

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: The European Union's (EU) circular economy strategy aims to increase recycling and re-use of products and waste materials. According to strategy, the use of industry waste material and side flows should be more effective. In this research, a chemical precipitation method to simultaneously remove phosphate and nitrogen using calcined paper mill sludge was tested. Paper mill sludge is a waste material formed in the paper-making process. It mainly contains calcium carbonate and cellulose fibers. Objective of this research was to test whether the industrial waste could be used as low cost precipitation chemical for ammonium and phosphate removal from wastewaters or the precipitate could be suitable for fertilizer use. The study results indicated that calcined paper mill sludge removed as much ammonium nitrogen and phosphate as commercial CaO. Furthermore, the results showed that calcined paper mill sludge removed efficiently phosphate from the liquid phase of anaerobic digestate, which leads to formation of hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. In this study we have shown, that calcined paper mill sludge can be used to manufacture recycled, slow-release fertilizers. Other possible mechanisms for the removal of phosphate and ammonium were also considered.

Keywords: ammonium; calcined paper mill sludge; phosphate; precipitation; recycled fertilizer

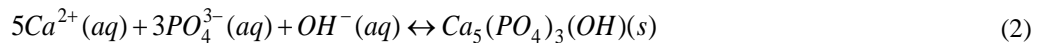
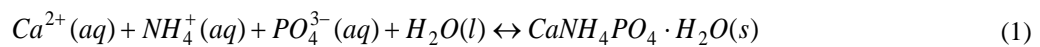
1. Introduction

The European Union's (EU) circular economy strategy aims to increase recycling and re-use of products and waste materials [1]. The use of industry waste material and side flows should be more effective. The strategy is closely linked to the EU Waste Framework Directive (2008/98/EC), which includes the five-step waste hierarchy [2]. The first goal of the waste hierarchy is the prevention of waste streams. If this is not possible, the next step is the preparation of waste for re-use, followed by recycling and other recovery (e.g. energy recovery). Finally, if none of the initial four steps are feasible, waste should be disposed of using ecologically beneficial methods. According to Sokka et al., re-use and symbiosis products manufactured from side flows or waste material in local industry carry a very small environmental load [3].

Phosphorus and nitrogen are the main nutrients in wastewaters that promote the growth of organic matter and algae that cause eutrophication in water bodies. Discharges of phosphorus and nitrogen are known to occur in, for example, agriculture and the reject water of anaerobic digestion plant. Anaerobic digestion is a widely used sustainable method for the management of organic solid wastes and sludge. Anaerobic digestion plant can use various biomass materials for renewable energy production. The composition of anaerobic digestate can differ significantly because of the numerous raw materials used in the gasification process [4]. Anaerobic digestate, used for agriculture purposes is specifically regulated by both European and Finnish national legislations [5], namely, Regulation (EU) No. 2003/2003 of the European Parliament and of the Council related to fertilizers [6], Animal by-products Regulation (EU) No. 1069/2009 of the European Parliament and of the Council [7], and the Finnish Act on Fertilizer Products 539/2006 [8], among others. The liquid phase of anaerobic digestate contains high concentration of nutrients. Therefore, it can be used as such as fertilizer, but it should be converted into a more slow-release solid form to decrease transport costs.

Currently, phosphorus can be removed by chemical precipitation using aluminium or iron precipitants or by a biological process [9, 10]. There are also various methods for phosphate removal, such as adsorption [11, 12], ion exchange [13], electro-coagulation [14, 15], and electro-Fenton treatment [16]. Nitrogen is typically present in the form of ammonium. Ammonium ions are quite difficult to precipitate because ammonium–ammonia equilibrium depends

strongly on pH, and therefore ammonium volatilises easily as ammonia gas in alkaline conditions [17]. Nitrogen cannot be removed with traditional Al or Fe salts, and therefore is removed in the biological process by nitrification and denitrification as nitrogen gas. Therefore, the simultaneous removal of phosphate and ammonium nitrogen is not possible using these traditional methods [18]. As known, phosphorus is essential for all life. However, it is non-renewable mineral and it has been calculated that phosphorus resources would last for only hundred years at the present depletion rate [19]. Therefore, it is a great need to develop alternative, recycled phosphorus fertilizers. It has been estimated that there is an enormous economic potential in the recycled fertilizer market. In Finland alone, the economic potential of recycled fertilisers is approximated to be € 500 million annually [20]. One answer to recycled fertiliser market would be to convert phosphate and ammonium into a product that enhances nutrient value. Chemical precipitation as struvite from wastewater by using Mg-salts is commonly used method of phosphorus and ammonium nitrogen recovery [21-23]. Whereas commercial Ca-salts such as CaO and Ca(OH)₂ are commonly used precipitants in Ca-phosphate precipitation. Ca-containing waste could also be used as a cheaper alternative in removal of nitrogen and phosphate from nutrient containing wastewaters. This would lead to the formation of a struvite-like Ca-mineral, such as calcium ammonium phosphate CaNH₄PO₄ (Eq. 1) and hydroxyapatite Ca₅(PO₄)₃(OH) (Eq. 2) [24].



In the research, industrial waste material Ca-rich paper mill sludge was studied as a low cost chemical precipitant in the simultaneous removal of ammonium nitrogen and phosphate from synthetic solution and from the liquid phase of anaerobic digestate. Comparison was made to commercial CaO. The effects of temperature and pH on the precipitation efficiency were studied and the nutrient contents of the formed precipitates were analyzed.

2. Materials and Methods

2.1 Materials

2.1.1 Precipitants

Paper mill sludge came from Finnish pulp and paper mill located in northern Finland. Precipitated calcium carbonate (PCC) is used as paper filling material and coating material to enhance paper's properties [25]. Wastewater produced at the pulp and paper mill contains calcium carbonate waste, cellulose fibres, 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 1000 °C in the lime kiln (Eq. 3) [26]:



The calcination process was carried out in the ramp controlled muffle furnace in our research. Calcination temperature was firstly elevated to 400 °C for 15 minutes. Subsequently, the temperature was elevated to 1000 °C and was then maintained for one hour. Thus, carbon and organic materials were burned. Calcination is necessary, as calcium carbonate in itself is not soluble in water and therefore cannot be directly used as a precipitant.

Commercial, analytically pure chemical CaO (VWR Chemicals, Radnor USA) was used as comparative precipitant. Synthetic (NH₄)₂HPO₄ 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 originated from an anaerobic digestion plant using pig and cow slurry for animal manure, fur waste from the leather industry, agricultural waste, and bio-waste as raw materials. The anaerobic digestion plant is located in western Finland.

2.2 Experimental methods

Saturated solutions were prepared from calcined paper mill sludge, and commercial CaO. Ammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ 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 the each precipitation experiment, the temperature of the $(\text{NH}_4)_2\text{HPO}_4$ solution was adjusted to a regulated temperature of 20 ± 2 °C, 40 ± 2 °C or 60 ± 2 °C. In the experiments, the $(\text{NH}_4)_2\text{HPO}_4$ solution (500 mL) was stirred with a magnetic stirrer at a speed of 160 rpm, and a pH meter (Knick Portable, Berlin, Germany) was connected to the system.

Saturated precipitant was added at 1 min intervals 1 mL at a time up to 30 mL. The experiment was continued by adding the precipitant at 1 min intervals 5 mL at a time until the total volume of the added precipitant was 50 mL. After each addition, the pH value was read. Water samples were taken after 5, 10, 15, 20, 30, 50 mL additions. Total reaction time of the experiments was 40 min. The water 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 ± 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. 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 (500 mL) while stirring the solution with a magnetic stirrer at a constant speed of 750 rpm for 1 minute 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 (2h). Water 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. The schematic description of the chemical precipitation system is shown in Fig. 1.

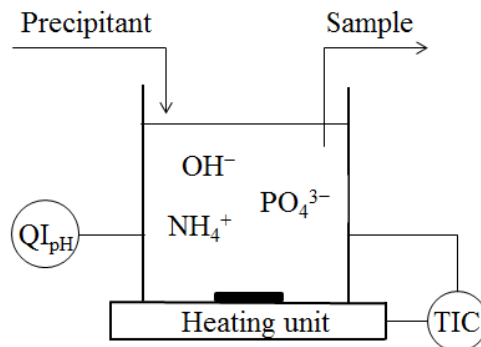


Fig. 1 Precipitation reactor consists of 800 mL decanter glass, a heating unit (TIC), and a pH-meter (QI_{pH})

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

$$R_{\text{eff}} = [(C_0 - C_t)/C_0] \cdot 100\%, \quad (4)$$

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

2.3 Description of analytical equipment

The ammonium concentration of the liquid samples was measured using a NH_4 -selective electrode (HACH HQ40d, Model ISENH418101, Loveland, CO, USA). The phosphate concentration of the liquid samples was measured by ion chromatography (METROHM 761 Compact IC, Herisau, Switzerland). The concentrations of trace elements were analyzed using inductively coupled plasma optical emission spectrometry (Perkin Elmer Optima 5300 DV, Shelton, CT, USA) and atomic absorption spectroscopy (Perkin Elmer AAS 200, Waltham, MA, USA). The composition of the formed precipitates was measured by x-ray diffractometer. X-ray diffraction patterns were recorded

by a PANalytical X'Pert Pro X-ray diffraction equipment using monochromatic CuK α 1 radiation ($\lambda=1.5406 \text{ \AA}$) at 45 kV and 40 mA. Diffractograms were collected in the 2θ range $10-80^\circ$ at 0.017° intervals and with scan step time of 100 s. The crystalline phases and structures were analyzed by HighScore Plus program. The composition of the formed precipitates was measured by scanning electron microscope (SEM). Paper mill sludge and calcined paper mill sludge were characterized using FESEM, and X-ray fluorescence spectrometer (S4 Pioneer, Bruker AXS, Billerica USA). The microstructure shown in FESEM images were obtained using a Zeiss Sigma field emission scanning electron microscope (Zeiss Sigma, Rödermark, Germany) at the Centre of Microscopy and Nanotechnology in the University of Oulu operated at 5 kV. For XRF measurement, the sample powders were added 6% C-wax as binder and press into pellet specimen with diameter of 37mm in a steel ring. The detectable element concentration is 5-10 ppm for XRF. The distribution of the particle size of calcined paper mill sludge was measured using a MALVERN Mastersizer 3000 (Malvern, England). The particle size distribution measurements were based on laser diffraction technique. The analyser utilises 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.

Table 1 XRF characterization of the main compounds of calcined paper mill sludge

CaO (%)	Al ₂ O ₃ (%)	MgO (%)	P ₂ O ₅ (%)	FeO (%)	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	MnO (%)
97.3	1.1	0.9	0.3	0.2	< 0.1	< 0.1	< 0.1	< 0.1

Singular cellulose fibres can be observed in the SEM image of raw paper mill sludge, Fig. 2a) 1000x, whereas calcined paper mill sludge contains homogenous calcium oxide, Fig. 2b) 1000x.

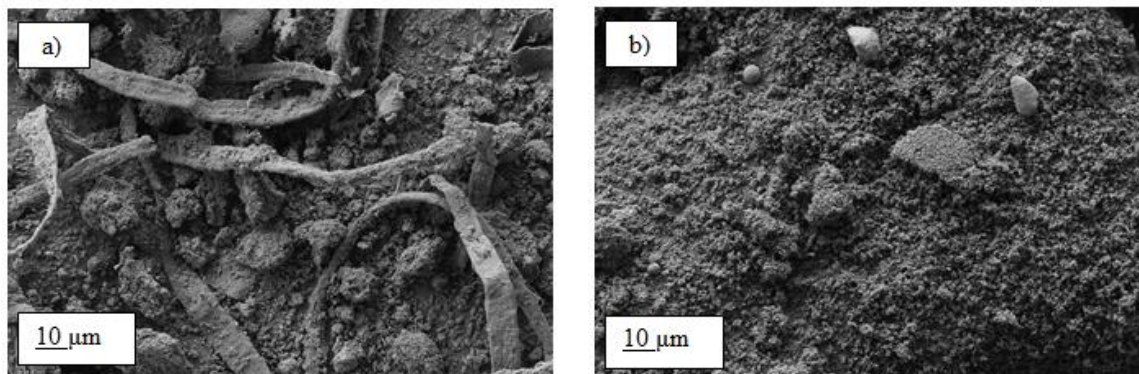


Fig. 2 a) SEM image of raw paper mill sludge, the bar indicates 10 μm length; b) SEM image of calcined paper mill sludge, the bar indicates 10 μm length

Fig. 3 illustrates the distribution of the particle size of calcined paper mill sludge. The particle size distributions of the calcined paper mill powder were $D_v(10)$ 8.7 μm i.e. 10% of the particles are smaller than 8.7 μm , (D_v = volume mean diameter) $D_v(50)$ 32.9 μm , and $D_v(90)$ 145 μm . All particles were smaller than 500 μm in the calcined paper mill sludge.

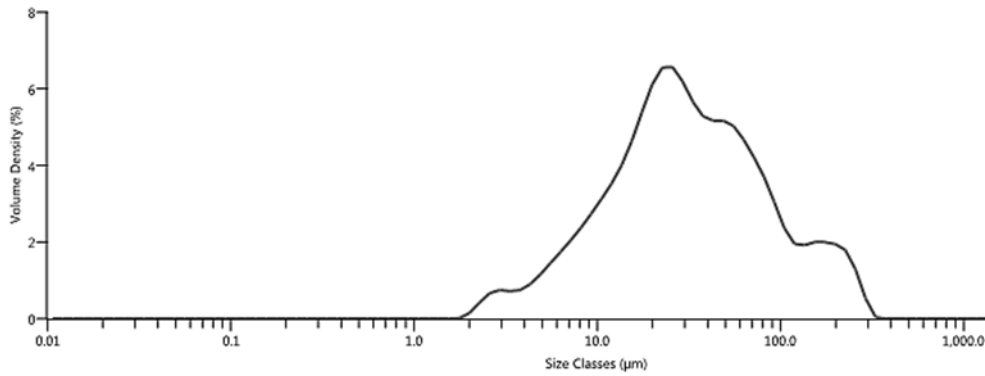


Fig. 3 Particle size distribution of calcined paper mill sludge

Concentrations of harmful elements in the calcined paper mill sludge and their limit values listed in the Finnish Fertiliser Product Act (24/2011) are presented in Table 2 [27]. Harmful element contents in paper mill sludge are clearly lower than the Finnish limits for forest fertilisers.

Table 2 XRF characterization of harmful element contents, (mg/kg, dw = dry weight) and a comparison to the limit values of Finnish fertiliser decree [27]

	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Calcined paper mill sludge	< 20	< 10	< 20	< 20	< 20	< 20	< 20
Limit value field/forest fertilizers	25/40	1.5/25	300	600/700	100/150	100/150	1500/4500

3.2 Liquid phase of the anaerobic digestate

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

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

pH	NH₄⁺ (mg/L)	PO₄³⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	K⁺ (mg/L)
8.4	1460	470	3.6	0.2	69.0

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±2 °C are presented in Fig. 4a. Calcined paper mill sludge removed 100% of ammonium. Commercial CaO removed 99% of ammonium. Therefore, calcined paper mill sludge removed as much ammonium as commercial salt. As shown in Fig. 4b, the results indicated that the pH increased throughout the treatment time 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. As ammonium occurs completely as ammonia gas at that pH, it is highly possible that at all of the ammonium evaporated as ammonia gas. The error bars of the parallel experiments were calculated by standard deviation in Fig. 4a.

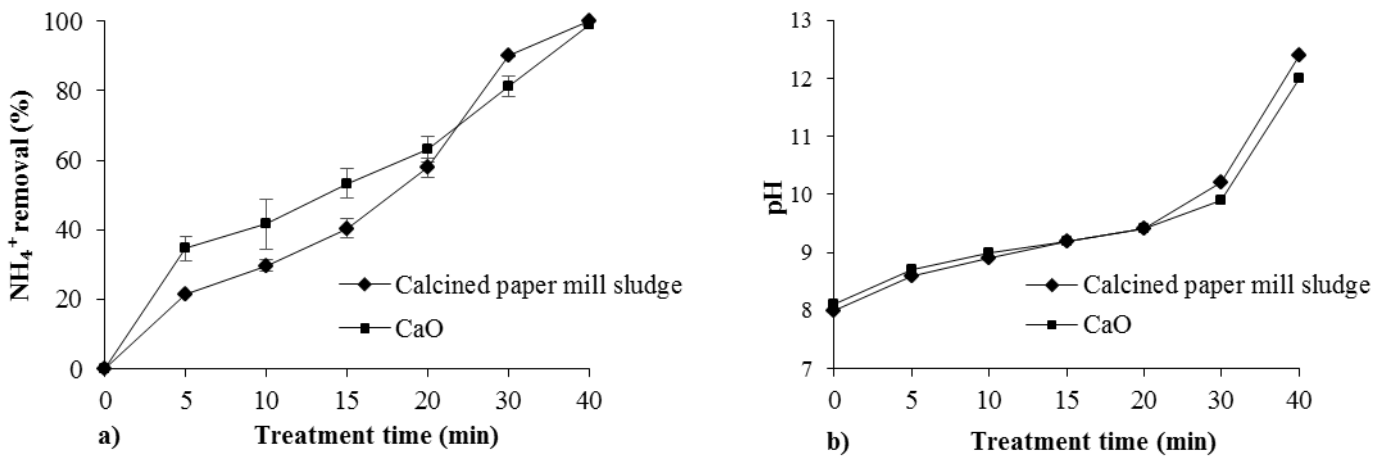


Fig. 4 a) Ammonium removal percentages of different precipitants at 20±2 °C as a function of treatment time, and b) pH as a function of treatment time

3.3.2 Phosphate removal

Fig. 5 illustrates the phosphate removal at 20±2 °C. Calcined paper mill sludge and commercial CaO removed over 99% of phosphate. Therefore, calcined paper mill sludge removed as much phosphate as commercial salt.

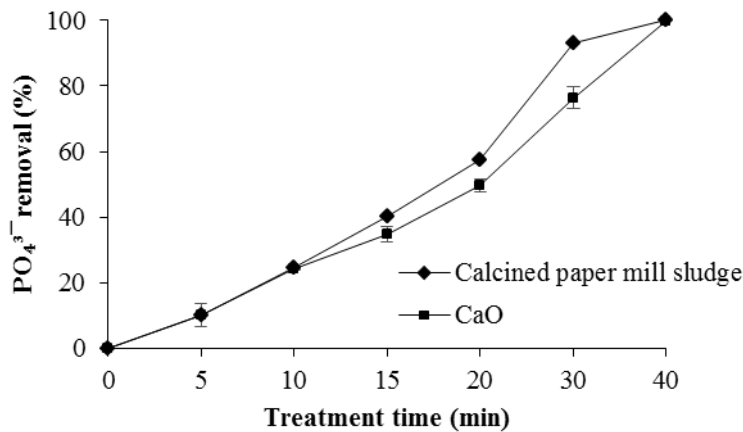


Fig. 5 Phosphate removal percentages of different precipitants at 20±2 °C as a function of treatment time. The error bars of the parallel experiments were calculated by standard deviation. Due to small SD (0.0–1.0), the error bars are not clearly visible in the case of calcined paper mill sludge

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 change in temperature appears to have no essential effect on the removal of ammonium or phosphate using either calcined paper mill sludge or commercial CaO. Therefore, precipitation at room temperature would be the preferred option because no heating is required.

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

3.3.4 Residual concentration of Ca²⁺

Fig. 6 illustrates the residual concentration of Ca²⁺ that remained in the solution. The soluble Ca²⁺ ions participate readily in the precipitation reaction as long as there are ions that can precipitate available in the solution. Therefore, the concentration of Ca²⁺ was at a very low level during the experiments. However, the residual Ca²⁺ concentration was up to 171 mg/L with calcined paper mill sludge and 124 mg/L with CaO. It is obvious that the added Ca²⁺ ions have almost quantitatively participated in precipitation reaction. The results were at the same level at all the different temperatures; therefore, the temperature did not have any impact on the residual calcium ion concentration.

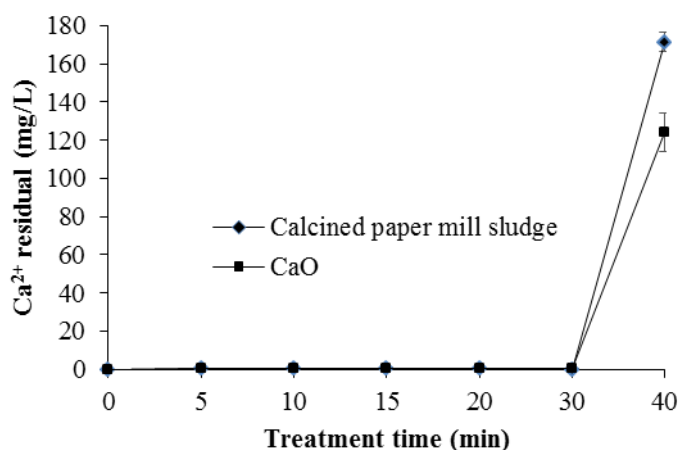


Fig. 6 Residual concentration of Ca²⁺ at the end of the experiments at 20±2 °C. The error bars of the parallel experiments were calculated by standard deviation

3.4 Characterization of the precipitate

The X-ray diffraction patterns for calcined paper mill sludge are presented in Fig. 7. Hydroxyapatite, Ca₅(PO₄)₃(OH), (JCPDS card numbers 04-011-06221 and 04-008-4763) was found in all samples. Calcite, CaCO₃, (JCPDS card number 04-007-8659) was only found when the precipitation temperature was 20 °C. The content of hydroxyapatite was up to 82%.

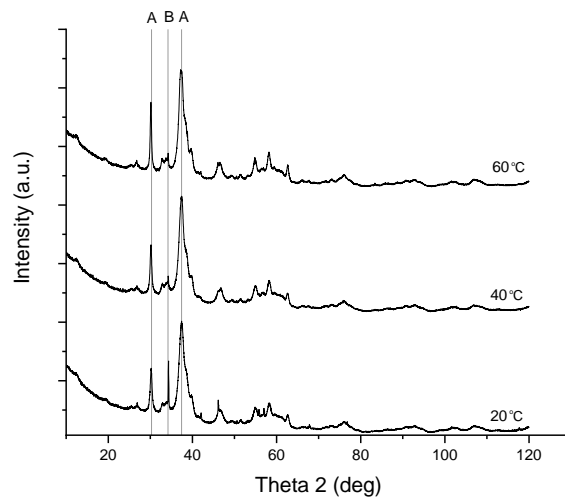


Fig. 7 X-ray diffraction patterns of calcined paper mill sludge at different temperatures. A: $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$; B: CaCO_3

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 minutes. After that, removal efficiency did not improve. When comparing the effectiveness of synthetic solution with the authentic solution, the ammonium removal efficiency was significantly worse. 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).

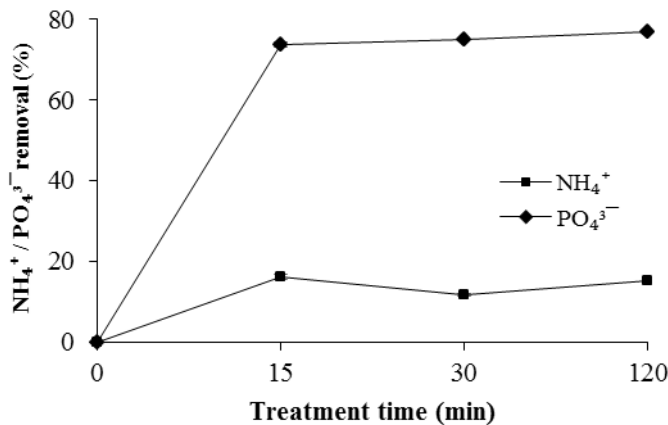


Fig. 8 Ammonium and phosphate removal percentage as a function of time at 20 ± 2 °C. The error bars of the parallel experiments were calculated by standard deviation. Due to small SD (0.2–0.7), the error bars are not clearly visible

3.5.2 Residual concentration of Ca^{2+} .

Fig. 9 illustrates the residual concentrations of Ca^{2+} that remained in the authentic solution. The zero value illustrates the Ca^{2+} concentration (770 mg/L) after addition of calcined paper mill sludge as a precipitant. As shown in

Fig. 9, the soluble Ca^{2+} ions have almost quantitatively participated in the removal of phosphate ions from the solution. Therefore, the concentration of Ca^{2+} was at a very low level during the experiment.

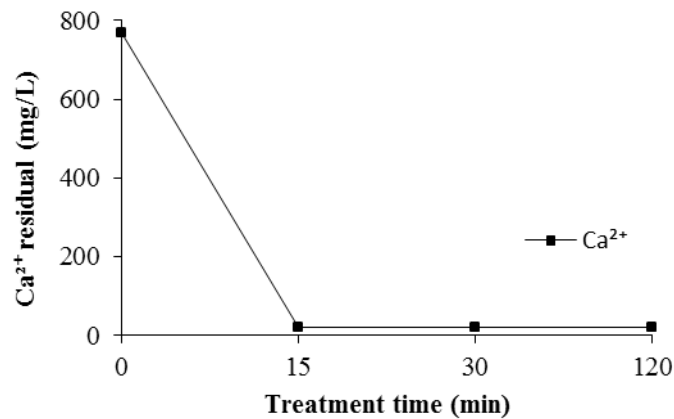


Fig. 9 Residual concentrations of Ca^{2+} during the experiment at 20 ± 2 °C. The error bars of the parallel experiments were calculated by standard deviation. Due to small SD (0.4–1.8), the error bars are not clearly visible

3.5.3 Characterization of precipitates

The X-ray diffraction patterns in the authentic solution experiments for calcined paper mill sludge are presented in Fig. 10. Peak A shows hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, peaking at $2\theta = 25.8^\circ$, at $2\theta = 31.8^\circ$, and at $2\theta = 49.5^\circ$. SEM images of the precipitates from authentic experiments are presented in Fig. 11. Large hydroxyapatite particles are completely covered with fine precipitate particles in the Fig. 11 b.

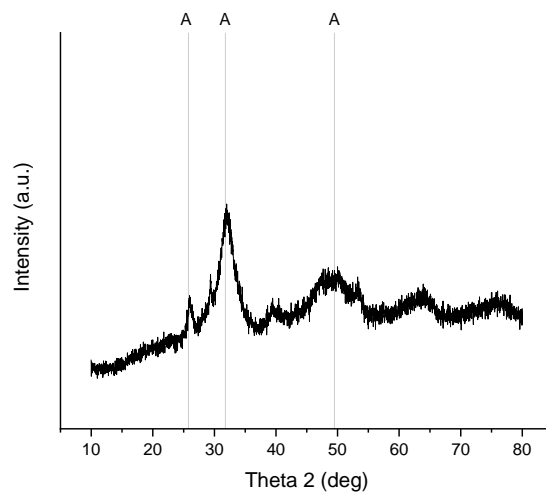


Fig. 10 X-ray diffraction patterns of the solid precipitate in the authentic solution experiment. A: $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$

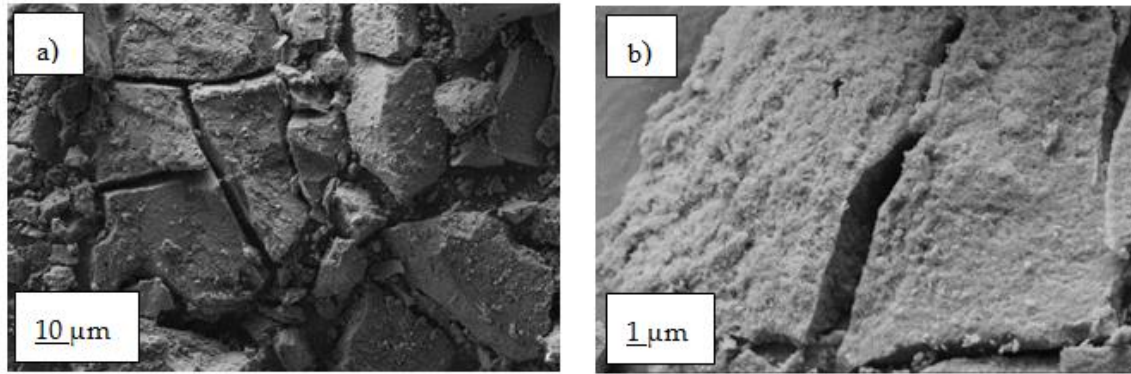


Fig. 11 SEM images of the precipitate from authentic experiments. a) The bar indicates 10 μm length, 2 500x; b) The bar indicates 1 μm length, 10 000x

4. Discussion

In this research, calcined paper mill sludge was specifically used for the removal of phosphate. At the same time, Frazier's method for removal of ammonium as calcium ammonium phosphate was tested. Ammonium removal efficiency was at a very low level in the authentic experiments. However, due to the high ammonium concentration of 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 volatilizes into air as ammonia gas under alkaline conditions as a function of pH (pKa 9.2) or ammonium ions transform to aqueous ammonia [17, 28]. Another reason that Frazier's method for removal of ammonium as calcium ammonium phosphate was unsuccessful, Frazier et al. used saturated ammonium phosphate solutions.

Several researchers obtained similar phosphate removal results with other, inexpensive waste materials. Johansson precipitated phosphate as hydroxyapatite, $\text{Ca}_{10}\text{OH}_2(\text{PO}_4)_6$, from wastewater with fly ash [29]. Moriyama et al. 2001 achieved 75–85% efficiency of hydroxyapatite formation using Ca-rich media in phosphorus removal [30]. Chemical precipitation as struvite is the best known method of simultaneous phosphorus and ammonium nitrogen recovery from wastewater [22, 23]. 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, Ca-rich media could also be used in the simultaneous removal of nitrogen and phosphate, which leads to the formation of a struvite-like Ca-mineral [24]. The phosphate removal efficiencies were comparable to results obtained with other Ca-containing waste materials, such as fly ash [31], bottom ash [32], waste bones ash [33] and calcined paper waste [34].

Due to the different species of phosphate, the calcined paper mill sludge dosage plays an important role in the phosphate precipitation. Between pH 4 and pH 6 dihydrogen phosphate species (H_2PO_4^-) is dominant, between pH 8 and 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 previous, the calcined paper mill sludge dosage must be at the required level [31, 35]. The removal of phosphorus may include, aside the precipitation reaction, some adsorption reactions [36, 37]. Phosphate can be adsorbed by calcite (CaCO_3) [38]. Since there was calcite found in our synthetic experiments (Fig. 7), this is more than likely.

The results from the study indicate that nutrient-rich liquid phase of anaerobic digestate can be converted to a solid form containing phosphate. The conversion can make the plant more feasible by lowering the costs for waste treatment.

5. Conclusions

Objective of this study was to test whether industrial waste material (calcined paper mill sludge) could be used as low cost precipitation chemical in the simultaneous removal of ammonium nitrogen and phosphate from the liquid phase of anaerobic digestate, and whether the precipitate could be suitable for fertilizer use. The results obtained in this study indicated that calcined Ca-containing paper mill sludge removed 17% of ammonium nitrogen and 73% of phosphate. The change in temperature had no effect on the removal of ammonium nitrogen and phosphate. The formed precipitates contain hydroxyapatite that can be used as recycled, solid, fertilizer. However, more research is needed to

optimize the precipitation conditions, as well as such as solubility and growth tests in greenhouses and fields to confirm the suitability of the precipitate for fertilizer use. The utilization of industrial waste material as secondary raw material is important for developing new sustainable removal methods from nutrient containing wastewaters.

Acknowledgments: The authors would like to thank laboratory assistant Mr. Jaakko Pulkkinen and student Mr. Ilkka Vesavaara for their assistance with the laboratory analysis.

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