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Article

# Use of Calcined Dolomite as Chemical Precipitant in the Simultaneous Removal of Ammonium and Phosphate from Synthetic Wastewater and from Agricultural Sludge

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**Abstract:** Phosphorus as phosphate and nitrogen as ammonium or nitrate are the main nutrients in wastewaters and agricultural sludges. They runoff easily to waterways and cause eutrophication in water bodies. However, ammonium and phosphate could be precipitated simultaneously and used as recycled nutrients. In this research, dolomite calcined at 650 °C, 750 °C, or 950 °C and commercial MgO were used as precipitants in simultaneous phosphate and ammonium removal from synthetic (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> solution and agricultural sludge. Calcination at 750 °C was the preferred option as dolomite was decomposed to MgO and CaCO<sub>3</sub> for optimal struvite precipitation. Molar ratios of 1.1–1.6:1–2:2 (Mg:P:N) were employed in the experiments. Very robust ammonium removal was obtained with MgO (57%), dolomite 650 °C and dolomite 750 °C (75%). MgO removed almost all phosphate, while dolomite 650 °C removed 65%, and dolomite 750 °C removed 60% (70% from agricultural sludge). Some part of the phosphate was adsorbed, most likely by CaCO<sub>3</sub>, during dolomite precipitation. Struvite was the only identified reaction product in all samples after 24 h of precipitation. Calcined dolomite had great potential in ammonium and phosphate precipitation from both synthetic waters and agricultural sludges and the precipitates could be used as recycled fertilizers.

**Keywords:** dolomite; precipitant; struvite; ammonium; phosphate

## 1. Introduction

Phosphorus as phosphate and nitrogen as ammonium or nitrate are the main nutrients in wastewaters and agricultural sludges. They runoff easily to waterways, especially when agricultural sludges are used as fertilizers. This promotes the growth of organic matter and algae, which causes eutrophication in water bodies. In addition, nitrogen is typically present in the form of ammonium, which volatilizes easily as ammonia gas under alkaline conditions [1]. These factors reduce the effect of fertilization.

In the optimum case, both ammonium and phosphate would be precipitated simultaneously and employed as recycled fertilizer. Especially seeing that the European Commission has released a proposal for the revision of the EU's fertilizer legislation, the usage of recycled fertilizers will rise [2]. The proposal is still under discussion, but the use of bio-based and recycled fertilizers

will be encouraged in the revised directive. In Finland alone, the economic potential of nutrient circulation is approximated to be €0.5 billion annually [3]. Moreover, traditional nitrogen fertilizers are produced mainly through use of energy-intensive Haber–Bosch reactions, which cause large amounts of greenhouse gas emissions as production consumes high amounts of natural gas [4]. It has been estimated that, in the following decades, exploitable phosphate resources will be significantly depleted [5]. The geographic distribution of exploitable reserves is very inhomogeneous with 77% of global reserves being located in Morocco [6]. In addition, the remaining rock phosphate reserves are characterized by decreasing quality (higher Cd and U concentrations) and more expensive mining technology is necessary [7]. Therefore, the need for the recovery of phosphorus is very significant.

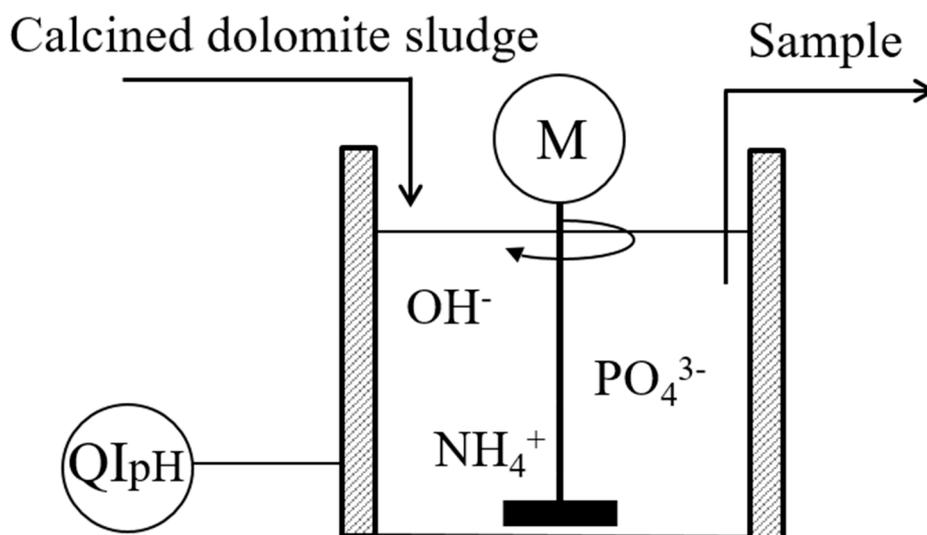
Ammonium and phosphate can be simultaneously precipitated as a phosphate mineral, struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ), which could be used as a slow-release fertilizer, reducing the nutrient supply to the waterways and diminishing ammonium losses as ammonia gas. Typical precipitants for struvite precipitation are commercial  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{MgO}$ , and  $\text{Mg}(\text{OH})_2$  [8]. Owing to the relatively high price of these commercial salts, there is a need to find other suitable cost-efficient precipitants for struvite precipitation. Inexpensive magnesium sources, such as magnesite [9], brucite [10], a byproduct of marine salt manufacturing and the thermal treatment of meat waste and bone meal [11],  $\text{MgO}$ -saponification wastewater [12], seawater [13,14], and wood ash from a residential fireplace [15], to produce struvite have been tested previously.

In this study, dolomite was utilized as a precipitant. Dolomite is a carbonate mineral composed of calcium magnesium carbonate,  $\text{CaMg}(\text{CO}_3)_2$ , and it is used, e.g., as a soil improver to increase the pH of acidic soils [16]. However, it could also be applied for struvite precipitation but there exists a very limited amount of research on this subject. Xiao et al. [17] used dolomite to neutralize waste sulfuric acid from the mining industry and employed the magnesium sulfate-containing supernatant to precipitate struvite from swine wastewater. However, as waste sulfuric acid can contain large amounts of toxic compounds [18] that can possibly precipitate together with nutrients, this procedure cannot necessarily be recommended. Chen et al. [19] used commercial dolomite calcined at  $750\text{ }^\circ\text{C}$  to precipitate struvite from model wastewater but did not perform any tests with authentic wastewaters. Waste dolomite has not been previously tested for struvite precipitation, and there has been no research on authentic wastewaters.

In this research, calcined dolomite (a waste fraction) was used to simultaneously precipitate phosphate and ammonium from agricultural sludge in addition to synthetic  $(\text{NH}_4)_2\text{HPO}_4$  solution. Effects of calcination temperature, precipitation time and precipitant dosing on the removal efficiency of phosphate and ammonium were studied. Comparisons were made to commercial  $\text{MgO}$ .

## 2. Materials and Methods

A Finnish lime quarry provided dolomite for this study. It was of a small-sized ( $<0.05\text{ mm}$ ) fraction that is leftover as the dolomite is sieved to desired-size fractions. The demand for these small particle sizes is very limited and is currently mostly considered a waste fraction for the lime quarry. Before the experiments, dolomite was calcined at  $650\text{ }^\circ\text{C}$ ,  $750\text{ }^\circ\text{C}$  or  $950\text{ }^\circ\text{C}$ . As a comparison, pure  $\text{MgO}$  was utilized as a precipitant. Molar ratios for the precipitation experiments were chosen using the MineQL program. Molar ratios, Mg:P:N of 1.1–1.6:2:2 (dolomite) or 1.1–1.6:1:2 ( $\text{MgO}$ ), were employed in the experiments. Precipitant solutions were prepared by dissolving 0.5–2.3 g of precipitant in 10 mL of de-ionized water. The formed suspension was hence saturated. Synthetic  $(\text{NH}_4)_2\text{HPO}_4$  solution ( $200\text{ mg}\cdot\text{L}^{-1}\text{ NH}_4^+$  and  $1050\text{--}2100\text{ mg}\cdot\text{L}^{-1}\text{ PO}_4^{3-}$ ) was prepared from ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and potassium hydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) salts. Precipitation experiments were conducted at room temperature ( $20\text{ }^\circ\text{C}$ ) and the schematic diagram of the batch-mode reactor used in the experiments is presented in Figure 1.



**Figure 1.** Precipitation reactor consists of a curved blade connected to a motor (M); a 2 L decanter glass with stators attached to the wall of the glass; and a pH-meter (QI<sub>pH</sub>).

In the experiments, 10 mL of the saturated precipitant solution was added to 1.6 L of the ammonium phosphate solution while stirring the solution at a constant speed of 450 rpm for 1 min to mix up the two solutions properly. Afterwards, the rotor speed was reduced to 50 rpm for the duration of the experiment (4 h, 24 h, or 48 h) and the pH was adjusted to either 8.5 (MgO and dolomite 650 °C and 750 °C) or 9.0 (dolomite 950 °C) and kept constant. Water samples (25 mL) were taken in the beginning, and then after every half hour until the end of the experiments. They were filtered through 4–12 µm filter paper before analysis.

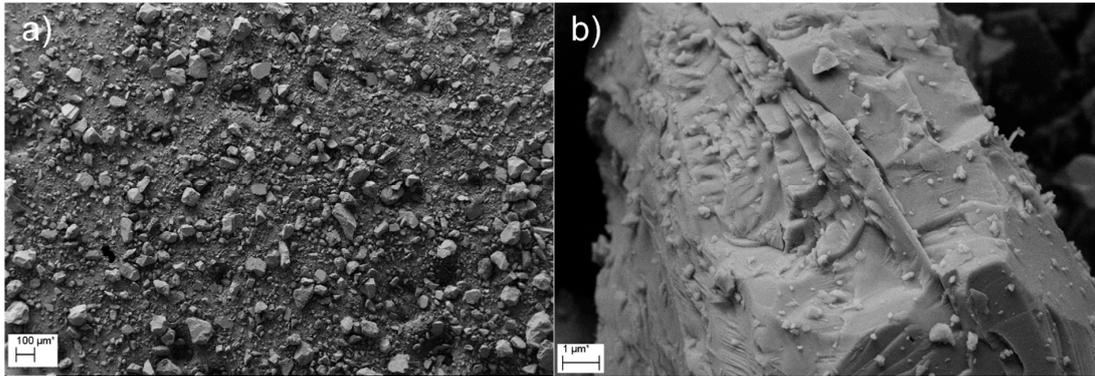
Further, one experiment with agricultural sludge was performed. Sludge was first filtered through 13–15 µm filter paper before the experiment. Filtrate had a pH of 8.95, a phosphate concentration of 25 mg·L<sup>-1</sup>, and an ammonium concentration of 137 mg·L<sup>-1</sup>, therefore KH<sub>2</sub>PO<sub>4</sub> was added to adjust the N:P ratio to 1:1. Dolomite 750 °C was used as a precipitation agent (pH 9; reaction time, 24 h).

Ammonium concentration was measured from the water samples with the use of an NH<sub>4</sub><sup>+</sup> selective electrode and phosphate concentration was measured by ion chromatography (IC; Methrom 761 Compact IC). Precipitate was collected after the experiments and dried at 105 °C (4 h experiments) or room temperature (24 h experiments). It was analyzed using a CHNS analyzer, x-ray diffractometer (XRD), and scanning electron microscope (SEM). Dolomite was characterized with SEM, an X-ray fluorescence spectrometer (XRF) and a thermogravimetry differential scanning calorimeter (TG-DSC). The microstructure shown in the FESEM images were obtained with a Zeiss Sigma field-emission scanning-electron microscope (FESEM) at the Centre of Microscopy and Nanotechnology at the University of Oulu operated at 5 kV. A Bruker AXS S4 Pioneer was used for XRF measurement. The sample powders were added 6% C-wax as binder and pressed into pellet specimens with a diameter of 37 mm in a steel ring. The detectable element concentration was 0–5 mg·kg<sup>-1</sup> for XRF. A Rigaku SmartLab 9 kW XRD was applied for the phase and structure evaluation. Elemental analysis was performed with a Flash 2000 CHNS-O Organic elemental analyzer produced by Thermo Scientific. The TG-DSC was performed at the research unit of Process Metallurgy at the University of Oulu using a Netzsch STA 449F3 thermal analyzer.

### 3. Results and Discussion

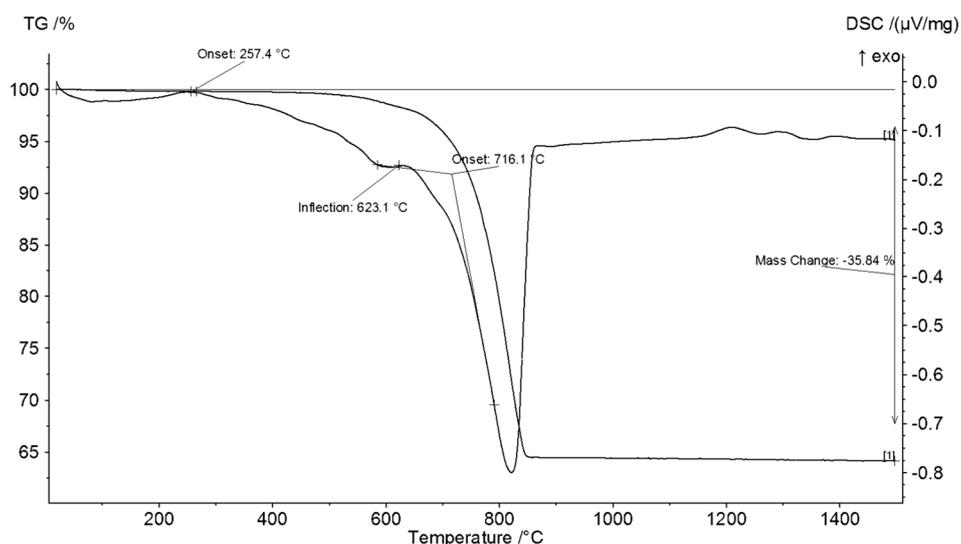
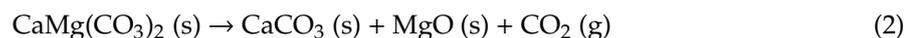
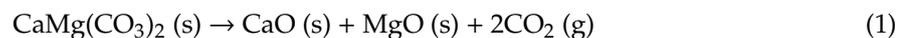
#### 3.1. Characterization of the Dolomite

SEM images of the dolomite before the calcination are presented in Figure 2. Figure 2a is a general image of the dolomite, while Figure 2b is a magnification of a single dolomite particle. Dolomite contains mainly irregularly shaped particles and therefore has no clear morphology.



**Figure 2.** SEM images of the dolomite. Scale bars: (a) 100  $\mu\text{m}$ ; and (b) 1  $\mu\text{m}$ .

TG-DSC analysis of the dolomite is presented in Figure 3. Complete decomposition of the calcium and magnesium carbonates is achieved approximately at 850  $^{\circ}\text{C}$ , as presented in Equation (1). Therefore, the calcination at 950  $^{\circ}\text{C}$  is more than enough to transform these carbonates into the reactive oxide form. However, as CaO easily precipitates phosphate as hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) [20], lower CaO concentration would be better suited for struvite precipitation. Therefore, calcination at lower temperatures should be preferred. At 750  $^{\circ}\text{C}$ , most of the  $\text{MgCO}_3$  is decomposed to MgO, but  $\text{CaCO}_3$  should still be mostly in carbonate form (Equation (2)) [21].



**Figure 3.** TG-DSC analysis of the dolomite.

The main components of the calcined (950 °C) dolomite are presented in Table 1 and harmful element contents along with a comparison of the limit values of Finnish fertilizer decree [22] are found in Table 2. Calcined dolomite contains mainly CaO, MgO, and SiO<sub>2</sub>. The molar ratio between MgO and CaO is therefore 1:1.3.

**Table 1.** Main components as mass fractions (XRF) of the calcined (950 °C) dolomite.

Sample	CaO (%)	MgO (%)	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	FeO (%)	P <sub>2</sub> O <sub>5</sub> (%)	K <sub>2</sub> O (%)	Na <sub>2</sub> O (%)	S (%)	TiO <sub>2</sub> (%)	Others (%)
Dolomite	50.6	27.4	15.3	1.3	1.0	0.3	0.2	0.2	0.1	0.1	3.5

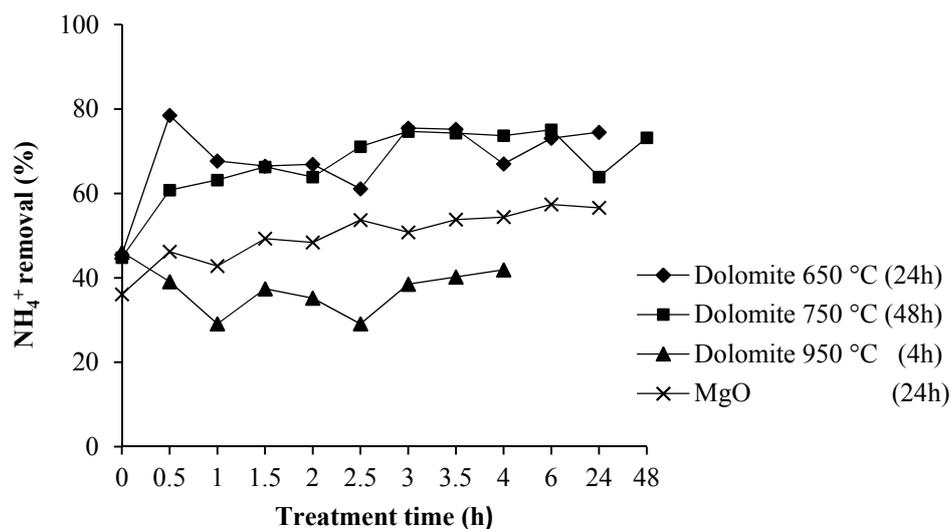
Concentrations of harmful elements are reasonably low and clearly below the limit values of Finnish fertilizer decree, i.e., dolomite could be used as a soil improver in Finland. The Cd concentration was below the detection limit value of the XRF equipment, therefore it cannot be stated with certainty if the Cd concentration is also below the limit for field fertilizers. It should be noted, however, that the limit values of Finnish fertilizer decree are for nitric acid digestion. XRF measures the total concentration of the elements, and the concentrations obtained with nitric acid digestion are typically evidently lower than the total concentrations [23]. Therefore, the results obtained with XRF overestimate the actual availability of these elements.

**Table 2.** Harmful element contents (XRF) and a comparison to the limit values of Finnish fertilizer decree [22].

Sample	As (mg·kg <sup>-1</sup> )	Cd (mg·kg <sup>-1</sup> )	Cr (mg·kg <sup>-1</sup> )	Cu (mg·kg <sup>-1</sup> )	Ni (mg·kg <sup>-1</sup> )	Pb (mg·kg <sup>-1</sup> )	Zn (mg·kg <sup>-1</sup> )
Dolomite	21	<5	68	30	36	10	41
Limit value field/forest fertilizers	25/40	1.5/25	300	600/700	100/150	100/150	1500/4500

### 3.2. Ammonium Removal

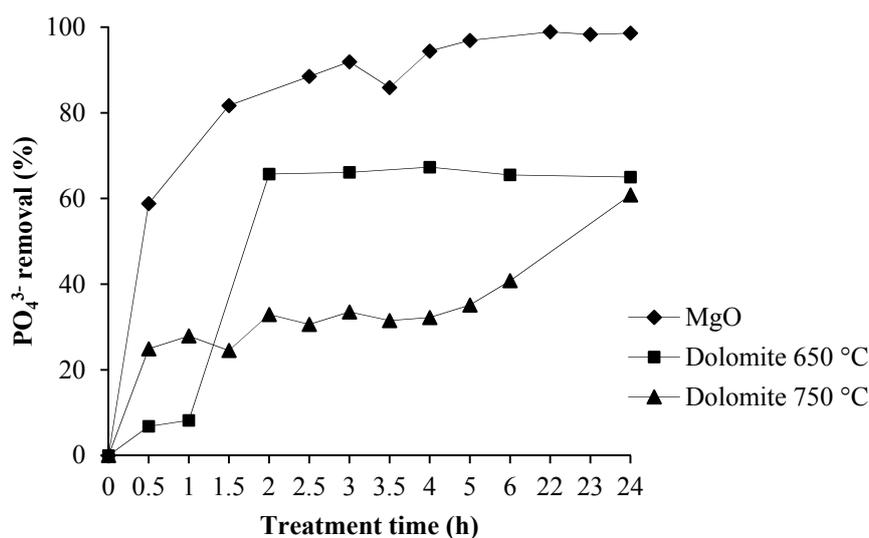
Ammonium removal percentages of different precipitants as a function of time are presented in Figure 4. The molar ratio did not have an impact on the ammonium removal and only results for ratios Mg:P:N 1.3:1:2 for MgO and 1.3:2:2 for dolomite are presented. The electrode used cannot detect ammonia, which explains the quite high percentage of removal at the beginning of the experiments where pH was adjusted from 4.6 to 8.5–9—ammonium transforms into ammonia under alkaline conditions as a function of pH (pKa 9.2). However, as ammonia is highly soluble in water (a mass fraction of 34% at 20 °C), no major ammonia losses occurred during these experiments [24]. For dolomite 950 °C, the removal percentage was roughly the same (41%) throughout the 4 h experiment, thereby indicating poor precipitation. With dolomite 650 °C and MgO, the precipitation continued for 24 h, and with dolomite 750 °C, for 48 h, to determine whether the increase in precipitation time would lead to increased recovery. The percentage of ammonium removal was up to 57% for MgO and 75% for dolomite 650 °C and dolomite 750 °C. There was excess ammonium in all cases present and the removal percentage could be at best be around 75%, therefore, removal was strong with MgO, dolomite 650 °C and dolomite 750 °C.



**Figure 4.** Percentage of ammonium removals of MgO, dolomite 650°, dolomite 750 °C, and dolomite 950 °C (Mg:P:N molar ratios 1.3:1:2 for MgO and 1.3:2:2 for dolomites).

### 3.3. Phosphate Removal

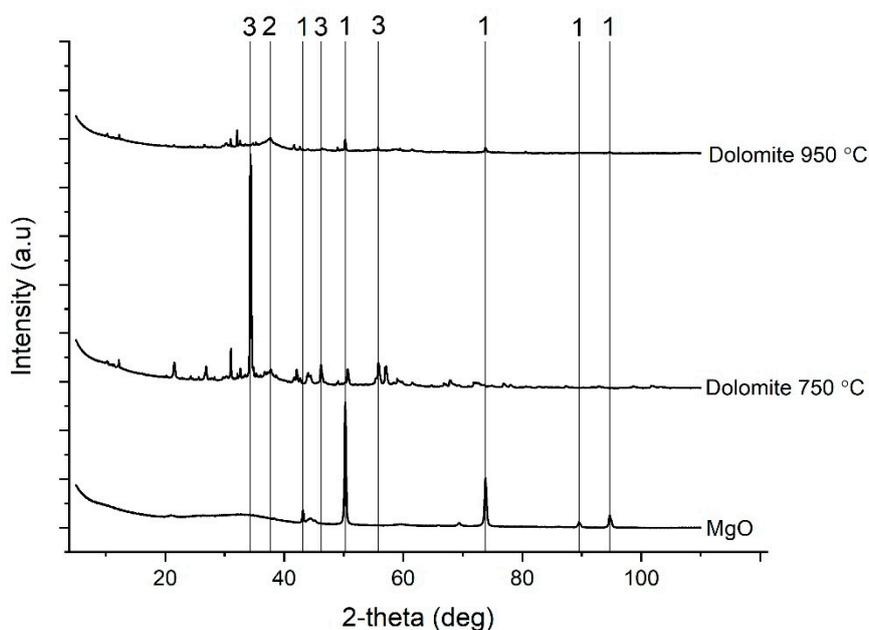
Phosphate removal percentages of different precipitates as a function of time are illustrated in Figure 5. Molar ratio did not have an impact on the phosphate removal and only results for ratios Mg:P:N 1.3:1:2 for MgO and 1.3:2:2 for dolomite are presented. MgO removed almost 100% of phosphate, dolomite 650 °C removed 65% of phosphate after a 24 h experiment. It should be noted that the concentration of phosphate in the dolomite precipitation was double compared to that with MgO, and only a 50% reduction was reached with struvite precipitation. Therefore, either some of the phosphate was adsorbed by the dolomite or it was precipitated as another component, such as hydroxylapatite. As there was no indication of other precipitation products besides struvite in the XRD graphs (Figure 8), adsorption is the more likely alternative, and  $\text{CaCO}_3$  especially can be used to effectively adsorb phosphate [25].



**Figure 5.** Phosphate removal percentages of MgO, dolomite 750 °C, and dolomite 950 °C (Mg:P:N molar ratios 1.3:1:2 for MgO and 1.3:2:2 for dolomites).

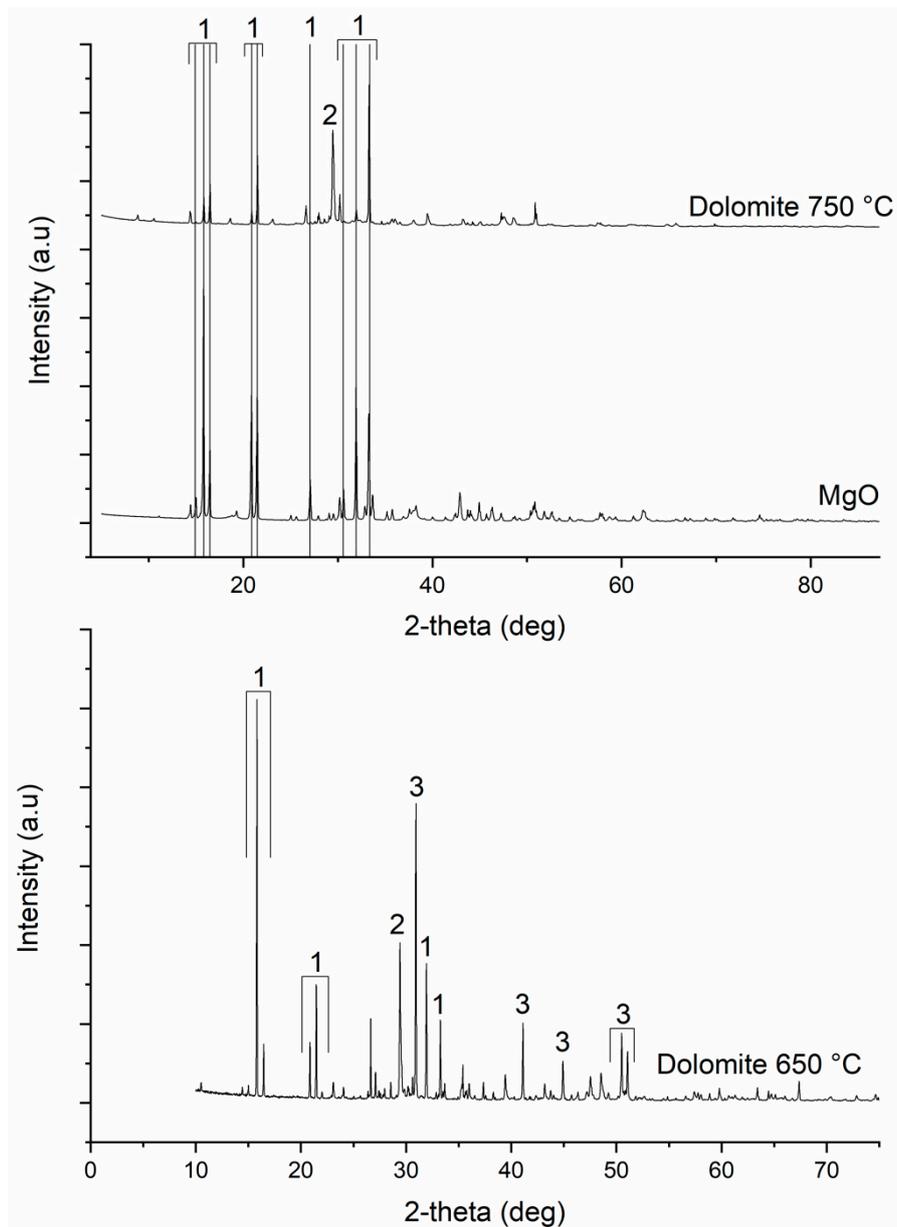
### 3.4. Characterization of the Precipitates

XRD diffractograms of the precipitates (Mg:P:N 1.3:1:2 for MgO and 1.1:2:2 for dolomite) are presented in Figure 6 (4 h experiments) and 7 (24 h experiments). Molar ratios did not have an impact on the diffractogram shape. The only crystalline compounds in the MgO precipitate from the 4 h experiments were MgO and a broad amorphous hump detected below 40 °C. CHNS analysis indicated that a mass fraction of around 1% of nitrogen was present in the precipitate, therefore some struvite was formed. Struvite peaks should be found between 10 and 40 °C in the XRD diffractograms, but, due to the amorphicity and relatively low struvite concentration, these peaks could not be detected. Similar amorphicity was found from the dolomite 750 °C precipitate in the 4-h experiment, where a struvite-like magnesium ammonium phosphate compound was observed. However, the peaks had low intensity and are not marked in Figure 6. CHNS analysis confirmed a low concentration of nitrogen in the precipitate (a mass fraction less than 1%). In addition, a CaCO<sub>3</sub> peak was found, confirming that the decomposition of dolomite was not complete. Only MgO and hydroxylapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)) peaks were noted from the dolomite 950 °C precipitate in the 4 h experiment, indicating that the CaO precipitated the phosphate as hydroxylapatite before struvite began to form. Therefore, calcination at a lower temperature is preferred. In practice, calcination should be performed at such a low temperature that a minimum amount of CaCO<sub>3</sub> and maximum amount of MgO would be decomposed. No nitrogen was found from the precipitate via CHNS analysis. It is possible that some of the nitrogen was lost while drying the precipitates at 105 °C [26].



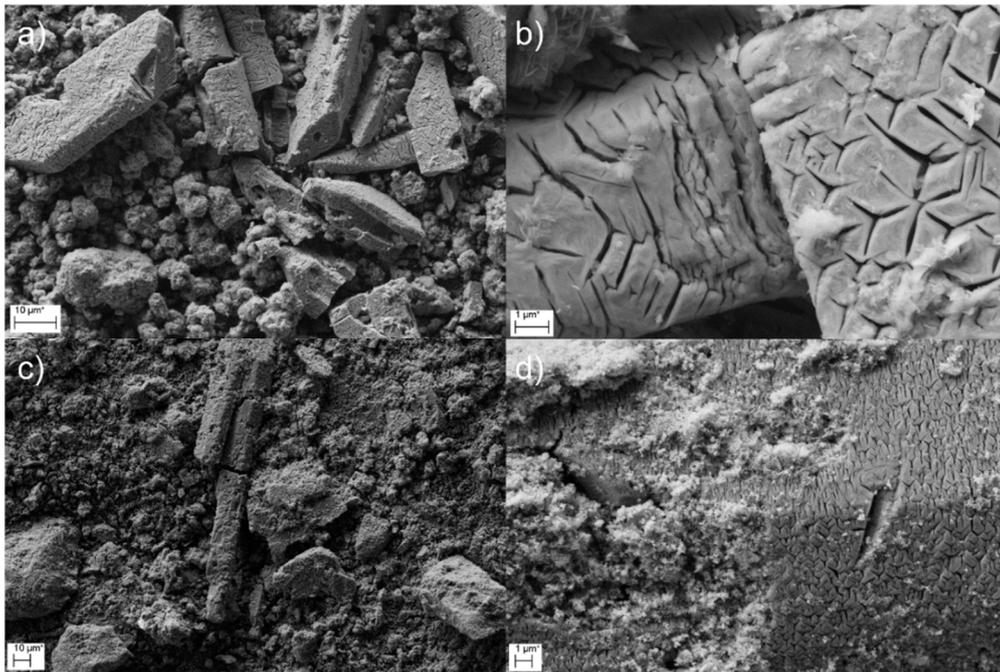
**Figure 6.** XRD diffractograms of the precipitates after the 4 h experiments (Mg:P:N 1.3:1:2 for MgO and 1.3:2:2 for dolomite): 1 = MgO; 2 = Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH); 3 = CaCO<sub>3</sub>.

As the precipitation time was increased to 24 h, struvite was found in all precipitate samples (Figure 7). Some CaCO<sub>3</sub> was found from the dolomite 750 °C sample as in the 4-h experiments. In addition, undecomposed dolomite was found from the dolomite 650 °C samples. Therefore, calcination at 650 °C was insufficient to decompose all MgCO<sub>3</sub> to MgO. The XRD graph for the 48 h experiment with dolomite 750 °C was similar to that for the 24-h experiment presented in Figure 8.



**Figure 7.** XRD diffractograms of the precipitates after the 24-h experiments (Mg:P:N 1.3:1:2 for MgO and 1.3:2:2 for dolomite 650 °C and 750 °C): 1 =  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ; 2 =  $\text{CaCO}_3$ ; 3 =  $(\text{CaMg}(\text{CO}_3)_2)$ .

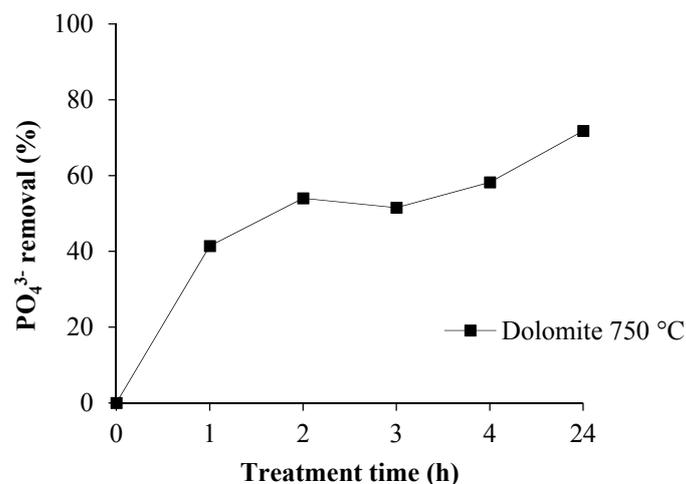
SEM images of the precipitates (Mg:P:N = 1.3:1–2:2) are portrayed in Figure 8a,b for MgO and Figure 8c,d for dolomite 750 °C. Large struvite crystals are clearly visible among the finer, more amorphous particles in all cases.



**Figure 8.** SEM images of the precipitates (Mg:P:N 1.3:1:2 for MgO and 1.3:2:2 for dolomite): (a,b) MgO; and (c,d) dolomite 750 °C. Scale bars: (a,c) 10 μm; and (b,d) 1 μm.

### 3.5. Agricultural Sludge

Phosphate removal from agricultural sludge using dolomite 750 °C (Mg:P:N = 1.3:1:1; pH 9) is depicted in Figure 9. The percentage of phosphate removal rose as a function of time from 40% after 1 h of precipitation time to approximately 70% after 24 h. It is possible that the precipitation reaction would proceed with even longer contact time. Unfortunately, based on the heavy fouling of the ammonium electrode caused by the agricultural sludge, the ammonium reduction could not be measured reliably and therefore no conclusions can be made surrounding ammonium reduction. However, if it is assumed that all of the phosphate was precipitated as struvite, then the ammonium reduction would also be approximately 70%.

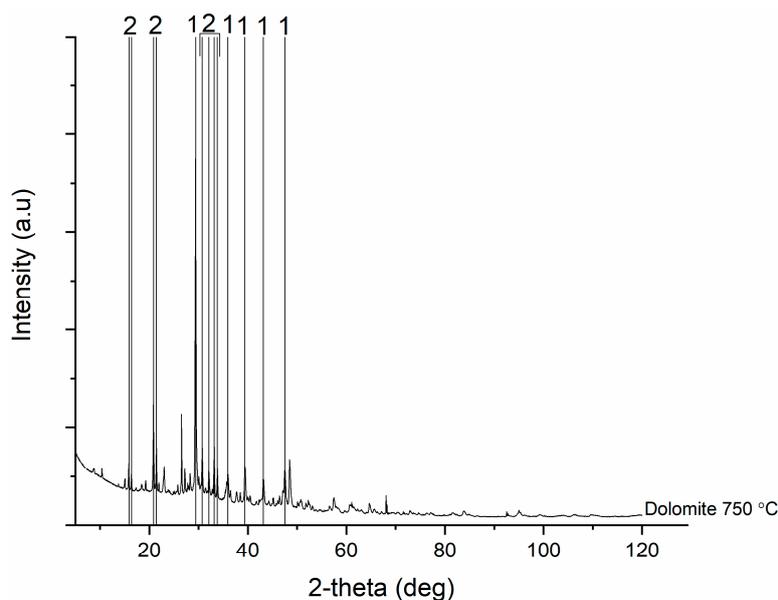


**Figure 9.** Phosphate removal percentages of dolomite 750 °C (Mg:P:N molar ratios 1.3:1:1) from agricultural sludge.

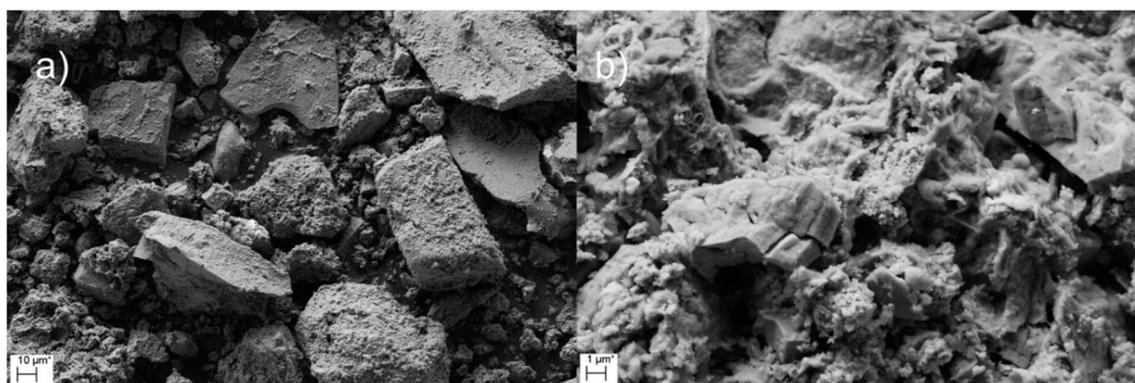
The XRD diffractogram of the precipitate is presented in Figure 10. CaCO<sub>3</sub> originating from the dolomite was found, but the only identified reaction product was struvite. SEM images of the

precipitates from the precipitation of agricultural sludge are shown in Figure 11. Larger particles that appear to be  $\text{CaCO}_3$  are completely covered with fine precipitate particles.

These results indicate that the calcined dolomite can be used as a precipitant with agricultural sludges as well. However, as the phosphate concentration of the studied sludge was relatively low compared to the ammonium concentration ( $25 \text{ mg}\cdot\text{L}^{-1}$  of  $\text{PO}_4^{3-}$ ;  $137 \text{ mg}\cdot\text{L}^{-1}$  of  $\text{NH}_4^+$ ), the phosphate concentration had to be adjusted for optimal precipitation. Another, possibly more cost-effective, option could be to remove the excess ammonium with other methods, such as adsorption with zeolites [27] or geopolymers [28] before or after the precipitation.



**Figure 10.** XRD diffractogram of the precipitate from the precipitation of agricultural sludge (Mg:P:N = 1.3:1:1) using dolomite 750 °C (Mg:P:N = 1.3:1:1): 1 =  $\text{CaCO}_3$ ; 2 =  $(\text{NH}_4\text{MgPO}_4\cdot 6\text{H}_2\text{O})$ .



**Figure 11.** SEM images of the precipitate from the precipitation of agricultural sludge with dolomite 750 °C (Mg:P:N = 1.3:1:1). Scale bars: (a) 10  $\mu\text{m}$ ; and (b) 1  $\mu\text{m}$ .

#### 4. Conclusions

Dolomite from a Finnish lime quarry was used as a precipitant for phosphate and ammonium uptake from a synthetic  $(\text{NH}_4)_2\text{HPO}_4$  solution and agricultural sludge. Dolomite was calcined at three temperatures (650 °C, 750 °C, and 950 °C) and its effectiveness as a precipitant was compared with commercial  $\text{MgO}$ . Calcination at 750 °C was found to be the most effective pretreatment for dolomite. Good ammonium and phosphate removals were achieved with  $\text{MgO}$ , dolomite 650 °C and dolomite 750 °C. Twenty-four-hour contact time was needed for struvite formation. In addition to struvite formation, some of the phosphate was adsorbed by the dolomite, most likely by  $\text{CaCO}_3$ .

Strong phosphate removal was also obtained for agricultural sludge and the only identified reaction product was struvite. The results indicate that calcined dolomite has great potential in ammonium and phosphate precipitation from both synthetic waters and agricultural sludges. Further, the precipitate could be used as a recycled fertilizer. However, more research is needed (such as solubility and growth tests in greenhouses and fields) to confirm suitability for fertilizer use.

**Author Contributions:** Conceptualization, J.P., P.M., S.T. P.T., and U.L.; investigation, G.V., T.H., and H.P.; writing—original draft preparation, J.P., P.M. and S.T.; and writing—review and editing, P.T. and U.L.

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