

Sustainable sorbents for phosphorus and pathogen removal from wastewater and their potential reuse

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Abstract. Excessive phosphorus from agricultural runoff and wastewater discharge is a major contributor to eutrophication in aquatic ecosystems, highlighting the urgent need for effective removal strategies in wastewater treatment. This study evaluates the dual functionality of calcium and iron oxide composites (CaFeOxide) for removing pathogens and phosphorus from wastewater, aiming to mitigate environmental pollution and promote sustainable reuse of spent sorbents. Phosphorus adsorption tests demonstrated that a 2 g/L dosage of CaFeOxide achieved an average removal efficiency of 84%. The composite also exhibited antimicrobial properties comparable to ferric sulphate, reducing *Bacillus subtilis* spore concentrations. When applied to soil, CaFeOxide improved pH levels and enhanced nutrient availability, underscoring its potential for integrated environmental benefits.

1. Introduction

Phosphorus (P) accumulation in aquatic systems, primarily driven by human activities such as agricultural runoff and wastewater discharge, has resulted in widespread eutrophication. This phenomenon, characterized by harmful algal blooms and oxygen depletion, poses significant ecological risks, degrading water quality and threatening aquatic life [1],[2]. In addition to nutrients, wastewater often contains pathogens and resilient spores [3]. Spores, particularly those of *Bacillus* spp., are highly resistant to chemical treatments and are frequently found in surface waters [4], [5] and agricultural wastewaters [6], [7].

Traditional P removal techniques methods in wastewater treatment, such as using ferric or aluminium salts, often have environmental downsides, including excessive sludge production, high dose dependency, and narrow temperature range [8]. Calcium-and-iron-rich composite materials have emerged as a promising alternative for removing P from wastewater. After adsorption, they can serve as fertilizers, supplying essential nutrients to crops while reducing the environmental impact of traditional chemical treatment methods [9].



This study aims to evaluate the effectiveness of calcium and iron oxide composites (CaFeOxide) in removing phosphorus and pathogens from wastewater, with the dual objectives of mitigating environmental pollution and enabling the reuse of spent sorbents.

2. Materials and Methods

The raw materials used in this study, iron oxide-containing pigments, were sourced from local deposits in Latvia, specifically Talicka (Madona region) and Steicele (Limbaži region). These pigments were subsequently thermally treated to synthesize CaFeOxide-T and CaFeOxide-S, following the methodology outlined by Karasa et al. [10].

2.1. Effect of competing ions on sorption

Previous studies were carried out to evaluate P removal from real wastewater, where it was found that an optimal dose of sorbent – CaFeOxide - is 2 g/L [10], [11]. The experimental setup to study the effects of competing ions on P removal from solution was adapted from [12]. Anions commonly found in wastewater - sulphate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-) were chosen.

Competing ion stocks were prepared in 1 L volumetric flasks by dissolving Na_2SO_4 , NaNO_3 , NaCl in an ultra-pure water. Then stocks were diluted to achieve a final phosphate and ion concentration of 1 g/L. The concentrations of each competing ion were calculated based on stoichiometric principles to ensure proper ionic interactions without compromising the desired phosphorus concentration.

To establish the initial phosphorus removal rate (without competing ions), 0.20 grams of CaFeOxide-S or CaFeOxide-T were added to 0.1 L of phosphate solution (2 g/L). In parallel, 100 mL of phosphate/individual competing ion solution was added to 0.20 grams of each CaFeOxide (2 g/L ratio). All mixtures were shaken continuously for 24 hours at 160 rpm and room temperature to facilitate thorough interaction. Residual phosphorus concentrations were measured using a Hach Lange DR3900 spectrophotometer via the molybdovanadate method with acid persulfate digestion (LCK 348), with results expressed in total PO_4^{3-} mg/L units.

The phosphorus removal rate from wastewater per gram of CaFeOxide was calculated using the following equations:

$$\text{Removal \%} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where, C_o refers to the initial concentration of P in the solution (mg/L), C_e indicates the final concentration of P in the solution.

2.2. The Impact of the CaFeOxide composite on *Bacillus subtilis* spores reduction in wastewater

The jar test method used for P sorption [11] was also used to evaluate the effectiveness of CaFeOxide composites and commercially available coagulant - iron(III) sulphate $\text{Fe}_2(\text{SO}_4)_3$ — in reducing *Bacillus subtilis* spores in wastewater.

Bacillus subtilis ATCC 6051 was initially cultured on Luria-Bertani agar. Bacterial colonies were then collected using a sterile spatula and transferred into a sterile phosphate-buffered saline solution (7 mM Na_2HPO_4 , 3 mM NaH_2PO_4 , 130 mM NaCl , pH 7.2). After a 6-day incubation at 37°C, the suspension was stained with malachite green and safranin to confirm the presence of spores, achieving approximately 98% sporulation. To eliminate any remaining vegetative cells, the suspension underwent a 10-minute heat shock at 80°C, followed by cooling and storage at 4°C.

A spore suspension was prepared at a concentration of 10^5 spores/mL in real wastewater. To compare spore concentration decrease in wastewater, 2 g of CaFeOxide-S was introduced to one set of beakers, and 2 g of Fe (as $\text{Fe}_2(\text{SO}_4)_3$) to other set of beakers. Control beaker contained only wastewater and the spore suspension.

To ensure that only spores were analyzed and vegetative cells were eliminated, after treatment with CaFeOxide-S and iron(III) sulphate all samples underwent heat treatment at 80°C

for 10 minutes. The decimal dilutions were made if necessary and the heat-treated samples were distributed on R2A agar plates. The plates were then incubated in 37°C for 24 h. Afterwards, colony forming units (CFU) were counted.

Wastewater samples were taken from the Daugavgrīva Wastewater Treatment Plant (WWTP) in Riga, Latvia from the inlet after the grit chambers. Wastewater characteristics: pH 7.14 ± 0.16 , electrical conductivity $1556 \pm 338 \mu\text{S}/\text{cm}$, UV absorbance at 254 nm of $1.49 \pm 0.44 \text{ cm}^{-1}$, UV absorbance at 410 nm of $1.32 \pm 1 \text{ cm}^{-1}$, turbidity of $233 \pm 113 \text{ NTU}$, and a total phosphorus concentration of $22.74 \pm 10.29 \text{ mg}/\text{L}$.

2.3. The Impact of spent sorbents for soil treatment

Spent sorbents from previous P adsorption experiments were collected, then distributed in a thin layer and dried at room temperature for 48 h. To evaluate the impact of spent sorbents on soil pH 0, 25 g, and 250 g of spent dried sorbent were added to 1 L of a soil.

The soil, classified as anthropogenic heavy clayey sand with 7.11% organic matter, was collected in November 2023 by the "Bruži" agricultural farm in Dunalka parish, Latvia. Its granulometric composition, determined using the ISO 11277:2020 [13] method, comprised 77% sand, 7% silt, and 16% clay.

The standard method for the determination of soil pH described in LVS EN ISO 10390:2022 was used [14], applicable to soils, biowaste, and sludge. Measurements were conducted in water, 1 mol/L potassium chloride, and 0.01 mol/L calcium chloride suspensions to capture variations under different ionic conditions.

2.4. Statistical Analysis

All experiments were performed in triplicate, and results are presented as mean \pm standard deviation (SD). Data points in the figure are annotated with error bars.

3. Results and discussion

3.1. Effect of competing ions on P removal

The influence of competing ions on phosphate removal was investigated to understand the interaction of CaFeOxide sorbents with anions commonly found in wastewater. CaFeOxide-T samples exhibited higher reduction of phosphate levels compared to the CaFeOxide-S (Figure 1). Addition of selected competing ions (Cl^- , NO_3^- or SO_4^{2-}) to CaFeOxide-T improved the phosphate removal (for 17.4 - 22.5 %) of the composite materials. The average level of remaining phosphate in the solution after exposure to CaFeOxide-T was 414 mg/L PO_4 as initial value, and it decreased to 327 mg/L in the presence of Cl^- , to 342 mg/L for NO_3^- and resulted in 321 mg/L for SO_4^{2-} .

The addition of chloride ions to CaFeOxide-S slightly improved the phosphate removal from the solution (from initial residual value of 636 mg/L to 604 mg/L PO_4). At the same time the addition of nitrate decreased the sorption of phosphate for 4.8 % resulting in 667 mg/L. Sulphate ions did not compete with the phosphate showing the remaining concentration of 644 mg/L PO_4 in the solution.

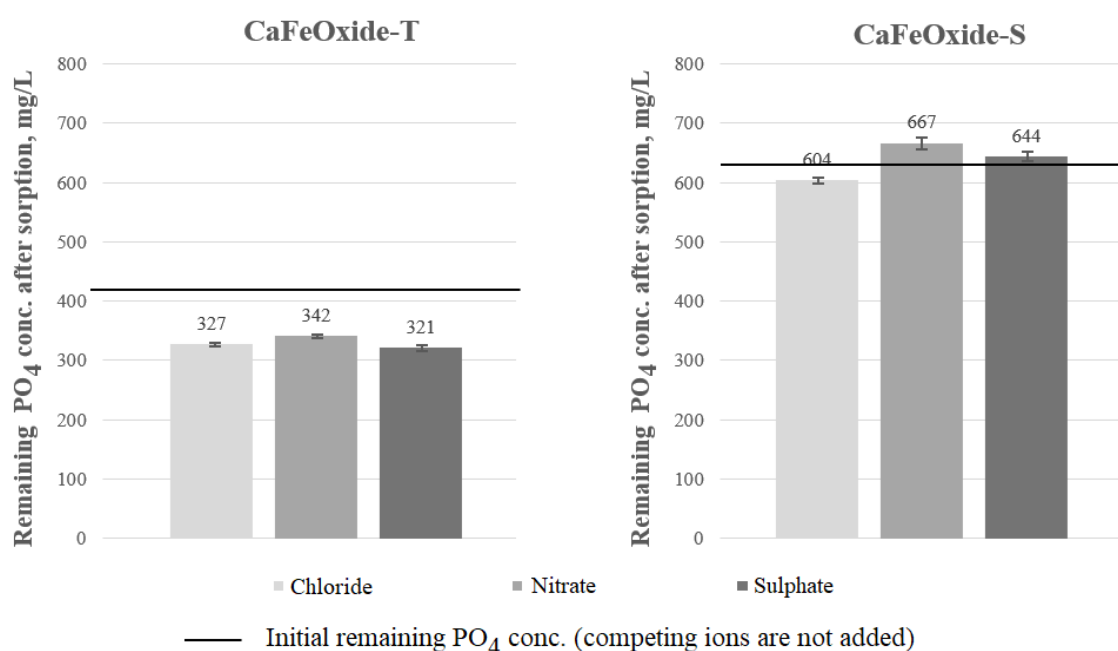


Figure 1. Effect of competing ions on phosphate removal (remaining concentration of PO₄ in the solution) by two CaFeOxides. Error bars represent mean \pm SD ($n=3$).

Obtained data demonstrates that nitrate ions (NO₃⁻) the most negatively interfere with the phosphate sorption process for CaFeOxide-S. This is because of the competition with P for sorption sites due to its smaller ionic size. Whereas CaFeOxide-T exhibited better phosphate removal in the presence of competitive ions. Surprisingly, the addition of the chloride (Cl⁻) improved the phosphate removal for both composites. These findings show the potential of CaFeOxide application for the treatment of saline waters.

Compared with commercial sorbents Ferrolox and Katalox, which achieved 310.42 mg/g and 14.58 mg/g phosphate adsorption capacities respectively from wastewater [15], CaFeOxide-T and CaFeOxide-S showed substantially higher capacities - exceeding 600 mg/g and 300 mg/g even in the presence of competing ions. Maintaining high adsorption under complex conditions highlights CaFeOxides potential as promising, high-capacity sorbents for wastewater treatment applications.

3.2. Effect of CaFeOxide-S and Fe₂(SO₄)₃ on *Bacillus subtilis* reduction

Both CaFeOxide-S and iron(III) sulphate (Fe₂(SO₄)₃) exhibited similar effectiveness in reducing *Bacillus subtilis* spores. CaFeOxide-S achieved an average reduction of 46.6 \pm 0.5 % within 1 hour, while Fe₂(SO₄)₃ demonstrated 40.3 \pm 2.8 % reduction. Fe₂(SO₄)₃ showed a faster initial reduction. In similar experiments \geq 99 % of enterobacteria (naturally present in wastewater) were removed using 120 mg/L FeCl₃ coagulant [16]. Using 220 - 350 mg/L of Al₂(SO₄)₃ [17] achieved 98.3 - 99.4% decrease of bacteria in treated wastewater. In the current study the dose of coagulant was significantly higher, which according to [18] may also reverse charge neutralization, causing re-stabilization of the colloidal system. Also, spores are much more resistant to chemicals than bacteria. Due to these reasons our inactivation rates may be smaller.

3.3. Effect of spent sorbents on soil properties

The study revealed that soil pH values varied depending on the amount of spent sorbent added. In control samples, where no spent sorbent was applied, pH was 8.86 \pm 0.01. The application of CaFeOxide-S exhibited a clear dose-dependent alkalizing effect on soil pH. A 25 g/L dose increased

the pH to 9.33 ± 0.02 , while a 250 g/L dose raised it significantly to 12.08 ± 0.01 . These findings suggest that CaFeOxide-S can effectively raise soil pH, making it a suitable soil amendment, particularly for acidic soils. Such improvement in the soil could be particularly beneficial for acidic soils, as it improves nutrient availability and creates a more conducive environment for root development and microbial activity, ultimately promoting healthier plant growth [19],[20].

4. Conclusions

This study demonstrated that calcium and iron oxide composites can be used for phosphorus and pathogen removal from wastewater, thereby contributing to pollution mitigation and facilitating the reuse of spent sorbents.

Specifically, the CaFeOxide-T reduced phosphate concentrations from 414 mg/L to 327 mg/L with Cl^- , 342 mg/L with NO_3^- , and 321 mg/L with SO_4^{2-} . Meanwhile, CaFeOxide-S decreased phosphate levels from 636 mg/L to 604 mg/L with Cl^- and 644 mg/L with SO_4^{2-} , though an increase to 667 mg/L with NO_3^- resulted in lower efficiency (4.8% reduction). In terms of pathogen removal, the spore removal efficiency of CaFeOxide-S (46.6 %) was comparable to that of iron(III) chloride (40.3 %).

Additionally, when spent CaFeOxide-S from phosphate removal processes was mixed into soil, it increased the soil pH in a dose-dependent manner, indicating its potential use as an amendment for acidic soils.

Overall, these findings illustrate the promise of using calcium and iron oxide composites for pollution control. However, further economic assessments and pilot-scale trials are needed to determine cost-effectiveness and feasibility.

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