_e) was measured and used to calculate the equilibrium adsorption capacity (q_e). The distribution coefficient (K_d) was calculated as follows:

$$K_d = \frac{q_e}{C_e}. \quad (4)$$

The distribution coefficient (K_d) is calculated from the equilibrium aqueous-phase phosphorus concentration and apparent equilibrium uptake. Because K_d has units of L/g, it was normalized by a reference value of 1 L/g to obtain the dimensionless coefficient K_d^* .

$$K_d^* = \frac{K_d}{1 \text{ L g}^{-1}}. \quad (5)$$

The dimensionless K_d^* was used as an apparent equilibrium parameter for evaluating the relative temperature dependence of phosphorus partitioning under the fixed experimental conditions. This normalization permits logarithmic treatment in the van't Hoff analysis. However, K_d is an empirical distribution parameter derived from concentration-based batch measurements rather than a rigorous activity-based thermodynamic equilibrium constant. Therefore, the resulting ΔG° , ΔH° , and ΔS° values are interpreted as apparent thermodynamic parameters that describe relative temperature-dependent behavior under the tested conditions.

The apparent thermodynamic parameters were estimated using the van't Hoff relationship:

$$\ln K_d^* = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \quad (6)$$

In this equation, R is the universal gas constant (8.314 J/(mol·K)), and T is the absolute temperature (K). The change in Gibbs free energy was calculated as follows:

$$\Delta G^\circ = -RT \ln K_d^*. \quad (7)$$

Linear regression of $\ln K_d^*$ against $1/T$ gave ΔH° and ΔS° from the slope and intercept, respectively.

2.2.3. Adsorption Isotherm Experiments

Isothermal adsorption experiments were conducted at 303 K. The initial phosphorus concentrations were 0.5, 1, 1.5, 2, 3, and 5 mg/L. For each treatment, 2.0 g of pyrite, limestone, or iron filings was mixed with 50 mL of phosphate solution. Preliminary tests indicated that all three materials approached equilibrium within 6–8 h. The contact time was extended to 12 h so that equilibrium could be approached at different initial concentrations. After reaction, each suspension was filtered through a 0.45 µm membrane, and the equilibrium phosphorus concentration was measured. The adsorption data were fitted with the Langmuir and Freundlich models.

The equilibrium data were fitted directly to the nonlinear Langmuir and Freundlich isotherm models using the experimental C_e and q_e values. The nonlinear forms of the Langmuir and Freundlich models are expressed as Equations (8) and (9), respectively:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (8)$$

$$q_e = K_F C_e^{1/n} \quad (9)$$

where $q_{\max}$ is the theoretical maximum adsorption capacity, K_L is the Langmuir constant, K_F is the Freundlich constant, and n is the adsorption-intensity parameter. Model performance was evaluated using the coefficient of determination (R^2) and root mean square error (RMSE) [14,19,26].

2.2.4. Kinetic Experiments

Before the formal kinetic experiment, preliminary tests were conducted to estimate the equilibrium time of each material. Pyrite and limestone approached steady removal after approximately 8 h, whereas iron filings reached relatively high removal efficiency at approximately 6 h before declining slightly. In the formal experiments, separate 0.5, 1, 2, 3, and 5 g samples of each mineral were placed in 100 mL conical flasks. Each flask contained 50 mL of synthetic phosphate solution with an initial phosphorus concentration of 2 mg/L. Removal efficiency was compared across all five dosages, while pseudo-second-order parameters were fitted at 40 g/L, equivalent to 2.0 g in 50 mL. A common dosage was used for the three minerals to permit direct comparison of their kinetic parameters. The flasks were shaken at 20 °C and 180 r/min. The residual phosphate concentration was measured after filtration through 0.45 µm membranes. The pseudo-second-order kinetic model was written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where q_t and q_e denote the adsorption capacities at time t and equilibrium, respectively, and k_2 denotes the pseudo-second-order rate constant [23–25].

The initial apparent uptake rate h was calculated as:

$$h = k_2 q_{e,cal}^2 \quad (11)$$

where $q_{e,cal}$ denotes the equilibrium adsorption capacity calculated from the pseudo-second-order model, and h is reported in mg/(g·h).

2.2.5. Composite Mineral Mixture Experiments

The three tested combinations were pyrite–iron filings, pyrite–limestone, and iron filings–limestone. A 1:1 mass ratio was used as a simple screening condition to compare the three binary mixtures under the same total dosage and with equal mass contributions from the two components. For each combination, 0.5, 1, 2, 3, or 5 g was added to 50 mL of phosphate solution, giving 10, 20, 40, 60, or 100 g/L. The corresponding contribution of each component was 0.25, 0.5, 1.0, 1.5, or 2.5 g. All mixtures were tested using the procedure applied to the single-material adsorption experiments. Phosphorus removal efficiency was measured to compare the performance of the three binary mixtures at different total dosages.

2.2.6. SEM Characterization

Pyrite, limestone, and iron filings before and after reaction were characterized by scanning electron microscopy (SEM) to evaluate changes in surface morphology. After reaction,

the solids were recovered and gently rinsed with a small volume of deionized water to remove loosely bound surface salts, and then dried at 60 °C to constant weight. Before SEM observation, the dried samples were mounted on conductive tape and sputter-coated with a thin layer of gold. Magnetic samples were observed using a MIRA3 scanning electron microscope (TESCAN, TESCAN, Brno, Czech Republic) at an accelerating voltage of 20 kV and a magnification of 2000 $\times$, while non-magnetic samples were observed using a Regulus 8100 cold-field-emission scanning electron microscope (Hitachi High-Tech Corporation, Tokyo, Japan) at an accelerating voltage of 3 kV and a magnification of 1000 $\times$. SEM observations were used to compare surface morphology before and after reaction and were not used to quantify specific surface area.

3. Results

3.1. Effect of Single-Material Dosage

The phosphorus removal effect of pyrite, iron filings, and limestone was evaluated at dosages of 10, 20, 40, 60, and 100 g/L. Figure 1 shows the relationship between dosage and phosphorus removal efficiency for the three minerals.

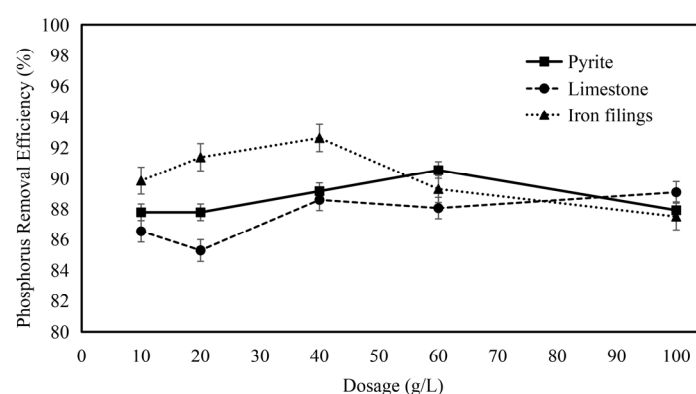


Figure 1. Effect of dosage on phosphorus removal by pyrite, limestone, and iron filings. Data are presented as mean $\pm$ SD ($n = 3$).

These three minerals showed different relationships. The phosphorus removal efficiency of iron filings increased from 10 g/L to 40 g/L as the dosage increased, reached a peak at 40 g/L, and then decreased with a further increase in the added amount. Pyrite showed little change between 10 and 20 g/L, followed by a gradual increase to a maximum at 60 g/L, before declining at 100 g/L. In contrast, limestone only showed slight fluctuations in the whole test addition range, and there was no obvious monotonic relationship between its dosages and phosphorus removal efficiency.

Based on the tested dosage range, 40 g/L was selected for iron filings because further increases in dosage did not improve phosphorus removal. For pyrite, 60 g/L was selected because the highest removal efficiency was observed at this dosage and decreased slightly at 100 g/L. For limestone, 40 g/L was selected based on the balance between phosphorus-removal performance and material input, because further increases in dosage produced only limited improvement.

The different dosage responses suggest that phosphorus removal was influenced by material-specific reaction characteristics rather than dosage alone. Iron filings reached their highest removal at 40 g/L, whereas pyrite required a higher dosage to reach its maximum. Limestone showed only modest changes across the tested dosage range, which is consistent with the potential influence of CaCO_3 dissolution and Ca-mediated phosphorus removal [29].

3.2. Adsorption Thermodynamics

Thermodynamic analysis at 298, 303, and 308 K was used to compare the apparent temperature responses of pyrite, limestone, and iron filings. The dimensionless normalized distribution coefficient, K_d^* , was used as an apparent equilibrium parameter. The $\ln K_d^*$ values were fitted to the van't Hoff relationship to estimate apparent ΔH° and ΔS° , while apparent ΔG° values were calculated from K_d^* . Because K_d^* is derived from concentration-based distribution data rather than thermodynamic activities, these parameters are interpreted as conditional indicators of temperature-dependent behavior under the tested batch conditions rather than rigorous standard-state thermodynamic quantities.

The van't Hoff curves are shown in Figure 2, and the corresponding thermodynamic parameters are listed in Table 1.

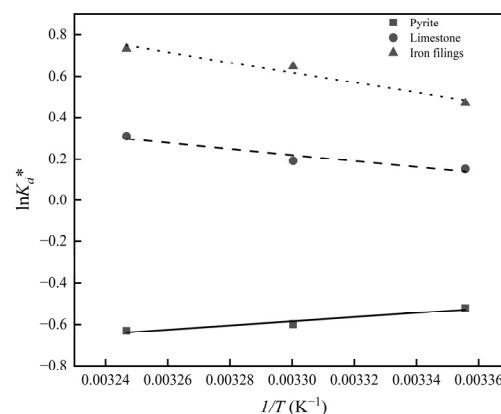


Figure 2. van't Hoff plots for phosphorus fixation by iron- and calcium-based minerals.

Table 1. Thermodynamic parameters for phosphorus adsorption by iron- and calcium-based minerals.

Adsorbent	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(mol·K))
Pyrite	298	1.30	−8.12	−31.64
	303	1.51		
	308	1.61		
Limestone	298	−0.38	11.75	40.61
	303	−0.49		
	308	−0.79		
Iron filings	298	−1.16	19.99	71.14
	303	−1.63		
	308	−1.87		

Figure 2 and Table 1 show that pyrite, limestone, and iron filings exhibited different apparent thermodynamic responses for phosphorus removal. The ΔH° and ΔS° values of pyrite were -8.12 kJ/mol and -31.64 J/(mol·K), respectively. A negative value of ΔH° indicated that the process was an exothermic process, while a negative value of ΔS° indicated that the interface order increased during the phosphorus fixation process. At 298, 303, and 308 K, the ΔG° values were 1.30, 1.51, and 1.61 kJ/mol respectively. Under the adopted K_d^* normalization, the positive apparent ΔG° values indicate a relatively less favorable equilibrium partitioning of phosphorus for pyrite within the tested temperature range. The slight increase in ΔG° with temperature is consistent with the exothermic nature of the process, indicating that the increase in temperature did not enhance the equilibrium driving force. Nevertheless, the reason why pyrite can achieve high-efficiency phosphorus removal may be attributed to the high amount of addition and the continuous generation of iron oxides and hydroxides. Possible phosphorus removal mechanisms include oxidative

dissolution of pyrite, the formation of Fe(III) oxides or oxyhydroxides, ligand exchange between phosphate and surface hydroxyl groups. Iron-oxide or iron-phosphate coatings may also gradually cover the mineral surface, thus limiting the further oxidation reaction and the renewal of the active sites [20,32,37].

The ΔH° and ΔS° values of limestone are 11.75 kJ/mol and 40.61 J/(mol·K) respectively, indicating that the process was an endothermic process accompanied by an increase in entropy. Its ΔG° value changes slightly, from -0.38 kJ/mol at 298 K to -0.79 kJ/mol at 308 K. The negative apparent ΔG° values indicate that phosphorus partitioning became more favorable for limestone under the tested conditions as temperature increased. The positive ΔS° may be related to the release of phosphate dehydration, hydrated water or carbonate ions, and the increase in ion mobility during surface complexation. The process of removing phosphorus from calcite-containing materials began with the adsorption of phosphorus at the Ca site on the surface; when local supersaturation was reached, calcium phosphate nucleation or precipitation further occurred [26–28]. At low phosphate concentrations and short contact times, surface binding may dominate, whereas precipitation may become more important at higher concentrations or longer contact times. In addition, the phosphorus removal performance of limestone was also affected by factors such as CaCO_3 dissolution, pH value, bicarbonate competition and calcium-phosphate crystallization kinetics [27,28,39]. Long-term research on drainage filtration systems shows that limestone is more sensitive to changes in water flow and phosphorus load than iron-rich filter materials.

For iron filings, the corresponding ΔH° and ΔS° values are 19.99 kJ/mol and 71.14 J/(mol·K) respectively. The increasingly negative apparent ΔG° values indicate a more favorable temperature response for iron filings under the tested conditions. The larger positive value ΔS° may reflect the desolventization of phosphate, the release of interfacial water and counterions, and structural rearrangement in the process of iron corrosion and phosphate binding [40,41]. Fe^0 corrosion produces Fe^{2+} , Fe^{3+} , which may then converted into iron oxides or hydroxides; phosphate can be removed by adsorption on corrosion products, inner-sphere complexation, coprecipitation and formation of Fe-P precipitates [42–44]. Higher temperature may accelerate corrosion, ion diffusion and the formation of reactive iron hydroxides. However, the small ΔG° values indicate that the equilibrium driving force is limited under the tested conditions. Dense oxide or phosphate layers may also hinder electron transfer and limit the exposure of fresh Fe^0 sites [41,45].

These research results are of great significance to the control of agricultural non-point pollution, because in the process of runoff and subsurface drainage, low phosphorus concentrations often occur under fluctuating flow, seasonal temperature changes, soluble organic matter and competitive anions. Constructed wetlands based on pyrite have achieved continuous phosphorus interception, among which Fe- and Al-bound fractions combined phosphorus usually account for the main part of the intercepted phosphorus [20–22]. Using the electrolytic-assisted wetland of pyrite, the removal effect of nutrients is also improved by accelerating the iron cycle and producing additional reaction surfaces [32–34]. Other combined processes using biochar or microelectrolysis technology also enhance the removal of nutrients and the formation of reactive surfaces [35,36]. On-site and filtration experiments further show that treatment efficiency depends on the flow rate, phosphorus load, contact time and the stability of the newly generated iron phase [10–12].

Overall, pyrite showed an exothermic apparent response, whereas limestone and iron filings showed endothermic apparent responses. For limestone and iron filings, the apparent ΔG° values became more negative as temperature increased, indicating more favorable relative phosphorus partitioning within the tested temperature range. For pyrite, the positive apparent ΔG° values indicate relatively less favorable partitioning under the

adopted K_d^* normalization. These results should be interpreted as comparative temperature responses under the tested batch conditions rather than as rigorous standard-state thermodynamic behavior.

The tested 298–308 K range represents only a limited temperature interval and does not cover the full seasonal temperature range of agricultural runoff.

3.3. Adsorption Isotherm Models

The equilibrium data were fitted to the Langmuir and Freundlich models using nonlinear regression based directly on the experimental C_e and q_e values. Both models described the experimental data to different degrees, but the Freundlich model provided the better overall fit for all three mineral media, as indicated by its consistently higher R^2 values and lower RMSE values, as shown in Figure 3 and Table 2.

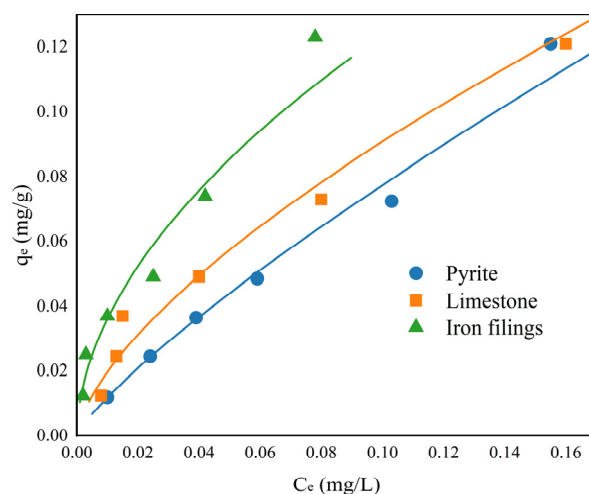


Figure 3. Nonlinear Freundlich isotherm fitting for phosphorus removal by pyrite, limestone, and iron filings at 303 K.

Table 2. Nonlinear Langmuir and Freundlich isotherm parameters for phosphorus removal by the three mineral media at 303 K.

Material	Langmuir				Freundlich			
	q_{max}	K_L	R^2	RMSE	K_F	n	R^2	RMSE
Pyrite	1.4032	0.5957	0.9839	0.00457	0.6496	1.0913	0.9867	0.00415
Limestone	0.2091	8.0492	0.9660	0.00664	0.3950	1.5446	0.9821	0.00481
Iron filings	0.2795	9.5304	0.9273	0.00987	0.5972	1.5667	0.9648	0.00687

For the Freundlich model, the R^2 values were 0.9867, 0.9821, and 0.9648 for pyrite, limestone, and iron filings, respectively, with corresponding RMSE values of 0.00415, 0.00481, and 0.00687 mg/g. The corresponding Langmuir R^2 values were 0.9839, 0.9660, and 0.9273. These results indicate that the Freundlich model provided a slightly better description of the equilibrium behavior of the three mineral media under the tested conditions [14,19,26]. Although the Langmuir model also produced relatively high R^2 values for pyrite and limestone, the fitted q_{max} values should be interpreted cautiously because a clear saturation plateau was not reached within the tested concentration range. The Freundlich model was therefore used primarily to describe the heterogeneous equilibrium behavior of the tested mineral surfaces.

Among the Freundlich fits, pyrite showed the highest K_F value (0.6496), followed by iron filings (0.5972) and limestone (0.3950). The corresponding n values were 1.0913,

1.5667, and 1.5446, respectively. These parameters indicate different equilibrium responses among the three mineral media. However, the model-fitting results alone do not establish a specific phosphorus-removal mechanism. The slightly better Freundlich fits are consistent with non-ideal and heterogeneous equilibrium behavior. Possible contributions from pyrite oxidation [20,32,37], CaCO_3 dissolution and Ca-mediated phosphorus removal [27,39], and Fe^0 corrosion and secondary iron-bearing surfaces [23–25,40,41,45] should therefore be considered together with the kinetic, pH, and SEM observations rather than inferred from the isotherm model alone.

3.4. Adsorption Kinetics

Figure 4 presents phosphorus removal over time for all three materials at 10, 20, 40, 60, and 100 g/L.

Figure 4a shows that the phosphorus-removal efficiency of pyrite varied with dosage and contact time. The treatment of 60 g/L reached the highest removal efficiency in 8 h, while the treatment of 100 g/L increased to about 90% in 6 h, and then decreased to 87.8% in 8 h. The variation was relatively small, indicating that increasing the dosage above 60 g/L did not further improve phosphorus removal under the tested conditions [32,37,38].

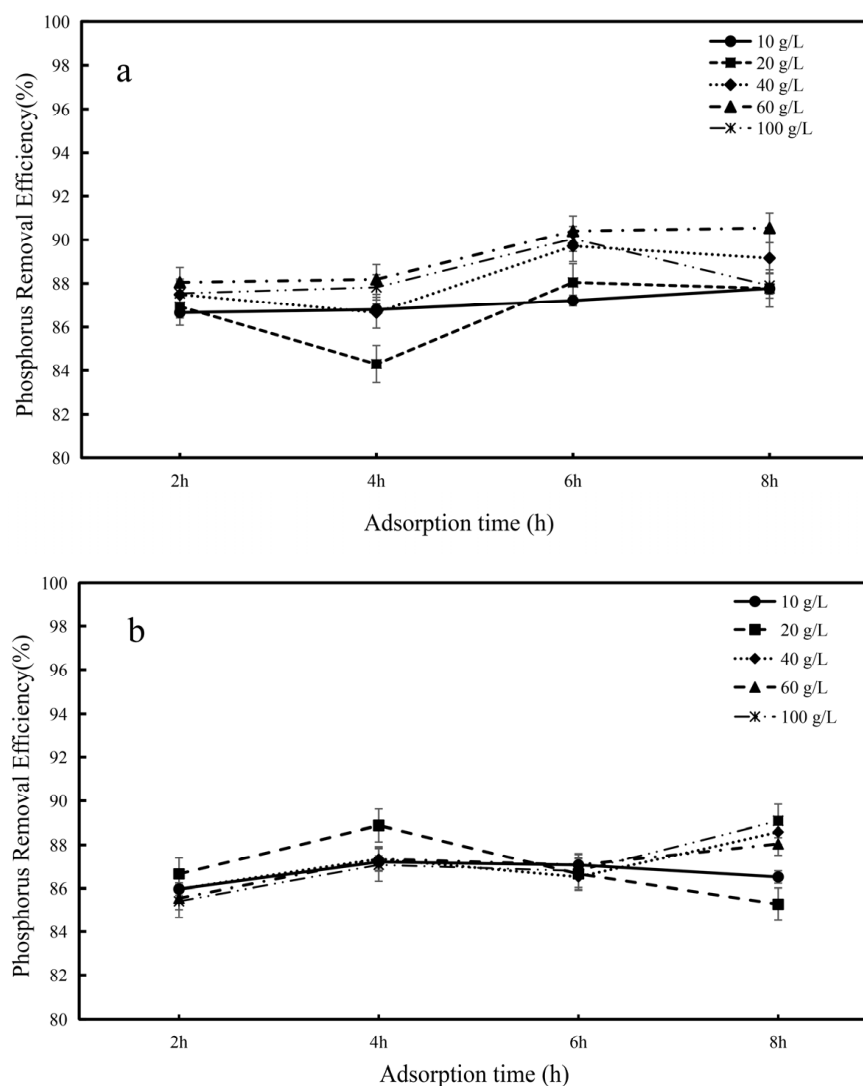


Figure 4. Cont.

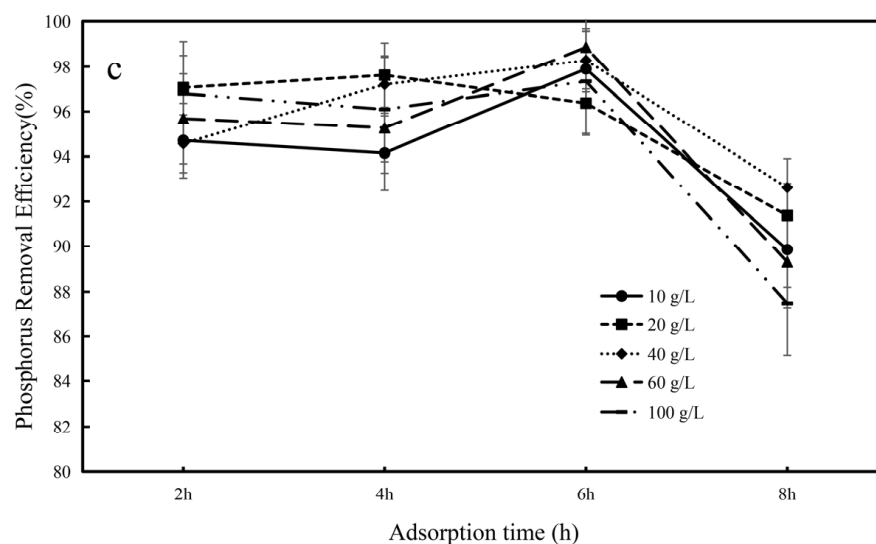


Figure 4. Kinetic characteristics of phosphorus removal by iron- and calcium-based minerals: (a) pyrite; (b) limestone; (c) iron filings. Data are presented as mean $\pm$ SD ($n = 3$).

The phosphorus-removal efficiency of limestone was slightly different, indicating that the process was constrained by the dissolution of CaCO_3 and the release rate of Ca^{2+} . When the dosage was 40 g/L, limestone showed a relatively high phosphorus-removal efficiency. Further increasing the amount did not improve the phosphorus-removal efficiency, which was consistent with the restrictions brought about by dissolution equilibrium and particle aggregation. These results suggest that limestone may be more useful as an auxiliary calcium source than as a stand-alone medium. Increasing the dosage alone may not substantially improve its performance [26,39].

Iron filings showed high phosphorus removal during the early stage of the reaction, reaching the highest removal at approximately 6 h before decreasing at 8 h across the tested dosages. This non-monotonic behavior indicates that aqueous-phase phosphorus removal did not approach equilibrium monotonically. The corrosion of Fe^0 and the formation of early Fe(II)/Fe(III) corrosion products may have promoted the rapid removal of phosphorus [23–25]. In the later stage, changes in the corrosion-product layer, coverage of reactive sites, or partial re-release of previously removed phosphorus may have contributed to the decrease in removal efficiency [40,41,45]. This result also shows that phosphorus removal from the aqueous phase does not necessarily represent irreversible phosphorus retention.

For direct comparison, the pseudo-second-order kinetic model was fitted to data collected at 40 g/L for all three minerals. Figure 5 and Table 3 present the fitted results.

At the dosage of 40 g/L, the pseudo-second-order model gives a physically reasonable fit for pyrite and limestone, and the R^2 value is 0.9995. The calculated equilibrium adsorption capacity is 0.04518 mg/g of pyrite and 0.04451 mg/g of limestone, and the corresponding rate constants are 152.132 and 167.168 g/(mg·h) respectively. The initial apparent uptake rate is $h = 0.3105$ mg/(g·h) of pyrite and 0.3312 mg/(g·h) of limestone, respectively. Therefore, the calculated equilibrium capacity of pyrite is slightly higher, while the apparent rate constant and initial adsorption rate of limestone are slightly higher.

For iron filings, the $q_{e,cal}$ value obtained by linear regression was 0.04639 mg/g, with $k_2 = -159.04$ g/(mg·h) and $R^2 = 0.9963$. Despite the high R^2 value, the negative k_2 has no physical meaning. In addition, phosphorus removal peaked at approximately 6 h and decreased at 8 h. Therefore, the fitted parameters are reported only for completeness and are not used for kinetic interpretation or material comparison.

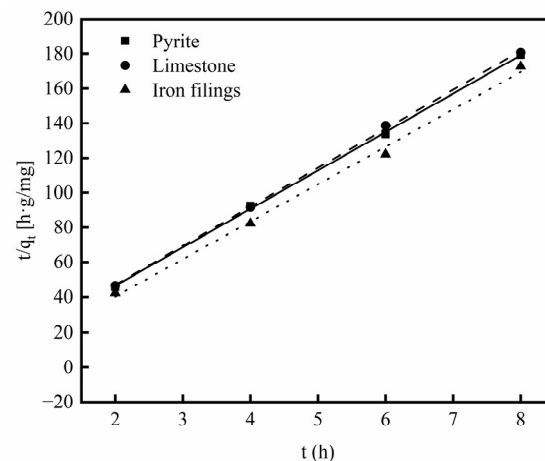


Figure 5. Linearized pseudo-second-order kinetic plots for the three minerals at 40 g/L. The iron-filings line is presented only to show the mathematical regression; because the calculated k_2 value was negative, the fitted kinetic parameters were considered physically invalid.

Table 3. Pseudo-second-order kinetic parameters for phosphorus removal by the three minerals.

Material	Pseudo-Second-Order Kinetics		
	$q_{e,cal}$ (mg/g)	k_2 g/(mg·h)	R^2
Pyrite	0.04518	152.132	0.9995
Limestone	0.04451	167.168	0.9995
Iron filings	0.04639 ^a	−159.04 ^a	0.9963 ^a

^a The pseudo-second-order fitting of iron filings yielded a negative rate constant. Therefore, although the mathematical fitting results are reported, the calculated parameters lack physical meaning and were not used for kinetic interpretation or comparison.

Nevertheless, the time-course data show that iron filings can quickly remove phosphorus in the early stage of the reaction. This rapid initial reaction may be related to the corrosion of zero-valent iron and the formation of Fe(II)/Fe(III) oxides or hydroxides, which can provide Fe-OH sites for phosphate adsorption, ligand exchange, coprecipitation and iron-phosphate generation [23,25,44]. The decrease in removal efficiency after 6 h may be related to changes in the corrosion product layer, phosphorus-containing deposits covering the reaction site, or the redistribution or partial re-release of previously retained phosphorus. These possible processes show that the removal of phosphorus from iron filings is determined by a variety of reactions that change over time, rather than a single adsorption-controlled kinetic process.

The dynamic differences between pyrite and limestone may reflect their different phosphorus fixation paths. The slightly lower k_2 value of pyrite may be related to the gradual oxidation of FeS₂ and the subsequent active iron-containing phase. Limestone showed a slightly higher apparent rate constant, which may be related to the rapid interaction of phosphate with the calcium-rich surface site, followed by slower CaCO₃ dissolution and calcium-phosphate nucleation [26,39].

3.5. Phosphorus Removal by Composite Mineral Mixtures

Figure 6a shows the phosphorus removal efficiency of three composite mineral mixtures at different dosages, while Figure 6b compares the composite mineral mixtures with the corresponding single material. Among the three tested 1:1 binary mixtures, the iron filings–limestone combination showed the highest mean phosphorus-removal performance, with the highest mean removal observed at a total dosage of 40 g/L. As shown in

Figure 6b, the phosphorus removal efficiency of the composite mineral mixtures are generally higher than that of the three single materials. The improvement over iron filings alone was smaller than the improvements over pyrite or limestone alone, and the magnitude of the improvement varied with dosage. These results suggest that the combination of iron- and calcium-based materials may provide complementary phosphorus-removal pathways.

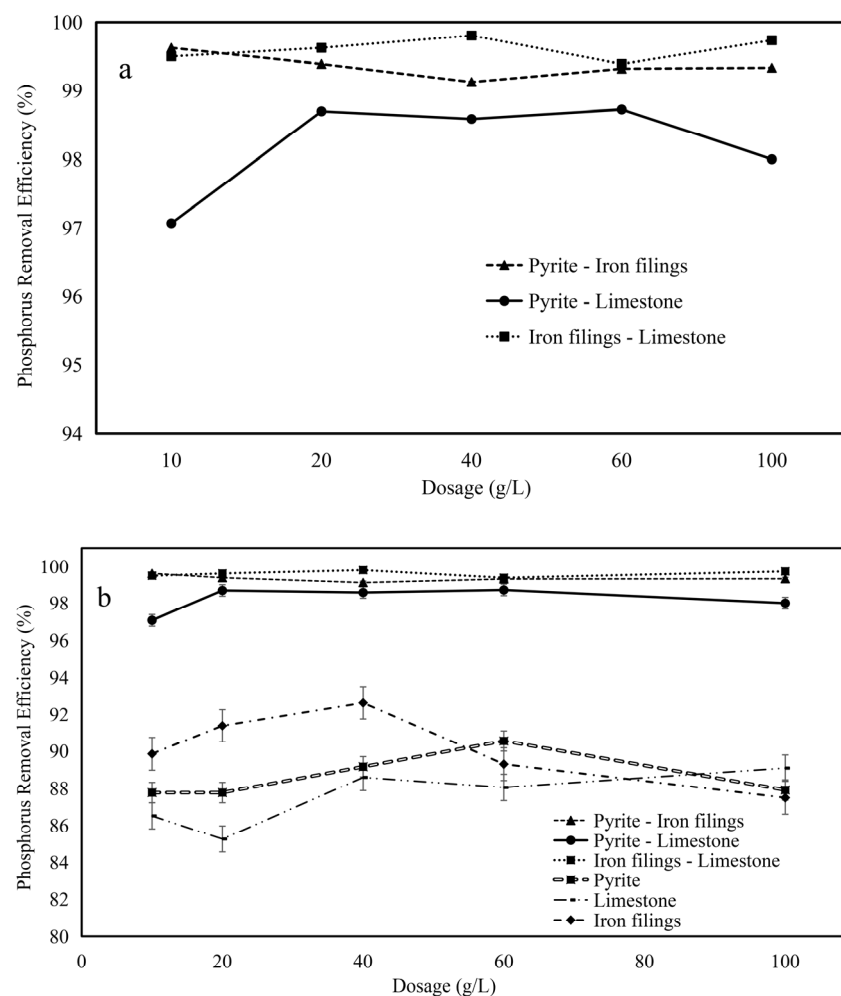


Figure 6. Phosphorus removal performance of composite mineral mixtures and individual minerals: (a) removal efficiencies of the three composite mixtures at different dosages; (b) comparison of the composite mixtures with the corresponding individual minerals. Data are presented as mean $\pm$ SD ($n = 3$).

The compound mixture may perform better because several removal processes can occur at the same time. In the iron filings–limestone system, Fe^0 corrosion will produce reactive iron-containing phases, which can adsorb or precipitate phosphates, while limestone dissolution will release Ca^{2+} and promote calcium-related phosphate precipitation [19,24]. These processes may provide complementary phosphorus-removal pathways: iron filings react quickly but may be passivated, while limestone provides a slower calcium-mediated removal pathway [25,40].

The pH measurements showed clear differences among the five treatments. During the 8 h shaking period, the pH of the mineral-free control increased from 6.10 to 7.10. The pH of the pyrite treatment increased from 5.71 to 6.74, while limestone and iron filings increased the pH from 7.76 to 9.36 and from 6.51 to 8.54, respectively. The 1:1 iron filings–limestone mixture showed the highest final pH, increasing from 7.50 to 9.81. The initial and final pH values are summarized in Table 4.

Table 4. Initial and final pH values under representative batch conditions.

Treatment	Dosage (g/L)	Initial pH	pH After 8 h	ΔpH
Control	0	6.10	7.10	+1.00
Pyrite	60	5.71	6.74	+1.03
Limestone	40	7.76	9.36	+1.60
Iron filings	40	6.51	8.54	+2.03
Iron filings–limestone	40	7.50	9.81	+2.31

These results indicate that the tested mineral media created different reaction environments. Limestone and the iron filings–limestone mixture produced more alkaline conditions, while pyrite maintained the lowest pH. Because the mineral-free control also showed an increase in pH and only the initial and final pH values were measured, the pH data are interpreted as supporting evidence for differences in solution chemistry rather than as direct evidence for the formation of specific Fe-P or Ca-P phases. The relatively high final pH of the iron filings–limestone treatment (9.81) should be further evaluated under real agricultural runoff and continuous-flow conditions.

From an application perspective, pyrite, iron filings, and limestone can be directly mixed without complex modification or synthesis, which may simplify material preparation [7–9]. Composite media may also provide greater functional diversity than single materials [11,29]. However, their performance under fluctuating hydraulic and water-quality conditions requires further validation using continuous-flow experiments [14,17,18]. Among the tested mixtures, the iron filings–limestone combination showed the highest mean phosphorus-removal performance and may be considered a candidate for further study [26,29,31].

Only a 1:1 mass ratio was evaluated for each binary mixture in the present study. Therefore, the results identify the best-performing combination under this fixed ratio but do not establish an optimal component ratio. Future studies should evaluate a wider range of iron/calcium ratios using real agricultural runoff under both batch and continuous-flow conditions.

3.6. SEM Characterization of the Three Minerals Before and After Reaction

SEM images were used to qualitatively compare surface morphological changes before and after reaction. As shown in Figure 7, the surfaces of pyrite, limestone and iron filings showed obvious morphological changes after contact with a phosphorus-containing solution. After the reaction, these minerals exhibited surface roughness and visible deposits. These changes are consistent with mineral dissolution or corrosion accompanied by possible surface deposition.

Before the reaction, the pyrite surface appeared relatively dense but uneven, with scattered particles and irregular areas (Figure 7a). After the reaction, the surface became rougher, with more evident pits, cracks, and fine deposits (Figure 7b). These changes are generally consistent with the oxidation of pyrite and the formation of secondary iron-containing surface phases. These phases may provide hydroxylation sites for phosphate binding, coprecipitation and iron-phosphorus precipitation [32,35,37].

The appearance of untreated limestone is relatively dense, but local pores, irregular particles and similar erosion characteristics can still be seen (Figure 7c). After phosphate removal, the surface was rougher and more heterogeneous, with flake-like and fine particulate deposits across the particles (Figure 7d). These features are consistent with partial CaCO_3 dissolution, Ca^{2+} release, and subsequent surface complexation or possible surface deposition associated with Ca-mediated phosphorus removal. The dissolution-deposition sequence agrees with limestone's endothermic response and the more favorable fixation

observed at higher temperatures. It may also explain limestone's lower and variable dosage response and weaker Freundlich fit than pyrite, because performance depends on mineral dissolution, solution chemistry, and Ca-P nucleation kinetics. The SEM morphology is therefore consistent with coupled dissolution and precipitation rather than adsorption on an unchanged surface.

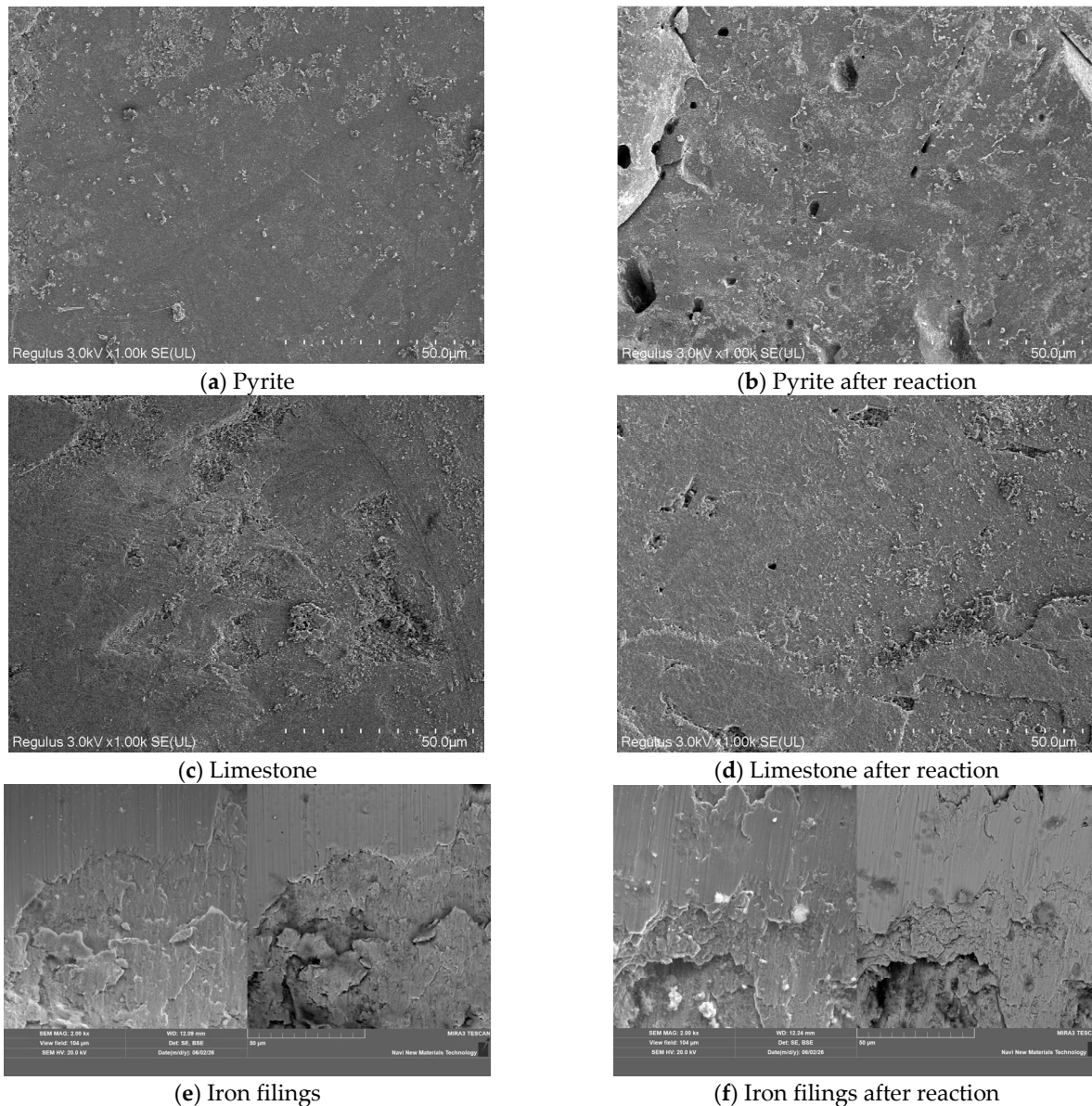


Figure 7. SEM images of the three minerals before and after reaction: (a,b) pyrite; (c,d) limestone; and (e,f) Iron filings.

The surface of unreacted iron filings is relatively flat (Figure 7e). After the reaction, obvious corrosion pits, cracks, rough areas and surface sediments were observed (Figure 7f). These morphological changes are consistent with Fe^0 corrosion and the development of a corrosion-product layer. These corrosion products may interact with phosphorus through ligand exchange, surface complexation, coprecipitation and Fe-P precipitation [42,44]. The observed morphology is also consistent with the time-course behavior of iron filings, that is, iron filings can quickly remove phosphorus in the early stage, but the removal efficiency decreases after 6 h. Because the pseudo-second-order fit for iron filings yielded a negative rate constant, the fitted $q_{e,cal}$ and k_2 values were not used to support the mechanistic

interpretation. The relatively dense surface deposition observed after the reaction may limit the exposure of fresh Fe^0 sites and lead to a decrease in the phosphorus removal rate in the later stage [40,41,45].

Overall, the SEM images show material-specific surface changes after reaction and provide qualitative supporting evidence for mineral transformation. These observations are consistent with possible contributions from pyrite oxidation, limestone dissolution, and Fe^0 corrosion, but they do not directly identify the composition of the surface deposits or confirm specific Fe-P or Ca-P phases. The proposed Fe- and Ca-mediated phosphorus-removal pathways should therefore be regarded as mechanistic interpretations based on the combined batch, pH, kinetic, and morphological results rather than direct phase identification.

4. Discussion

The three mineral media exhibited different phosphorus-removal behaviors under the tested batch conditions. As discussed in Section 3, these differences were reflected in their dosage responses, apparent thermodynamic behavior, equilibrium characteristics, and reaction kinetics. Overall, the results suggest that phosphorus removal was governed by the combined effects of mineral composition, particle size, surface characteristics, and reaction chemistry rather than by material dosage or adsorption alone. The Freundlich fitting, kinetic behavior, pH changes, and SEM observations together support the possible contributions of mineral dissolution, Fe^0 corrosion, surface binding, and precipitation-related processes. However, these results should be interpreted as complementary evidence rather than direct identification of specific Fe-P or Ca-P phases.

Among the three tested 1:1 binary mixtures, the iron filings–limestone combination showed the highest phosphorus-removal performance. Its performance may be related to the complementary behavior of the two components: iron filings can provide reactive iron-bearing surfaces through corrosion, while limestone can release Ca^{2+} and modify the solution environment, providing an additional Ca-mediated pathway for phosphorus removal. The pH and SEM results are consistent with this interpretation, although further solid-phase characterization would be required to confirm the specific phosphorus-containing products. The fixed 1:1 ratio used here should therefore be regarded as a screening condition rather than an optimized formulation.

From a sustainability perspective, the tested minerals are unmodified particulate materials that can be used without complex chemical preparation, supporting their potential as simple reactive media for decentralized phosphorus interception. Compared with highly engineered adsorbents, their use may reduce material-processing requirements. However, sustainability cannot be assessed solely from short-term phosphorus-removal efficiency. The present experiments were conducted using synthetic phosphate solutions under controlled batch conditions, whereas real agricultural runoff contains more complex water chemistry and variable hydraulic and temperature conditions. Therefore, further continuous-flow studies using real agricultural runoff should evaluate mixture composition, hydraulic behavior, phosphorus-retention stability, effluent pH, material service life, and long-term performance.

5. Conclusions

This study compared unmodified pyrite, iron filings, and limestone for phosphorus removal from low-concentration synthetic phosphate solutions. Based on the tested dosage range, 60 g/L was selected for pyrite and 40 g/L for both iron filings and limestone. The three mineral media exhibited different apparent thermodynamic, equilibrium, kinetic, and surface responses. Pyrite showed an exothermic apparent response, whereas limestone

and iron filings showed endothermic apparent responses and more favorable phosphorus partitioning with increasing temperature. Nonlinear isotherm analysis showed that the Freundlich model provided a slightly better description of the equilibrium data than the Langmuir model. Iron filings showed rapid phosphorus removal during the early reaction stage but a non-monotonic time response, while pyrite and limestone showed more stable short-term behavior. Among the three tested 1:1 binary mixtures, the iron filings–limestone combination showed the highest phosphorus-removal performance, with removal remaining above 99% across the tested dosage range. The combined pH, kinetic, thermodynamic, and SEM results are consistent with possible contributions from Fe^0 corrosion, CaCO_3 dissolution, surface binding, and precipitation-related processes. However, these observations should be regarded as supporting evidence for possible Fe- and Ca-mediated pathways rather than direct identification of specific phosphorus-containing phases. These findings provide a mechanistic basis for considering simple Fe- and Ca-based mineral media in sustainable agricultural phosphorus-management strategies.

The present results should be interpreted within the scope of a laboratory-scale batch screening study. The experiments were conducted using synthetic phosphate solutions, while the dosage and kinetic tests were performed at 20 °C and the apparent thermodynamic analysis covered 298–308 K. In addition, only a fixed 1:1 mass ratio was evaluated for the binary mixtures. Differences in particle size among the three materials were not normalized using BET specific surface area, and phosphorus removal was evaluated from changes in dissolved phosphorus concentration rather than from a complete aqueous–solid phosphorus mass balance. The pH measurements were limited to the initial and final values, and SEM provided qualitative morphological information rather than direct phase identification.

Future studies should focus on validation using real agricultural runoff under continuous-flow conditions. A wider range of Fe/Ca mixing ratios and temperatures, particularly lower temperatures, should be evaluated together with standardized particle-size fractions and BET specific-surface-area measurements. Desorption tests and direct solid-phase phosphorus measurements would help clarify phosphorus-retention stability and possible re-release. Continuous-flow experiments should also evaluate hydraulic performance, clogging, passivation, material service life, effluent pH, Fe/Ca release, and the potential for material reuse or phosphorus recovery. Such information is necessary for a more comprehensive assessment of the long-term applicability and sustainability of iron- and calcium-based mineral media for agricultural phosphorus interception.

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