Use of calcium/iron oxide composites for sorption of phosphorus from wastewater

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Abstract. The development of an effective, low-cost and natural sorbent is of great significance for phosphorus removal and recovery from small and medium size industrial and municipal wastewater. Commonly used phosphorus removal methods are costly and thus rarely applied in the small-scale WWTPs. This research was aimed at preparing and characterising three different calcium/iron composites for evaluating their sorption performance for the removal of phosphorus from aqueous solutions and domestic wastewater. The obtained composite materials belonging to the Brownmillerite mineralogical subgroup were characterised by the Powder X-ray Diffraction (PXRD), specific surface area analysis by Brunauer-Emmett-Teller (BET) method and scanning electron microscope (SEM). It was found that for aqueous solutions the sorption process is pH- dependent, showing the optimal sorption conditions for phosphorus removal at pH 3 to pH 6. However, all three proposed composites significantly increased the pH of wastewater. All three tested materials adsorbed phosphorus from wastewater. Maximal phosphorus adsorption capacity from the domestic wastewater was 17.75 mg g^{-1}, 8.25 mg g^{-1} and 4.46 mg g^{-1} for CaFeOxide, CaFeHydr and CaFeReg respectively. In further research it is planned to develop an environmentally friendly and cost-effective phosphorus recovery technology with the potential to apply the used sorbent as a slow-release fertiliser in agriculture.

Key words: Brownmillerite, Srebrodolskite, natural inorganic sorbents, phosphorus removal, resource recovery, wastewater treatment.

INTRODUCTION

In the EU phosphate rock and phosphorus (P) are included in the list of critical raw materials (CRMs) due to the risks of their shortage of supply and taking into account the fact that the impacts of a shortage on the economy are greater than those of most other raw materials. In the EU countries, there are no economically significant deposits of

phosphate rock (except for Finland) and demand for phosphorus-containing materials is satisfied entirely by imports. Morocco and Kazakhstan are the main countries providing P and phosphate rock to the EU. In 2020 the EU import dependency rate for phosphorus and phosphate rock was 100% and 84%, respectively (European Commission, 2020). Despite the natural sources of phosphates being depleted, the problem of the increase of eutrophication of waterbodies is driven by a discharge of untreated or semi-treated wastewater from small wastewater treatment plants, and runoff from agricultural soils being over-fertilised. Eutrophication of both freshwater and coastal marine ecosystems leads to a decrease in dissolved oxygen concentration and increases the abundance of toxic algae and aquatic plants. 415 coastal water bodies are defined as eutrophic and hypoxic worldwide and among them, the following five are the most critical: the Baltic Sea, the North Sea, The Gulf of Mexico, the Chesapeake Bay, and the Black Sea (Smol et al., 2020).

Among the many phosphorus sources, effluents from wastewater treatment plants (WWTPs) provide significant loading of P into the surface waters. Recovery of P from wastewater has been gaining more attention lately (Chrispim et al., 2019; Jupp et al., 2021). Chemical precipitation and enhanced biological (bacterial) uptake are the main methods for additional P removal used in the WWTPs. Although these methods are well-established and applied in the large WWTPs, their use in the small WWTPs is very rarely practised due to limited legislative acts. For instance, in the EU, the regulation on municipal wastewater treatment (Directive 91/271/EEC) does not state any limits for permissible P concentration in the effluent from the WWTPs operating in small agglomerations with less than 2000 population equivalents (Molinos-Senante et al., 2014). Scaling up the alternative P removal methods to the small WWTPs results in high capital and operational costs and overall system complexity and is rather detrimental as the obtained P reduction rates on a small scale are often insufficient and fail to meet the environmental safety standards. Furthermore, a concern arises that the environmental impact of phosphorus discharge from the small-scale WWTPs is greater than previously assumed (Bunce et al., 2018, Tihomirova et al., 2019; Denisova et al., 2020).

Among the various viable methods reported for the removal (and recovery) of phosphorus are ion exchange, coagulation/sedimentation or precipitation, and crystallisation, whereas adsorption stands out as one of the most sustainable solutions (Parasana et al., 2022). Some of the recent advances for P-capture include the use of carbonaceous (carbon-based materials) sorbents, such as activated carbon, and biochar (Almanassra et al., 2021), mesoporous silica, metal-organic frameworks, clay and zeolites as well as bio-derived materials, chitosan-based and other hydrogels (Othman et al., 2018; Jemeljanova et al., 2019; Jóźwiak et al., 2021), followed by more advanced engineered materials, including magnetic and granular adsorbents (Bacelo et al., 2020). Typically, sorbents for the P removal can be divided into the following categories: iron-based, silica-alumina-based, calcium-based, and biochar-based, wherein the metal and metal oxides are employed in phosphorus removal (Parasana et al., 2022).

The most common inorganic coagulants for wastewater treatment are soluble iron and aluminium salts (Kweinor & Rathilal, 2020). These reagents are cheap and effective for the turbidity reduction, removal of the natural organic matter, and other organic and inorganic pollutants (Park & Yoon, 2009). Furthermore, iron-based coagulants are proven to reduce phosphorus concentrations in polluted waters (Mishima et al., 2018; Mohamad et al., 2022). However, these chemicals have several disadvantages, including

excessive sludge generation and negative impact of the sludge on the environment (due to a high salt content) (Kweinor & Rathilal, 2020) and crops. In the current study, three calcium/iron composite materials of the Brownmillerite mineralogical subgroup were tested that can be used to adsorb phosphorus. Calcium/iron composite materials are environmentally friendly, and thus, can be used directly as fertilisers after the adsorption process, providing the crops with essential phosphorus content while lacking the disadvantages of common reagents. Furthermore, calcium/iron composite materials have other advantages, such as fast reactivity and good selectivity (Bacelo et al., 2020). Additionally, calcium/iron oxide materials can be found naturally (Chelyabinsk coal basin in the South Urals) (Chesnokov & Bazhenova, 1985) and it can be cheaply manufactured from Latvian resources - Staiceles, Kazuleja colour earth deposits. The process has the potential to be scaled up, thus meeting the demand for environmentally friendly sorbents in the wastewater treatment process.

The aim of the current research is to evaluate three calcium/iron oxide composites for their potential as an efficient and sustainable alternative for phosphorus removal from wastewater in the small and medium size WWTPs.

Usage of the sustainable materials for phosphorus removal as a complimentary technological step may be integrated into several stages of the WWTP operative process, allowing phosphorus recovery in the form of a ready-to-use fertiliser. The development of the ready-to-use fertiliser, especially from waste streams, has gained significant attention lately (Montemurro et al., 2017; Balogun et al., 2022).

MATERIALS AND METHODS

Synthesis of calcium/iron oxide composites
The raw adsorption composite for this research was obtained from raw natural material from the local deposits in Latvia. After the treatment material was transferred to Brownmillerite subgroup mineral - Srebrodolskite labelled as calcium/iron oxide (CaFeOxide). Two more composites for the research were derived from the initial CaFeOxide, e.g., calcium/iron hydroxide form and regenerated oxide. Calcium/iron hydroxide is a product of CaFeOxide interaction with water (labelled as CaFeHydr). Thereafter, the hydrated calcium/iron form was regenerated back to oxide form (labelled as CaFeReg). The detailed synthesis procedure of the proposed composites cannot be disclosed by the authors due to the protection of intellectual property rights (including manufacturing technology). The obtained calcium/iron composites were further used for the phosphorus removal from phosphate aqueous solutions and wastewater samples.

Characterization methods of calcium/iron oxide composites
Changes in the calcium/iron composite structures was characterised by the Powder X-ray diffraction (PXRD) performed with Bruker D8 Advance powder diffractometer equipped with LynxEye position-sensitive detector and Cu Kα radiation ($\lambda = 1.5418$ Å), 40 kV, 40 mA. The diffraction patterns were recorded with 0.02 step size and a scan speed of 0.5 s per step in the 2θ range from 5 to 65.

The scanning electron microscopy (SEM) data were obtained to study the morphological changes of samples using the scanning electron microscope FE-SEM Hitachi S4800 (Tokyo, Japan). The samples were measured in the secondary electron regime, with the SEM operating voltage being 3–5 kV.

The specific surface area (SSA) of the samples was determined by nitrogen adsorption–desorption isotherms at –196 °C (77 K) using the Quantachrome Autosorb-iQ-KR/MP automated gas sorption analyser. Prior to the analysis, the powder samples were outgassed in vacuum at 50 °C for 3 h. The SSA was calculated by using the Brunauer-Emmett-Teller (BET) equation. The pore size distribution was determined by applying the density functional theory (DFT). The total pore volume was measured from the adsorption isotherm by the uptake of nitrogen at a relative pressure of $p/p0 = 0.99$. All calculations were performed by the ASiQwin (Version 2.0) program developed by the Quantachrome Instrument.

Adsorption of phosphorus from aqueous solutions

To compare the efficacy of the studied calcium/iron composites with the efficacy of commercially available materials for phosphorus removal, the phosphate adsorption procedure in accordance with Delgadillo-Velasco et al. (2018) was carried out. The adsorption process was performed in batch systems with constant agitation of 150 revolutions per minute and 72 h equilibrium time at ambient temperature in the phosphate solution of pH 7 (adjusted with 2 M NaOH). The sorbent/phosphate solution mass-to-volume ratio is 2 g L^{-1}, e.g., 0.50 g of the selected calcium/iron composite and 250 mL of 500 mg L^{-1} phosphate solution. The phosphate solution was prepared by dissolving KH_2PO_4 in ultrapure water (Milli-Q).

An additional procedure was carried out to evaluate the adsorption efficacy of phosphorus from phosphate solutions depending on the pH level of the solution. 50 mL of 500 mg L^{-1} phosphate solution with known pH was added to 0.10 g CaFeOxide at a constant agitation of 150 rpm and 24 h equilibrium time at ambient temperature. The pH of the phosphate solutions varied from pH 2 to pH 10 (being adjusted with 1 M NaOH or 1 M HCl).

Measurements of the phosphorus concentrations in these experiments were made by the inductively coupled plasma optical emission spectrometry method (ICP-OES). The quantification of P was performed on the inductively coupled plasma optical emission spectrometer iCap 7000 (Thermo Scientific) using a calibration curve at 177.49 nm. The test solutions for the measurements were diluted 10 times. The obtained ICP-OES numerical data of the phosphorus determination for calcium/iron composites were then recalculated to mg P L^{-1}.

Adsorption of phosphorus from wastewaters (jar tests)

The calcium/iron oxide composites were tested for their ability to remove phosphorus from wastewater. Experiments were made using a simple Jar Test PB-700 (Phipps & Bird). The wastewater obtained from the wastewater treatment plant 'Daugavgrīva' (Riga, Latvia) was used (wastewater was collected after grit chambers). The average wastewater quality: pH 7.16 ± 0.13, electrical conductivity $1,690 \pm 62$ µS cm^{-1}, UV light absorption at 254 nm 1.59 ± 0.26 cm^{-1}, UV light absorption at 410 nm 1.83 ± 0.83 cm^{-1}, turbidity 285 ± 102 NTU, total phosphorus concentration of 30.4 ± 4.52 mg L^{-1}. 0 g L^{-1}, 1 g L^{-1}, 2 g L^{-1}, 3 g L^{-1}, 5 g L^{-1} and 10 g L^{-1} of CaFe oxide composites. The test consisted of 1 min of rapid mixing (313 rpm), 30 min of slow mixing (41 rpm), and 1 h of sedimentation. The experiments were conducted at the room temperature of 20 ± 2 °C.

Phosphorus in wastewater samples was analysed as described in Golovko et al. (2019) using the colourimeter Hach DR890 (Hach-Lange, Germany) and standard Hach protocol No. 8190. Before the analysis, samples were filtered through 0.45 μm syringe filters and diluted, if necessary.

The phosphorus removal rate from wastewater per gram of calcium/iron composite was calculated using the equations:

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

$$Q_e = \frac{C_0 - C_e}{M} \times V \qquad (2)$$

where C_0 is the initial concentration (mg L^{-1}) of phosphorus in the wastewater, Q_e represents the amount of phosphorus adsorbed per g of the calcium/iron composite (adsorption density), M is the mass (g) of the calcium/iron composite, V is the volume of the wastewater (L).

RESULTS AND DISCUSSION

Characterization of calcium/iron oxide composites

The obtained PXRD data (Fig. 1) were processed with the Diffrac Eva software and the crystallographic database ICDD PDF-2. The available data confirmed CaFeOxide composite sample as a $Ca_2Fe_2O_5$ compound - Srebrodolskite structure compound (subgroup of Brownmillerite) with traces of quartz. The comparison of the x-ray powder diffraction data for CaFeOxide and CaFeReg confirmed identical patterns for both samples, thus proving the efficacy of the CaFeHydr composite regeneration procedure employed. The PXRD pattern of the CaFeHydr sample showed significant changes in the initial calcium/iron oxide structure indicating a hydroxide phase formed as a result of CaFeOxide interaction with water.
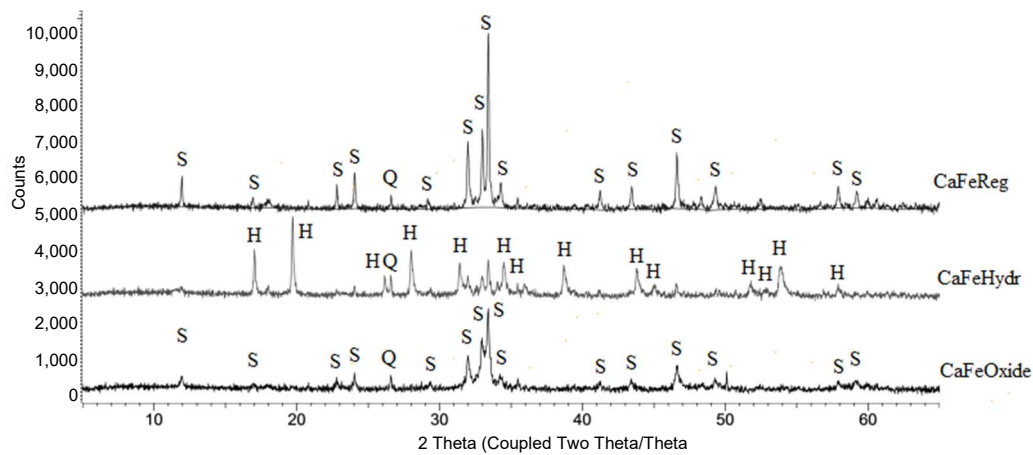

Figure 1. PXRD patterns of raw calcium/iron composites (S – Srebrodolskite $Ca_2Fe_2O_5$; H – Calcium iron hydroxide $Ca_3Fe_2(OH)_{12}$; Q – quartz SiO_2).

The SEM images showed that the surface morphology of the initial CaFeOxide consist of globular or spheroid shape particles that are densely arranged into larger agglomerations (Fig. 2, a) which are characteristic for the Brownmillerite samples (Gupta et al., 2015; Dhankhar et al., 2016). After water and thermal treatment, CaFeOxide morphology was slightly changed and additionally octahedral and wavy sheet-like particles were found (Fig. 2, b, c). Similar results were discovered in Gupta et al. (2015) work, where after carbonation-calcination, the morphology changed to sheet-like morphology.
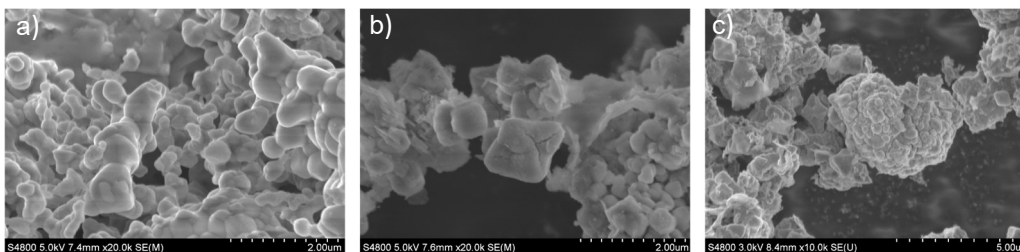

Figure 2. SEM images (20k and 10k magnification) of initial calcium/iron oxide composite (a); calcium/iron hydroxide form (b) and regenerated calcium/iron oxide (c).

The CaFeOxide samples also were characterised also by their specific surface area (SSA), as this parameter is often used for sorption interpretation. The SSA increased more than 4 times after thermal treatment and increased in the following order: initial CaFeOxide < CaFeOxide hydroxide form < regenerated CaFeOxide (Table 1).

These parameters indirectly indicate that the sorption capacity of regenerated CaFeOxide will be higher than for the initial and water-treated CaFeOxide samples. Similar results of SSA measurement (8.22 m^2 g^{-1}) were also found for other calcium and iron-containing materials (Gupta et al., 2015).

Table 1. Textural properties of calcium/iron oxide composites

Sample	Specific surface area (m^2 g^{-1})	Pore volume (m^3 g^{-1})	Average pore diameter (nm)
CaFeOxide	2.588	0.006	4.678
CaFeHydr	3.804	0.014	1.299
CaFeReg	10.616	0.044	7.524

Sorption efficacy of the calcium/iron oxide composites

Competitive analogues of calcium/iron oxide composites. The sorption capacity of the studied calcium/iron composites were compared with the commercially available analogues for phosphate adsorption. Eight commercial sorbents of different origins and nature were studied in the Delgadillo-Velasco et al. (2018) research for the removal of phosphate using synthetic solutions and wastewaters from an anodizing company (Table 2). The materials included activated carbons (CC, B), bone char (BC), catalytic carbon (CtC), natural silica (S), natural zeolite (Z), manganese (II) oxide composite (KL) and iron (III) hydroxide (F). The results obtained from the above mentioned research work established the iron (III) hydroxide (Ferrolox, F) and manganese (II) oxide composite (Katalox, KL) being as the most perspective, with the phosphate sorption values of 76.0 mg g^{-1} and 23.5 mg g^{-1}, respectively.

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Table 2. Specification of commercial sorbents used for the removal of phosphate from water (adapted from Delgadillo-Velasco et al., 2018)

Abbr.	Sorbent	Particle size (mm)	Surface area ($m^2 \, g^{-1}$)	Sorption value ($mg \, g^{-1}$)
CC	Coconut Shell activated carbon. Vegetal.	2.38–0.595	1,050	5.8
B	Bituminous coal activated carbon. Mineral.	2.38–0.595	1,000	6.3
BC	Bone char. Animal: bovine bones	2.38–0.595	104	16.5
Z	Natural zeolite	1.18	25	2.7
S	Natural Silica	3.175–1.58	n/a	5.2
F	Ferrolox. Patented granular Iron hydroxide (70–85%)	1.5–4.0	270	76.0
CtC	Catalyc Carbon. Coconut shell activated carbon (85%) with iron catalytic coating (FeO(OH) 15%)	2.4–0.6	2,000–2,500	1.9
KL	Katalox Light. ZEOSORB (clinoptilolite [85%]) with MnO_2 coating (10%) and $Ca(OH)_2$ (5%)	1.4–0.6	n/a	23.5

The suggested calcium/iron oxide composites were treated in the same way as analogues and showed higher sorption potential than iron (III) hydroxide (Ferrolox, F). The phosphate sorption results for some commercial sorbents and calcium/iron composites are summarised in Fig. 3.
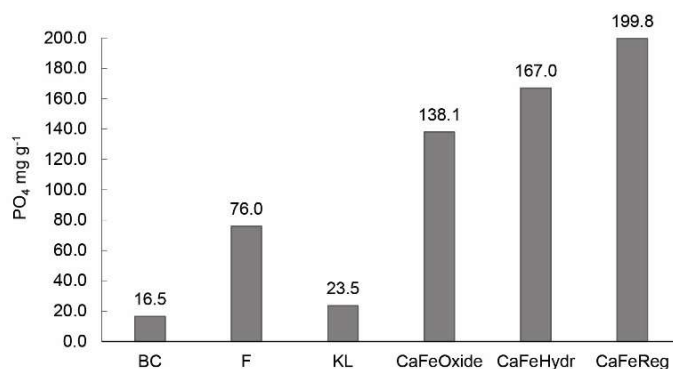

Figure 3. Sorption results for BC – bone char, F – Ferrolox, KL – Katalox Light (Delgadillo-Velasco et al., 2018) and Ca/Fe composites using phosphate solutions of 500 mg L^{-1} at pH 7, mass to volume ratio of 2 g L^{-1}.

The obtained data indicated that the highest phosphate sorption value of 199.8 mg g^{-1} was achieved when CaFeReg composite was used. This can be explained by the regenerated composite's finer structure and smaller particles, resulting in a larger surface area of 10.616 m^2 g^{-1} (confirmed by BET analysis, see Table 1).

pH levels of phosphate solutions. The initial CaFeOxide was selected for the evaluation of pH influence on the phosphorus uptake in the pH range from 2 to 10. The obtained sorption results are summarised in Fig. 4.
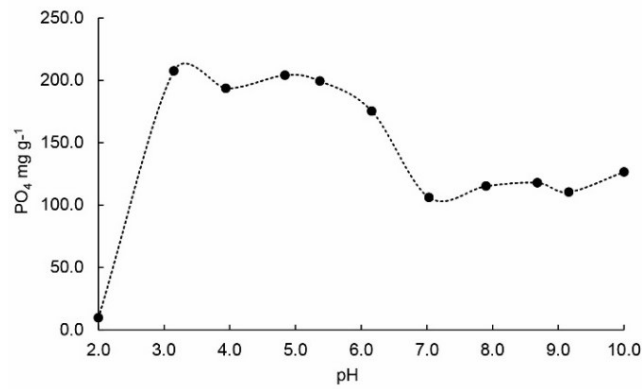
Figure 4. Phosphate sorption results for initial CaFeOxide composite at different pHs.

The sorption process is pH-dependent, showing the optimal sorption conditions for the phosphate removal at pH 3 to pH 6, which corresponds to the results of other studies involving the use of synthetic P solutions (Kang et al., 2003; Ajmal et al., 2018).

Phosphorus removal from wastewater

Three different calcium/iron oxide composites were tested for their ability to remove phosphorus (total) from the domestic wastewater by using a simple jar test. The results showed that with the addition of all tested materials, pH levels of the wastewater increased with the increase of concentration of calcium/iron oxide composite added (Fig. 5). The biggest incline of the pH level was observed in the sample containing CaFeReg, when the pH increased from 7.16 to 11.44 after 1 min (rapid mixing). After 1 h (after sedimentation) the pH reached the value of 11.69. The release of composite structural CaO in aqueous solutions led to an increment of pH value due to the formation of $Ca(OH)_2$, in the case of CaFeReg pH these values were higher due to finer particles of the suggested composite.
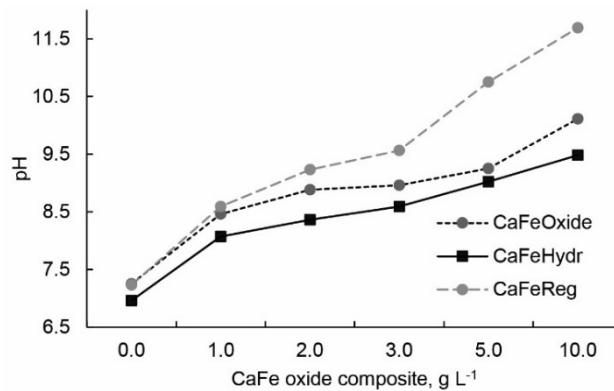

Figure 5. Changes in wastewater pH after the sedimentation depend on the amount of calcium/iron composite added.

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The concentration of total phosphorus decreased with the addition of all calcium/iron composite samples alone (Fig. 6). For the CaFeOxide the most significant decrease of phosphorus from 27.4 to 3.74 mg L^{-1} was observed after the addition of 2 g L^{-1} of composite resulting in 84% decrease of phosphorus concentration in wastewater. The further increase of concentration of CaFeOxide composite had insignificant effect on the phosphorus removal. Adding 10 g L^{-1} of CaFeOxide led to 96% removal of phosphorus. CaFeHydr demonstrated a more even phosphorus removal rate depending on the amount of composite added. 1 g L^{-1} of CaFeHydr resulted in a 16% decrease in the phosphorus concentration. CaFeHydr at 2 g L^{-1} showed the lowest result among the three tested materials (39% decrease of phosphorus). The addition of 10 g L^{-1} of CaFeHydr led to 85% removal of phosphorus. CaFeReg at 1 g L^{-1} showed a 36% decrease in phosphorus concentration. 10 g L^{-1} resulted in 81% decrease in P concentration, indicating that CaFeOxide was the most effective for phosphorus removal among the three composites tested. It was also the most effective at the lowest concentration of 1 g L^{-1}. The previous results with lower calcium/iron composite concentrations (data not shown) demonstrated a low efficiency in phosphorus removal. It should be noted that the phosphorus adsorption rates from domestic wastewater were much lower if compared to the results obtained with the synthetic phosphorus solutions carried at fixed pH of 7 for 72 h and a higher loading of "pure" phosphorus (Fig. 4). The competitive sorption processes are possible and should be additionally evaluated in future, when calcium/iron composites are applied to wastewater samples.
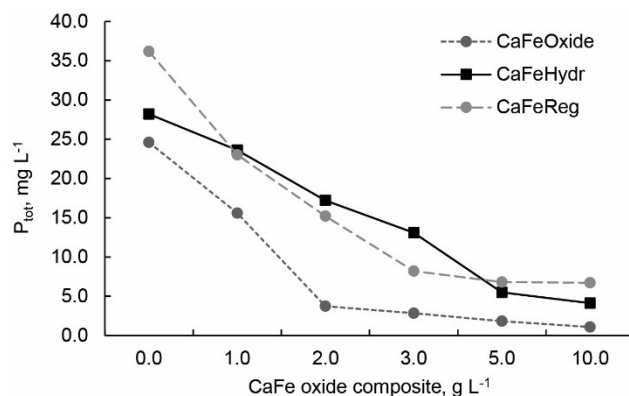

Figure 6. Changes in the concentration of phosphorus after the sedimentation versus the amount of calcium/iron oxide composite added.

Similar tests were performed for ferrihydrite, goethite, and magnetite using synthetic phosphorus solutions (Ajmal et al., 2018). Their results indicated maximal removal of 77%, 81% and 89% at 5 g L^{-1} adsorbent dosage for goethite, magnetite and ferrihydrite respectively. In the current study at 5 g L^{-1} it was 92%, 80.5% and 81%. However, the initial P concentration was lower in this study (30 mg L^{-1} P versus 100 mg L^{-1}). Relatively similar results (38.8 mg P g^{-1}) for phosphorus adsorption from lake water using modified iron oxide-based sorbents were achieved by Lalley et al. (2016). It should be noted that the composition of natural water and domestic wastewater is quite complex. Thus, the adsorption process is affected by many other factors

(including pH, water composition, salinity, and concentration of organic matter) and processes occurring within a solution, simultaneously. Also, in domestic wastewaters, the presence of calcium and magnesium compounds promotes phosphorus removal at higher pH values forming sparingly soluble precipitates including apatite and struvite. With more alkaline pH values precipitation of dolomite may occur (Kang et al., 2003). Higher pH values may be beneficial for the domestic wastewater treatment using iron compounds as concentrations of dissolved metals (copper, lead), benzo(a)pyrene and hexabromocyclododecane, as it was observed. Significant decreases in the concentration for dissolved cadmium, fluoranthene cypermethrin and biochemical oxygen demand (Comber et al., 2021) were also reported. A chemical reaction may be involved in addition to the adsorption process (high surface area and small particle size), where Ca_2^+ cations precipitate with condensed PO_4 (Park et al., 2021). Brushite $CaPO_3(OH)x2H_2O$ was identified by XRD in a current study, which is also in agreement with Park et al. (2021).

A negative control was used to understand if phosphorus concentration decrease was related to the adsorption or just phosphorus form changes due to the pH level increase. The results indicated a slight (13%) decrease of phosphorus concentration, when pH was adjusted to mimic pH increase caused by the addition of 2 g L^{-1} of the composites. Thus, indicating that the major phosphorus removal is attributed to the adsorption on the surface of composites.

There was no significant difference in the adsorption density (Q_e) for CaFeOxide (calculated using equation (2)) when 1 or 2 g L^{-1} of the composite was used. It was 17.70 and 17.75 mg (P) g^{-1}, respectively. For CaFeHydr, the maximal adsorption density was 8.25 mg g^{-1} (when 2 g L^{-1} of CaFeHydr was used). The lowest Q_e was for CaFeReg, it was 4.46 mg g^{-1} (when 3 g L^{-1} of CaFeReg was used). Recalculation of the results incorporating specific surface area indicated that CaFeReg demonstrated the lowest adsorption density per m^2 - 0.42 mg(P) m^{-2}. For CaFeOxide and CaFeHydr, Qe were 6.86 and 2.17 mg m^{-2} respectively.

CONCLUSIONS

In the current research three CaFe oxide materials were tested. The initial material (CaFeOxide) was obtained by treatment of natural origin material from local deposits of Latvia. Two more composites for the research were derived from the raw material, e.g., calcium/iron hydroxide form and regenerated oxide. The properties of the initial calcium/iron oxide composite were changed after water or thermal treatment, i.e., morphology transformed to a sheet-like structure, the specific surface area increased more than four times, and the composition was significantly altered. The ability of three calcium/iron oxide composites to adsorb phosphorus from domestic wastewater was evaluated. The results indicated that:

- The phosphorus sorption process from aqueous solutions is pH dependent, showing the optimal sorption conditions for the phosphate removal at pH 3 to pH 6 for CaFeOxide.

- All three calcium/iron oxide composites: CaFeOxide, CaFeHydr and CaFeReg adsorbed phosphorus from wastewater. The maximal adsorption density was 17.75 mg g^{-1}, 8.25 mg g^{-1} and 4.46 mg g^{-1}, respectively.

The suggested calcium/iron composites have a significant potential, compared to their commercially available analogues, as sustainable and regenerable materials for

removal of phosphorus from wastewater. The property of the CaFeOxide to increase the pH may be beneficial in wastewater with low pH levels.

Further studies of kinetics, thermodynamics and desorption of phosphorus must be performed to evaluate full potential of the developed calcium/iron oxide composites and possibilities to use them for the production of industrial sorbents. Additionally, toxicity studies should be performed to evaluate the possibility of direct application of used sorbent after phosphorus removal as fertilizer in agriculture.

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