Use of calcined dolomite as chemical coagulant in the simultaneous removal of nitrogen and phosphorus

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Abstract

Phosphorus and nitrogen 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 the optimum case, both nitrogen and phosphorus from wastewaters and agricultural sludges would be precipitated simultaneously and used as recycled nutrients. In this research, calcined dolomite was used as a coagulant for phosphorus and nitrogen removal from synthetic $(NH_4)_2HPO_4$ solution. Molar ratios Molar ratios Mg:P:N of 1.1-1.6:1-2:2 was used in the experiments. Calcination at 750 °C decomposed most of the $MgCO_3$ to MgO, but $CaCO_3$ was mostly as carbonate, while calcination at 950 °C decomposed the dolomite completely. Ammonium removal was 32 % for dolomite 750 °C, 41 % for dolomite 950 °C and 44 % for MgO. CHNS analysis indicated that around one m% of nitrogen was present in the MgO precipitate, therefore some struvite was formed. A small amount of struvite-like magnesium ammonium phosphate compound was found from the dolomite 750 °C precipitate. Only hydroxylapatite ($Ca_5(PO_4)_3(OH)$) was found from the dolomite 950 °C precipitate, indicating that CaO precipitates the phosphate as hydroxylapatite before struvite begins to form. Therefore, the calcination should be performed in such a low temperature that a minimum amount of $CaCO_3$ and a maximum amount of MgO would be decomposed. Results indicated that calcined dolomite have some potential in the nitrogen and phosphorus precipitation from synthetic samples.

Keywords: dolomite, coagulant, struvite, fertilizer.

1. Introduction

Phosphorus and nitrogen 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. Also, nitrogen is typically present in the form of ammonium, which volatilizes easily as ammonia gas at alkaline conditions [1]. These factors reduce the effect of fertilization.

In the optimum case, both nitrogen and phosphorus would be precipitated simultaneously and used as recycled fertilizer. Especially, since the European Commission has released a proposal for the revision of the EU's fertilizer legislation, the usage of recycled fertilizers will be increased [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]. Also, traditional nitrogen fertilizers are produced mainly by using the energy-intensive Haber-Bosch reaction, which causes large amounts of greenhouse gas emissions, as production consumes high amounts of natural gas [4].

Ammonium and phosphate can be simultaneously precipitated as a phosphate mineral, struvite ($NH_4MgPO_4 \cdot 6H_2O$), which could be used as a slow-release fertilizer, reducing the nutrient supply to the waterways and reducing the nitrogen losses as ammonia gas. Typical coagulants for struvite precipitation are commercial $MgCl_{2,}$ $MgSO_4$, MgO and $Mg(OH)_2$ [5]. Due to the high price of these commercial salts, there is a need to find other suitable cost-efficient coagulants for struvite precipitation.

Dolomite is a carbonite mineral composed of calcium magnesium carbonate ($CaMg(CO_3)_2$ and it is used e.g. as a soil improver to increase pH of acidic soils [6]. However, it could also be used for struvite precipitation.

In this research, calcined dolomite was used as a coagulant for phosphorus and nitrogen removal from synthetic $(NH_4)_2HPO_4$ solution. It's effectiveness as coagulant was compared with commercial MgO.

2. Materials & Methods

A Finnish lime quarry provided the dolomite used in this study. Before the experiments, dolomite was calcined at 750 °C or at 950 °C. As a comparison, pure MgO was used as a coagulant. The optimal conditions for the precipitation experiments were calculated using MineQL program. Molar ratios Mg:P:N of 1.1-1.6:2:2 (dolomite) or 1.1-1.6:1:2 (MgO) was used in the experiments. Coagulant solutions were prepared by dissolving 0.5 – 2.3 g of coagulant in 10 mL of de-ionized water. Formed suspension was hence saturated. Ammonium phosphate $(NH_4)_2HPO_4$ solution (200 mg/L NH_4^+ and 100-200 mg/L PO_4^{3-}) was prepared from ammonium chloride (NH_4Cl) and potassium hydrogen phosphate (KH_2PO_4) salts. Precipitation experiments were conducted at room temperature (20 °C) and the reactor used in the experiments is presented in Fig. 1.

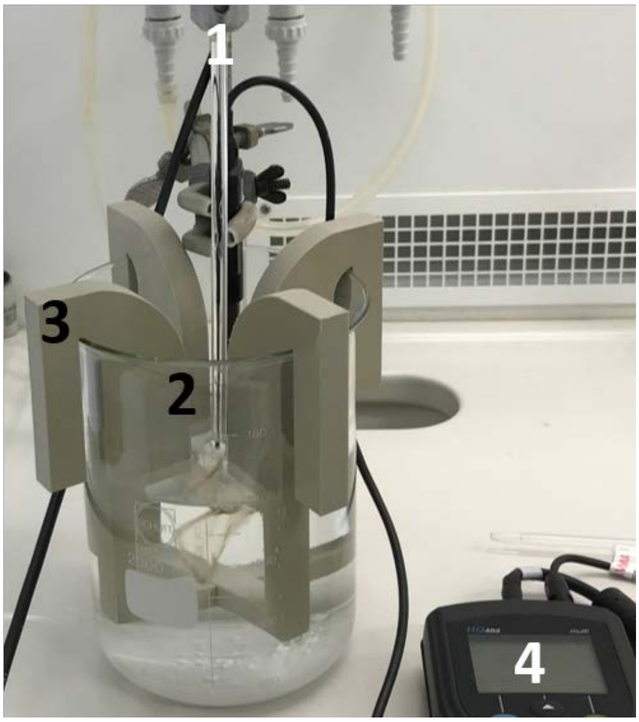

Fig. 1 Precipitation reactor consists of a curved blade (1) connected to a rotor; a 2 L decanter glass (2); stators (3); and a pH-meter (4)

In the experiments, 10 mL of the saturated coagulant 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 minute in order to mix up the two solutions properly. After that, the rotor speed was reduced to 50 rpm for the duration of the experiment (240 min) and the pH was adjusted to either 8.5 (MgO and dolomite 750 °C) or 9.0 (dolomite 950 °C) and kept constant. Small amount of struvite (10 mg) was added as seed crystals to enhance the precipitation. Water samples were taken in the beginning, and then after every half an hour until the end of the experiments. They were filtered through 4-12 µm filter paper before analyzing. Ammonium concentration was measured from the water samples with the use of NH_4-selective electrode and phosphate concentration was measured by IC. Precipitate was collected after the experiments, and dried at 105 ˚C. It was analyzed using CHNS-analyzer, XRD and SEM. Dolomite was characterized using SEM, XRF and TG-DSC.

3. Results & Discussion

3.1 Characterization of the dolomite

SEM-image of the dolomite before calcination is presented in Fig 2. Dolomite contains mainly irregular shaped particles and therefore it has no clear morphology.

Fig. 2 SEM-image of the dolomite

TG-DSC analysis of the dolomite is presented in Fig 3. Complete decomposition of the calcium and magnesium carbonates is achieved approximately at 850 °C. Therefore, the calcination at 950 °C is more than enough to transform these carbonates into the reactive oxide form. At 750 °C most of the $MgCO_3$ is decomposed to MgO, but $CaCO_3$ should still be mostly in the carbonate form [7]. However, the decomposition of $MgCO_3$ is not clearly visible in the TG-curve.

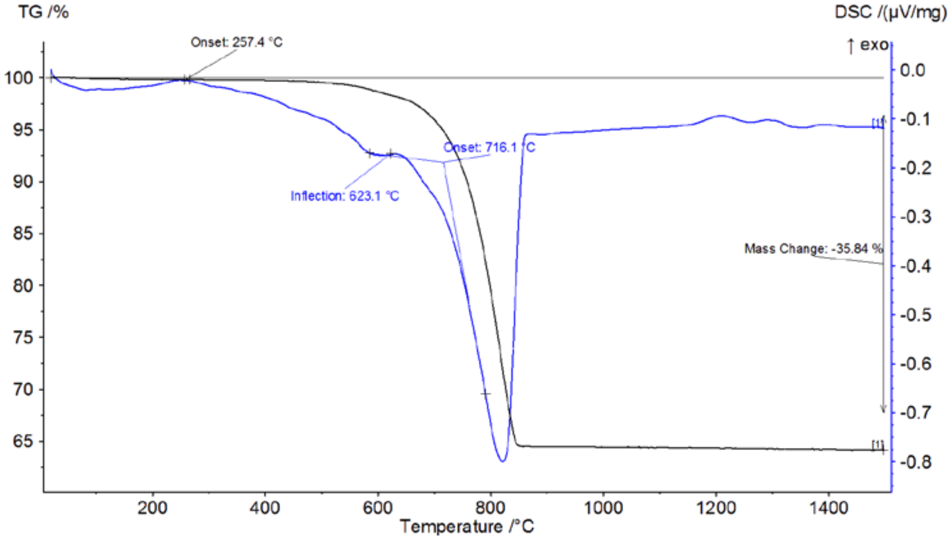

Fig. 3 TG-DSC analysis of the dolomite

Main components of the calcined (950 °C) dolomite are presented in Table 1. Calcined dolomite contains mainly CaO, MgO and SiO_2. The molar ratio between MgO and CaO is therefore 1:1.3.

Table 1 XRF analysis of the calcined (950 °C) dolomite

	Na_2O (%)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	P_2O_5 (%)	S (%)	K_2O (%)	CaO (%)	TiO_2 (%)	FeO (%)	MnO (%)
Dolomite	0.16	27.4	1.34	15.27	0.31	0.07	0.22	50.59	0.05	0.96	0.02

3.2 Ammonium removal

Ammonium removal percentages of different coagulants (Mg:P:N 1.3:1:2 for MgO and 1.3:2:2 for dolomite) as a function of time are presented in Fig 4. Ammonium removal was 32 % for dolomite 750 °C, 41 % for dolomite 950 °C and 44 % for MgO. Ammonium removal percentage increased as a function of time when MgO was used as a coagulant. However, for dolomite the removal percentage was roughly the same throughout the experiment indicating a poor precipitation. Ammonium transforms into ammonia in alkaline conditions as a function of pH (pKa 9.2), which explains the quite high removal percentage in the beginning of the experiments as pH is adjusted to 8.5-9. However, as ammonia is highly soluble in water (34 m% at 20 °C), no major ammonia losses occur during these experiments [8]. Partial reason for the poor ammonium removal could be the relatively short precipitation time (4 h) and therefore longer lasting experiments should be conducted.

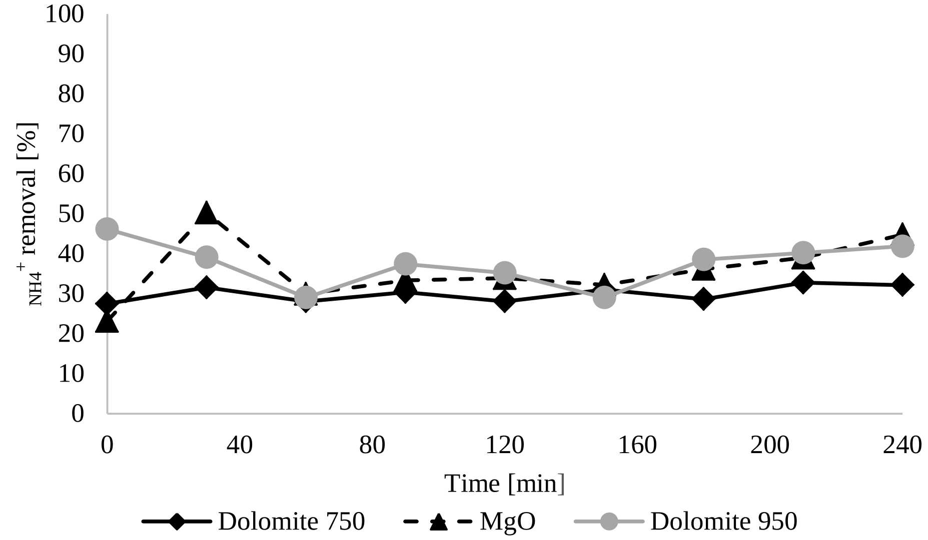

Fig. 4 Ammonium removal percentages of different coagulants (Mg:P:N 1.3:1:2 for MgO and 1.3:2:2 for dolomite)

3.3 Characterization of the precipitate

SEM-images of the precipitates (Mg:P:N 1.1:1-2:2) are presented in Fig. 5. Undissolved dolomite particles are completely covered with very fine precipitate particles in Figs. 5 a) and b). Larger precipitate crystals are visible among the rodlike MgO particles in Fig. 5 c). The precipitate from dolomite 750 °C precipitation was similar than the one from dolomite 950 °C precipitation.

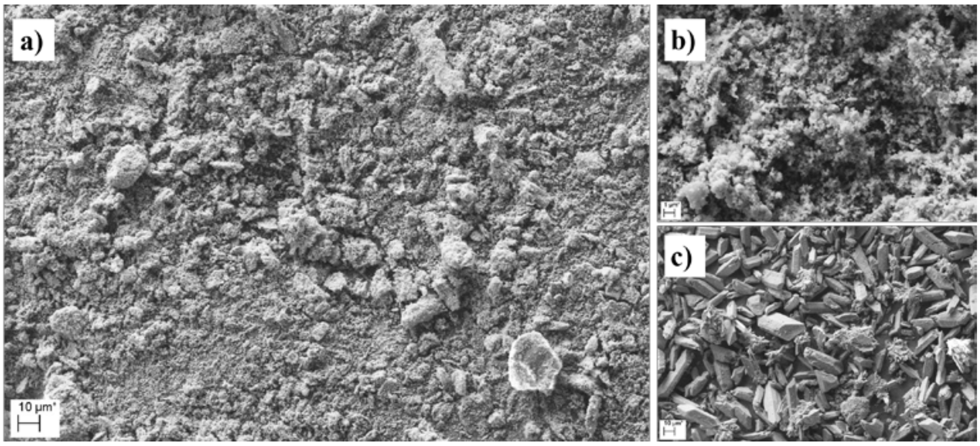

Fig. 5 SEM-images of the precipitates (Mg:P:N 1.1:1:2 for MgO and 1.1:2:2 for dolomite): a) and b) calcined dolomite 950 °C; c) MgO. The bars at a) and c) indicate 10 µm length and at b) 1 µm length

XRD diffractograms of the precipitates (Mg:P:N 1.1:1:2 for MgO and 1.1:2:2 for dolomite) are presented in Fig. 6. Molar ratios did not have an impact on the diffractogram shape. Only crystalline compound in the MgO precipitate was MgO and a broad amorphous hump was detected below 40 degrees. CHNS analysis indicated that around one m% of nitrogen was present in the precipitate, therefore some struvite was formed. Struvite spikes should be found between 10 and 40 degrees in the XRD diffractograms but due to the amorphicity and relatively low struvite concentration, these spikes could not be detected. Similar amorphicity was found from the dolomite 750 °C precipitate, where a struvite-like magnesium ammonium phosphate compound was found. However, the spikes are with low intensity and are not marked on Fig. 6. CHNS-analysis confirmed a low concentration of nitrogen in the precipitate (less than one m%). In addition, $CaCO_3$ spike was found, confirming that the decomposition of dolomite was not complete. However, many unidentified spikes remained. Only MgO and hydroxylapatite ($Ca_5(PO_4)_3(OH)$) spikes were found from the dolomite 950 °C precipitate, indicating that the CaO precipitates the phosphate as hydroxylapatite before struvite begins to form. Therefore, calcination at a lower temperature should be preferred. In practise, the calcination should be performed in such a low temperature that a minimum amount of $CaCO_3$ and a maximum amount of MgO would be decomposed. No nitrogen was found from the precipitate with CHNS analysis. It is possible that some of the nitrogen was lost while drying the precipitates at 105 °C [9].

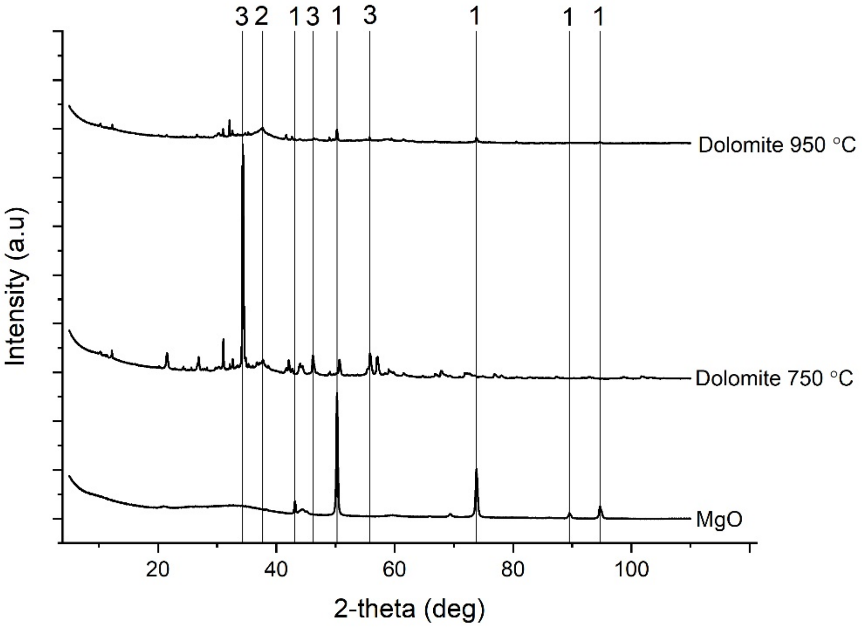

Fig. 6 XRD diffractograms of the precipitates (Mg:P:N 1.1:1:2 for MgO and 1.1:2:2 for dolomite): 1 = MgO; 2 = $Ca_5(PO_4)_3(OH)$; 3 = $CaCO_3$

4. Conclusions

In this paper, calcined dolomite from a Finnish lime quarry was used as a coagulant for phosphorus and nitrogen uptake from a synthetic $(NH_4)_2HPO_4$ solution. It's effectiveness as coagulant was compared with commercial MgO. Calcination at 750 °C decomposed most of the $MgCO_3$ to MgO, but $CaCO_3$ was mostly as carbonate, while calcination at 950 °C decomposed the dolomite completely. Ammonium removal was 32 % for dolomite 750 °C, 41 % for dolomite 950 °C and 44 % for MgO. CHNS analysis indicated that around one m% of nitrogen was present in the MgO precipitate, therefore some struvite was formed. A small amount of struvite-like magnesium ammonium phosphate compound was found from the dolomite 750 °C precipitate. Only hydroxylapatite ($Ca_5(PO_4)_3(OH)$) was found from the dolomite 950 °C precipitate, indicating that CaO precipitates the phosphate as hydroxylapatite before struvite begins to form. Therefore, the calcination should be performed in such a low temperature that a minimum amount of $CaCO_3$ and a maximum amount of MgO would be decomposed.

Results indicate that calcined dolomite have some potential in the nitrogen and phosphorus precipitation from synthetic samples and precipitate could be used as a recycled fertilizer. However, more tests with a lower calcination temperature, longer contact and sedimentation times should be conducted. Also, tests with real agricultural sludges should be performed.

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