The use of calcined paper mill sludge as a chemical precipitant in the simultaneous removal of ammonium and phosphate – paper mill waste recycling and reuse

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ABSTRACT

Currently, recycling and re-use of materials is extremely important due to the diminishing of natural resources. The objective of the European Union's circular economy strategy is to increase recycling and the use of industrial waste materials and side streams as secondary raw materials. In this study, a chemical precipitation method to simultaneously remove ammonium nitrogen and phosphate from the liquid phase of anaerobic digestate using calcined paper mill sludge was studied. Papermill sludge is a waste material that forms in the paper-making process. In addition, commercial calcium oxide (CaO) was used as a reference precipitant. The suitability of the formed precipitate's composition for recycled fertilizer use was also considered. The study results indicated that calcined paper mill sludge was as effective precipitant as commercial CaO in the removal of ammonium nitrogen and phosphate from the synthetic wastewater. In addition, the results indicated that calcined paper mill sludge removed efficiently phosphate from the liquid phase of anaerobic digestate, which led to the formation of hydroxyapatite, $Ca_5(PO_4)_3(OH)$. In this research we have shown, that calcined paper mill sludge can be used to produce recycled, slow-release, solid fertilizer. Another possible reaction, such as adsorption was also considered.

Keywords: Ammonium nitrogen; Calcined paper mill sludge; Hydroxyapatite; Phosphate; Precipitation; Recycled fertilizer

1. Introduction

Currently, recycling and re-use of materials is extremely important due to the diminishing of natural resources. The objective of the European Union's circular economy strategy is to increase the use of industrial waste materials and side streams as a secondary raw material [1]. The challenge of waste material used without increasing an environmental load can be met by improving the circulation of waste materials. 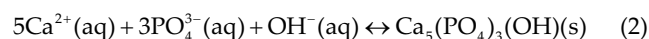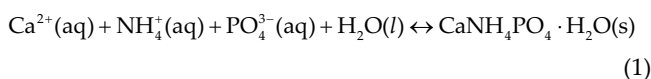The re-use and symbiosis products manufactured from side flows or waste materials in the local industry carry a minor environmental load [2].

Agriculture is the most significant diffuse source of nutrients in lakes and rivers. In addition, nitrogen and phosphorus are a major contributor to the eutrophication and deterioration in bodies of water in the ecological system. Anaerobic digestion plant uses various biomass materials originated from agriculture. Both Finnish National and European Union legislation must be taken into account as anaerobic digestate is used for agriculture purposes [3],

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principally, Regulation (EU) No. 2003/2003 of the European Parliament and of the Council related to fertilizers [4], Animal by-products Regulation (EU) No. 1069/2009 of the European Parliament and of the Council [5], and the Finnish Act on Fertilizer Products 539/2006 [6]. The nutrient containing liquid phase of anaerobic digestate can be used as such as fertilizer, but it should be converted into a more solid form to decrease transport costs.

Traditionally, phosphorus is removed by chemical precipitation using calcium, aluminum or iron salts or by a biological process [7,8]. Currently, different kinds of methods for phosphate removal, such as adsorption [9,10], ion exchange [11], electro-coagulation [12,13], and electro-Fenton treatment [14], have also been used. Nitrogen is typically present in the form of ammonium ion that is not easy to precipitate because ammonium volatilizes into the air as ammonia gas under alkaline conditions as a function of pH [15]. Nitrogen cannot be removed with traditional calcium, aluminum or iron salts, and therefore nitrogen is removed in the biological process by nitrification and denitrification as nitrogen gas. Therefore, the simultaneous removal of nitrogen and phosphorus is not possible using these traditional methods [16]. Phosphorous is a non-renewable mineral and it has been calculated that phosphorus resources will last for only a hundred years at the present depletion rate [17]. Therefore, there exists a great need to develop alternative, recycled phosphorus fertilizers for a more sustainable future. It has been estimated that there is enormous economic potential in the recycled fertilizer market. The economic potential of recycled fertilizers is approximated to be € 500 million per year, in Finland alone [18]. One solution to the recycled fertilizer market would be to convert ammonium nitrogen and phosphate into a product of more value. Chemical precipitation as struvite, $MgNH_4PO_4 \cdot 6H_2O$, from wastewater is a considerable method of ammonium nitrogen and phosphate recovery [19–21]. Commercial calcium salts such as CaO and $Ca(OH)_2$ are typically used precipitants in calcium phosphate precipitation. However, CaO can be prepared from paper mill sludge, a waste material formed in the paper-making process. Thus, it can be used as an inexpensive alternative precipitant in the removal of ammonium nitrogen and phosphate from nutrient containing wastewaters. This would lead to the formation of a struvite-like Ca-mineral, such as calcium ammonium phosphate $CaNH_4PO_4$ (Eq. 1) and hydroxyapatite $Ca_5(PO_4)_3(OH)$ (Eq. (2)) [22].

$$Ca^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) + H_2O(l) \leftrightarrow CaNH_4PO_4 \cdot H_2O(s)$$
(1)

$$5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq) \leftrightarrow Ca_5(PO_4)_3(OH)(s)$$
(2)

In the present research, the industrial waste material, Ca-rich paper mill sludge was applied as a low-cost chemical precipitant. It was used in the simultaneous removal of ammonium nitrogen and phosphate from synthetic wastewater and the authentic wastewater, the liquid phase of anaerobic digestate. The comparison was also made to

commercial CaO. The effect of temperature and pH on the precipitation efficiency was studied. The nutrient content of the formed precipitates was analyzed.

2. Materials and methods

The methodology used here is based on our previous papers [23,24].

2.1. Materials

2.1.1. Precipitants

Papermill sludge originated from Finnish pulp and paper mill located in northern Finland. Precipitated calcium carbonate is used as a paper filling material and coating material to enhance the paper's properties [25]. Wastewater produced at the pulp and paper mill contains calcium carbonate waste, cellulose fibers, and different kinds of organic and inorganic substances. In the pulp and paper mill, solid calcium carbonate waste sludge is returned to the lime kiln. Calcination in the lime kiln enables the reuse of paper mill calcium carbonate waste as a make-up chemical in the pulping process. Calcium carbonate is calcined at 1,000°C in the lime kiln (Eq. (3)) [26]:

$$CaCO_3(s) \xrightarrow{1000°C} CaO(s) + CO_2(g)$$
(3)
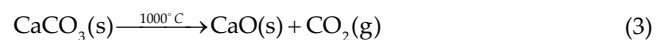
According to the previous example from the industry, the calcination process was carried out in the temperature ramp controlled muffle furnace. Calcination temperature was firstly elevated to 400°C for 15 min. Subsequently, the temperature was elevated to 1000°C and was then maintained for 1 h. Thus, residue carbon and organic materials were burned. The calcination is crucial, as $CaCO_3$ in itself is not water-soluble and cannot be directly used as a precipitant.

Commercial, analytically pure chemical CaO (VWR Chemicals, Radnor USA) was used as a reference precipitant. Synthetic $(NH_4)_2HPO_4$ solution (J. T. Baker, Phillipsburg, NJ, USA) was prepared from an analytically pure reagent.

2.1.2. Digestate from an anaerobic digestion plant

The anaerobic digestate (after hygienisation at 70°C) used in this research was provided by anaerobic digestion plant located in western Finland. The anaerobic digestion plant uses pig and cow slurry, fur animal manure, fur waste from the leather industry, agricultural waste, and bio-waste as raw materials. The composition of anaerobic digestate and also nutrient content can differ significantly because of the numerous raw materials used in the gasification process [27].

2.2. Experimental methods

Saturated solutions were prepared from calcined paper mill sludge and commercial CaO. Ammonium phosphate $(NH_4)_2HPO_4$ solution (10 mmol) (360 mg/L NH_4^+ and PO_4^{3-} 950 mg/L) was prepared from an analytically pure

diammonium hydrogen phosphate. Before each precipitation experiment, the temperature of the $(NH_4)_2HPO_4$ solution was adjusted in a regulated temperature at 20°C ± 2°C, 40°C ± 2°C or 60°C ± 2°C. The $(NH_4)_2HPO_4$ solution (500 mL) was stirred with a magnetic stirrer at a speed of 160 rpm, and a pH meter was connected to the experiment system.

Saturated precipitant was added to the synthetic wastewater at certain intervals. To be more specific, at 1 min intervals one mL at a time up to 30 mL. The experiment was continued by adding the precipitant at 1 min intervals five mL at a time until the total volume of the added precipitant was 50 mL. The pH value was read after each addition. Samples were taken after the 5, 10, 15, 20, 30, and 50 mL additions. The total reaction time of the experiments was 40 min. The samples were filtered through Whatman 4 filter paper (20–25 μm pores), and precipitates were air-dried before analysis.

Experiments with the liquid phase of anaerobic digestate were carried out at room temperature (20°C ± 2°C). Digestate was first filtered through a coarse fabric and then a filter paper (40 μm) before the experiments. The precipitant dosage was calculated, according to Frazier et al. [22] molar ratio Ca:P (2:1), for possible hydroxyapatite precipitation. In the experiment, saturated precipitant (30 mL) suspension was added to the liquid phase of digestate all at one time while stirring the solution with a magnetic stirrer at a constant speed of 750 rpm for 1 min in order to mix up the two solutions properly. After that, the rotor speed was reduced to 160 rpm for the duration of the experiment (2 h). Samples were taken in the beginning, 15, 30, and 120 min. Samples were filtered through 4–12 μm filter paper, and precipitates were air-dried before analyzing to prevent the volatilization of ammonium. The composition of the formed solid precipitates was characterized. A simplified schematic description of the chemical precipitation system is illustrated in Fig. 1.

The removal efficiency (R_{eff}) of ammonium nitrogen and phosphate from the aqueous solution was calculated by Eq. (4) as follows:

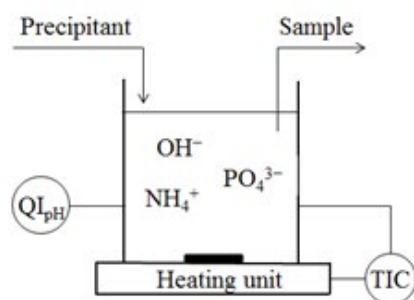$$R_{eff} = \left[\frac{(C_0 - C_t)}{C_0} \right] \times 100\% \qquad (4)$$

Fig. 1. Schematic description of the chemical precipitation system. The precipitation reactor consists of 800 mL decanter glass, a heating unit (TIC), and a pH-meter (QI_{pH}).

where C_0 and C_t are concentrations at time 0 and time t, respectively.

2.3. Description of analytical equipment

The pH value was measured using a portable pH meter (Knick Portable, Berlin, Germany) during the experiments. The ammonium concentration of the liquid samples was measured using a HACH HQ40d NH_4-selective electrode (Model ISENH418101, Loveland, CO, USA). The phosphate concentration of the liquid samples was measured by ion chromatography (METROHM 761 Compact IC, Herisau, Switzerland). Concentrations of trace elements were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer Optima 5300 DV, Shelton, CT, USA) and atomic absorption spectroscopy (AAS; Perkin Elmer 200, Waltham, MA, USA). The composition of the formed precipitates was characterized using an X-ray diffractometer (XRF; S4 Pioneer, Bruker AXS, Billerica USA). For X-ray fluorescence (XRF) measurement, the sample powders were added 6% C-wax as binder and press into pellet specimen with a diameter of 37 mm in a steel ring. The detectable element concentration is 5–10 ppm for XRF. The Rigaku SmartLab 9 kW X-ray diffraction (XRD) device with PDXL2 software was used to analyze the phase structure of the precipitates, and XRD patterns were also recorded by a PANalytical X´Pert Pro XRD equipment using monochromatic CuKα1 radiation (λ = 1.5406 Å) at 45 kV and 40 mA. Diffractograms were collected in the 2θ range 10°–80° at 0.017° intervals and with a scan step time of 100 s. The crystalline phases and structures were analyzed by the HighScore Plus program. The microstructure shown in FESEM images were obtained using a Zeiss Sigma field emission scanning electron microscope (FESEM; Zeiss Sigma, Rödermark, Germany) at the Centre of Microscopy and Nanotechnology in the University of Oulu operated at 5 kV. The particle size distribution of calcined paper mill sludge was analyzed using a MALVERN Mastersizer 3000 (Malvern, England). The particle size distribution measurement is based on a laser diffraction technique. The analyzer utilizes static light scattering and Mie theory to calculate the particle size distribution.

3. Results

3.1. Calcined paper mill sludge

The main components of the calcined paper mill sludge are illustrated in Table 1. It mainly contains CaO.

Singular cellulose fibers can be observed in the scanning electron microscope (SEM) image of raw paper mill sludge, Fig. 2a 1,000×, whereas calcined paper mill sludge contains homogenous calcium oxide, Fig. 2b 1,000×.

Fig. 3 illustrates the particle size distribution of calcined paper mill sludge. The particle size distributions is classified in Dv 10, Dv 50, and Dv 90 (Dv = volume mean diameter). For instance, Dv 10 means that 10% of the particles are smaller than 8.7 μm, etc. However, all particles are smaller than 500 μm.

Concentrations of harmful elements in the calcined paper mill sludge and their limit values listed in the Finnish

Table 1
Main compounds as mass fractions (XRF) of calcined paper mill sludge

CaO (%)	97.3
Al_2O_3 (%)	1.1
MgO (%)	0.9
P_2O_5 (%)	0.3
FeO (%)	0.2
Na_2O (%)	<0.1
K_2O (%)	<0.1
TiO_2 (%)	<0.1
MnO (%)	<0.1

Fertiliser Product Act (24/2011) are presented in Table 2 [28]. Harmful element contents in paper mill sludge are clearly lower than the Finnish limits for forest fertilizers.

3.2. Liquid phase of the anaerobic digestate

Essential nutrient content was measured from the liquid phase of anaerobic digestate (Table 3). Nutrient contents are at a high level and pH is slightly alkaline.

3.3. Results of the synthetic solution experiments

3.3.1. Ammonium nitrogen removal and effect of pH

Ammonium nitrogen removal percentages of different precipitants as a function of treatment time at 20°C ± 2°C are presented in Fig. 4a. Calcined paper mill sludge removed

100% of ammonium nitrogen, and commercial CaO removed 99%, respectively. Therefore, calcined paper mill sludge removed as much ammonium as commercial CaO. As shown in Fig. 4b, the results indicated that the pH increased throughout the experiment as more precipitant was added to the solution. During the experiments with CaO, and calcined paper mill sludge, the pH was 12.0, or 12.4 at the end of the precipitation. Since ammonium occurs completely as ammonia gas at that pH, it is most likely that all of the ammonium volatilized into the air as ammonia gas.

3.3.2. Phosphate removal

Fig. 5 illustrates the phosphate removal at 20°C ± 2°C. Calcined paper mill sludge and commercial CaO removed

Table 2
XRF characterization of harmful element contents, (mg/kg, dw = dry weight) and a comparison to the limit values of Finnish Fertiliser decree [28]

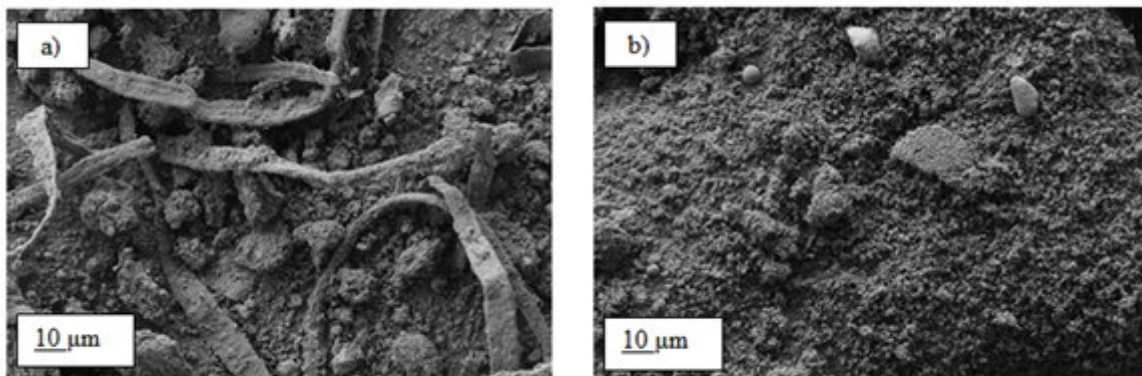|	Calcined paper mill sludge	Limit value field/ forest fertilizers
As (mg/kg)	<20	25/40
Cd (mg/kg)	<10	1.5/25
Cr (mg/kg)	<20	300
Cu (mg/kg)	<20	600/700
Ni (mg/kg)	<20	100/150
Pb (mg/kg)	<20	100/150
Zn (mg/kg)	<20	1,500/4,500

Fig. 2. (a) SEM image of raw paper mill sludge, the bar indicates 10 μm length and (b) SEM image of calcined paper mill sludge, the bar indicates 10 μm length.
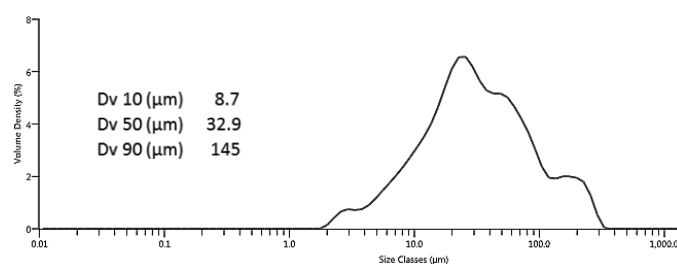

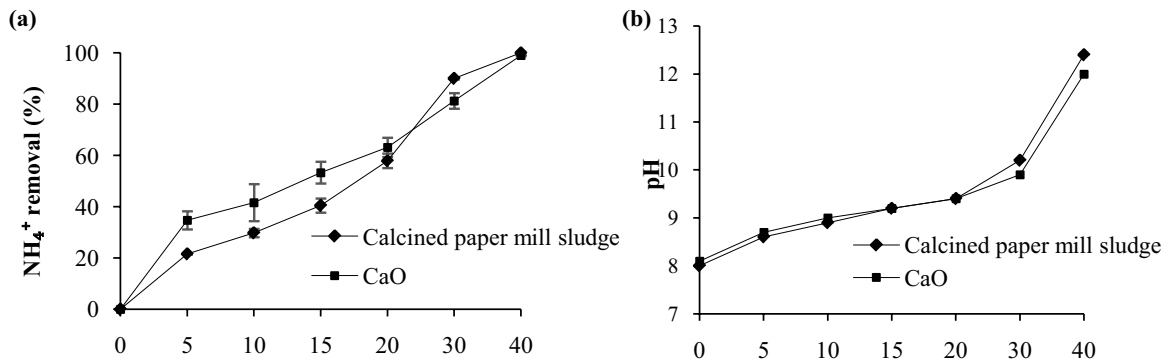Fig. 3. The particle size distribution of calcined paper mill sludge.

Fig. 4. (a) Ammonium removal percentages of different precipitants at 20°C ± 2°C as a function of treatment time. The error bars of the parallel experiments were calculated by standard deviation (SD) and (b) pH as a function of treatment time.

Table 3
Essential nutrient content of the liquid phase of anaerobic digestate

pH	8.4
NH_4^+ (mg/L)	1,460
PO_4^{3-} (mg/L)	470
Ca^{2+} (mg/L)	3.6
Mg^{2+} (mg/L)	0.2
K^+ (mg/L)	69.0

Table 4
Effect of different precipitants on the removal of NH_4^+ and PO_4^{3-} at different temperatures

Calcined paper mill sludge				CaO		
	20°C	40°C	60°C	20°C	40°C	60°C
NH_4^+ removal (%)	100	100	100	99.1	98.8	99.6
PO_4^{3-} removal (%)	100	100	100	99.9	100	100

commercial CaO. As a result, precipitation at room temperature would be preferred.

3.3.4. Residual concentration of Ca^{2+}

Fig. 6 illustrates the residual concentration of Ca^{2+} that remained in the solution. The soluble Ca^{2+} ions participate readily in the precipitation reaction as long as there are ions that can precipitate available in the solution. Therefore, the concentration of Ca^{2+} was at a very low level during the experiments. However, the residual Ca^{2+} concentration was up to 171 mg/L with calcined paper mill sludge and 124 mg/L with CaO. The added Ca^{2+} ions have almost quantitatively participated in aprecipitation reaction. The results were at the same level at all temperatures indicating that the temperature did not have any impact on the residual calcium ion concentration.

3.4. Characterization of the precipitate

The XRD patterns (a Rigaku SmartLab 9 kW XRD device) for calcined paper mill sludge are presented in Fig. 7. Hydroxyapatite, $Ca_5(PO_4)_3(OH)$, (JCPDS card numbers 04-011-06221 and 04-008-4763) were found in all samples. Calcite, $CaCO_3$, (JCPDS card number 04-007-8659) was only found when the precipitation temperature was 20°C. The content of hydroxyapatite was up to 82%.

Table 5 shows the composition, molecule formula and content (%) of precipitates formed by different precipitants at the temperatures used. When using calcined paper mill sludge and CaO, the formed precipitates contain nutrients, such as hydroxyapatite and calcium phosphate. The commitment of phosphate is seen in XRD patterns when using

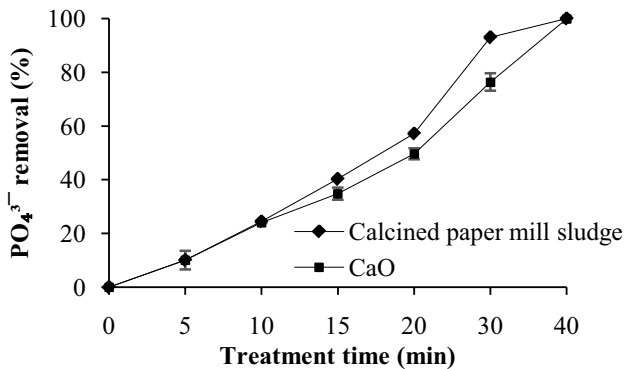Fig. 5. Phosphate removal percentages of different precipitants at 20°C ± 2°C as a function of treatment time. The error bars of the parallel experiments were calculated by the standard deviation (SD). Due to small SD (0.0–1.0), the error bars are not clearly visible in the case of calcined paper mill sludge.

over 99% of phosphate. Therefore, calcined paper mill sludge removed as much phosphate as commercial salt.

3.3.3. Effect of temperature

The effect of different temperatures in the removal of ammonium and phosphate using different precipitants is illustrated in Table 4. The results were at a similar level at all temperatures. Therefore, the temperature did not have any impact on the removal efficiency of ammonium nitrogen and phosphate using either calcined paper mill sludge or

calcined paper mill sludge (Fig. 7). The lack of ammonium compounds could be caused by high pH (Fig. 4b), which causes ammonium volatilization into the air as ammonia gas.

3.5. Results of the authentic solution experiments

3.5.1. Ammonium nitrogen and phosphate removal

Ammonium nitrogen and phosphate removal percentages as a function of treatment time are presented in Fig. 8. Calcined paper mill sludge removed 16.7% of ammonium nitrogen in the first 15 min. As seen in Fig. 8, removal efficiency did not improve essentially after that. When the ammonium removal of synthetic solutions are compared with the authentic solution, the ammonium removal efficiency is significantly worse in the latter case. Calcined paper mill sludge removed 73.7% of phosphate after 15 min experiment. After that, removal efficiency did not improve essentially. The removal efficiency was very good for hydroxyapatite formation (Fig. 10).

3.5.2. Residual concentration of Ca^{2+}

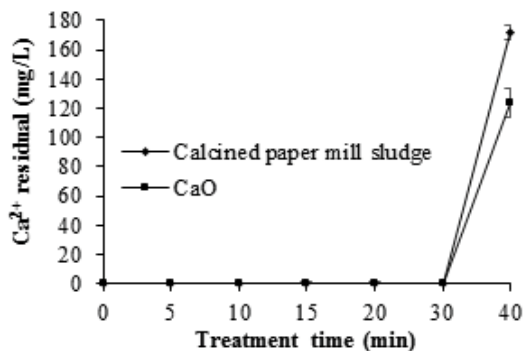The residual concentration of Ca^{2+} that remained in the authentic solution is illustrated in Fig. 9. The zero value

Fig. 6. Residual concentration of Ca^{2+} at the end of the experiments at 20°C ± 2°C. The error bars of the parallel experiments were calculated by the standard deviation (SD).

illustrates the Ca^{2+} concentration (770 mg/L) after the addition of calcined paper mill sludge as a precipitant. The concentration of Ca^{2+} was at a very low level during the experiment as the soluble Ca^{2+} ions have almost quantitatively participated in the removal of phosphate ions from the solution.

3.5.3. Characterization of precipitates

The XRD patterns (a PANalytical X´Pert Pro XRD device) in the authentic solution experiments for calcined paper mill sludge are presented in Fig. 10. Peak A shows hydroxyapatite, $Ca_5(PO_4)_3(OH)$, peaking at $2\theta° = 25.8°$ and at $2\theta° = 31.8°$. SEM images of the precipitates from authentic experiments are presented in Fig. 11. Large hydroxyapatite particles are completely covered with fine precipitate particles in Fig. 11b.

4. Discussion

In this research, calcined paper mill sludge was specifically used for the removal of phosphate. At the same time,
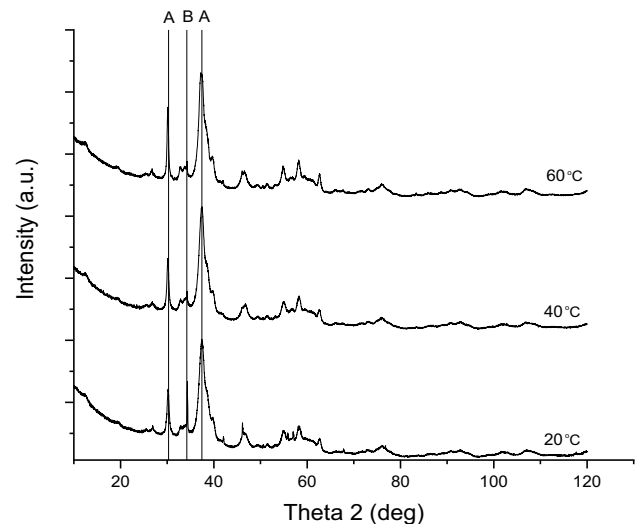

Fig. 7. X-ray diffraction patterns of calcined paper mill sludge at different temperatures, A: $Ca_5(PO_4)_3(OH)$ and B: $CaCO_3$.

Table 5
Composition of the formed precipitates when using different precipitants

Precipitant	Temperature (°C)	Precipitate	Formula	Content (%)
Calcined paper mill sludge	20	Hydroxylapatite, syn	$Na_{0.25}Ca_{4.5}(PO_4)_{2.25}(CO_3)_{0.75}(OH)$	77.0
		Hydroxylapatite, syn	$Ca_5(PO4)_3(OH)$	19.3
		Calcite, syn	$CaCO_3$	3.7
	40	Hydroxylapatite, syn	$Na_{0.25}Ca_{4.5}(PO_4)_{2.25}(CO_3)_{0.75}(OH)$	95.1
		Hydroxylapatite, syn	$Ca_5(PO4)_3(OH)$	4.9
	60	Hydroxylapatite, syn	$Na_{0.25}Ca_{4.5}(PO_4)_{2.25}(CO_3)_{0.75}(OH)$	96.6
		Hydroxylapatite, syn	$Ca_5(PO4)_3(OH)$	3.4
Commercial CaO	20	Calcium hydroxide phosphate	$Ca_{10}(OH)_2·(PO_4)_6$	100.0
	40	Calcium hydroxide phosphate	$Ca_{10}(OH)_2·(PO_4)_6$	100.0
	60	Hydroxylapatite, syn	$Ca_5(PO4)_3(OH)$	58.0
		Carbonate hydroxyapatite	$Ca_{3.4}(Ca_{5.9}(NH_4)_{0.1})((PO_4)_{4.95}(CO_3)_{1.08}(H_2O)_{0.45})((OH)_{1.65}(H_2O)_{0.75})$	42.0

Frazier's method [22] for the removal of ammonium as calcium ammonium phosphate was tested.

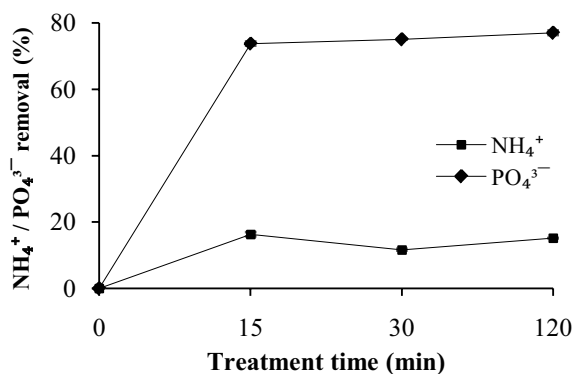Calcined paper mill sludge removed 100% of phosphate from the synthetic wastewater at all temperatures (Fig. 5) and 73% of the phosphate from authentic wastewater at 20°C ± 2°C (Fig. 8). Ammonium removal efficiency (99%) was also at a very high level in the experiments where synthetic wastewater was used (Fig. 4a) and at a very low level (17%) in the authentic experiments (Fig. 8). However, due to the high ammonium concentration of the authentic solution, calcined paper mill sludge dosage should be much higher, and pH then would consequently increase over pH 10. As a result, ammonium either volatizes into the air as ammonia gas under alkaline conditions as a function of pH (pKa 9.2) or ammonium ions transform to aqueous ammonia [15,29]. Therefore, this method cannot be recommended for ammonium removal from authentic wastewaters. Instead, the phosphate removal efficiencies were comparable to results obtained with other Ca-containing waste materials, such as fly ash [30], bottom ash [31], waste bone ash [32], calcined paper waste [33] and calcined paper mill sludge [23].

In this study, the phosphate was exclusively precipitated as hydroxyapatite (Figs. 8 and 10). Similar results were obtained by Johansson with fly ash [34]. Moriyama et al. [35] achieved 75%–85% efficiency of hydroxyapatite using

Fig. 8. Ammonium and phosphate removal percentage as a function of time at 20°C ± 2°C. The error bars of the parallel experiments were calculated by the standard deviation (SD). Due to small SD (0.2–0.7), the error bars are not clearly visible.
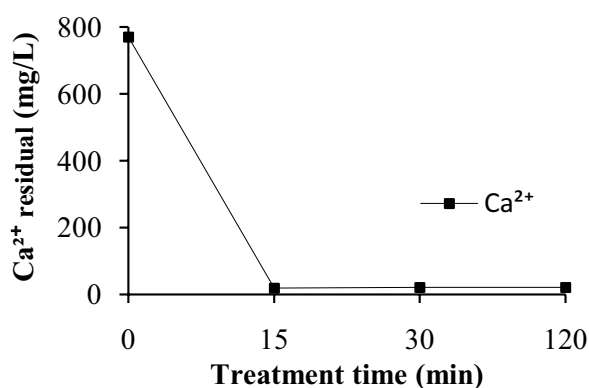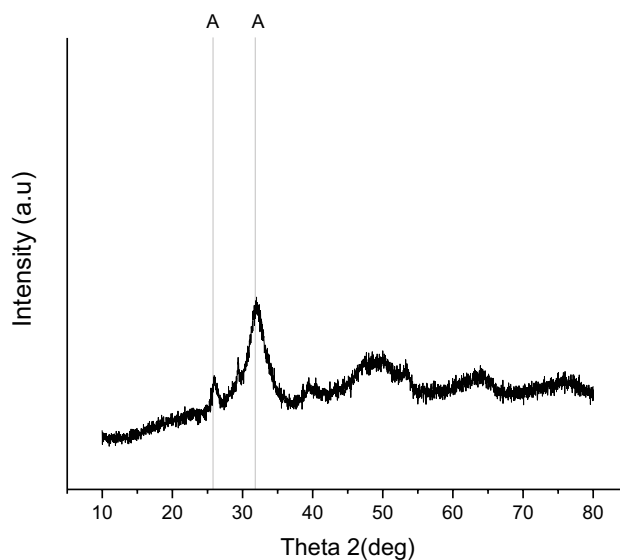
Fig. 9. Residual concentrations of Ca^{2+} during the experiment at 20°C ± 2°C. The error bars of the parallel experiments were calculated by the standard deviation (SD). Due to small SD (0.4–1.8), the error bars are not clearly visible.

Fig. 10. X-ray diffraction patterns of the solid precipitate in the authentic solution experiment. A: $Ca_5(PO_4)_3(OH)$.
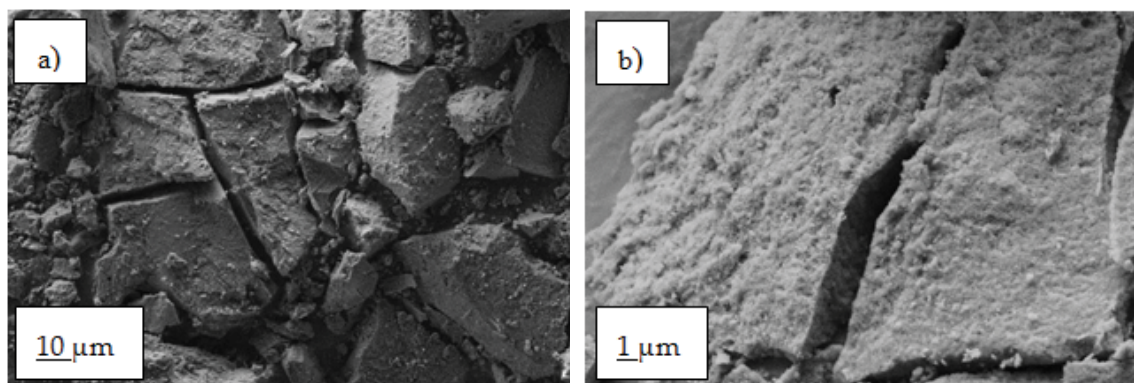
Fig. 11. SEM images of the precipitate from authentic experiments. (a) Bar indicates a 10 μm length and (b) bar indicates 1 μm length.

Ca-rich media in phosphorus removal. Myllymäki et al. [24] precipitated instead monetite, $CaPO_3(OH)$, from wastewater using fly ash, but in their study, the pH was between 8–10 instead of the pH over 12 (Fig. 4b) in this study. Due to the different species of phosphate, the calcined paper mill sludge dosage is important in the phosphate precipitation. Between pH 4–6 dihydrogen phosphate species ($H_2PO_4^-$) is dominant, between pH 8–11 hydrogen phosphate (HPO_4^{2-}) is the predominant form and when pH is more than 9 (PO_4^{3-}) dominates. The alkaline quality of calcined paper mill sludge converts acidic phosphate compounds. According to the previous, the calcined paper mill sludge dosage must be at the required level [30,36].

Chemical precipitation as struvite is the best-known method of simultaneous ammonium nitrogen and phosphate recovery from wastewater [20,21]. In our study, this was not possible because the magnesium concentration of calcined paper mill sludge and the liquid phase of digestate were at a too low level. However, it is possible to use also Ca-rich media for the simultaneous removal of nitrogen and phosphate, which leads to the formation of a struvite-like Ca-mineral as in Frazier et al. [22]. In this study, the formation of calcium ammonium phosphate was unsuccessful, most likely since Frazier et al. used saturated ammonium phosphate solutions in their experiments. This is an unrealistic situation with authentic wastewaters, and therefore Frazier´s method does not work with these authentic wastewaters.

The removal of phosphorus may include, aside from the precipitation reaction, some adsorption reactions [37,38]. Therefore, phosphate can be adsorbed by calcite ($CaCO_3$) [39]. Since there was calcite found in our synthetic experiments (Fig. 7), this is more than likely. However, since the adsorption can be a reversible process, as described in Fu and Wang [40], the whole reaction is more complicated.

5. Conclusions

In this research, paper mill sludge, waste material from the Finnish pulp and paper mill, was used as a precipitant for ammonium nitrogen and phosphate removal from synthetic wastewater and authentic wastewater, the liquid phase of anaerobic digestate. Papermill sludge was calcined at 1,000°C, and its effectiveness as a precipitant was compared with commercial CaO. The results showed that calcined paper mill sludge has excellent potential, especially in phosphate precipitation from the nutrient containing wastewater. Calcined paper mill sludge removed 73% of phosphate. Ammonium removal efficiency was 17%, due to the ammonium volatilization into the air as ammonia gas. The change in temperature had only a marginal effect on the removal efficiency. The formed precipitates contain hydroxyapatite that can be used as a recycled, solid, slow-release fertilizer. However, more research is needed to optimize the precipitation conditions. Solubility and growth tests are also needed to confirm the suitability of the precipitate for fertilizer use.

Acknowledgments

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