



# Article Phosphorus Recovery from Municipal Wastewater: Brucite from MgO Hydrothermal Treatment as Magnesium Source

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**Abstract:** Crystallization of struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O, MAPH) for both N and P recovery from municipal wastewater is an attractive alternative. The low magnesium concentration in municipal wastewater calls for low-cost magnesium sources. In the present work, the precipitation of struvite from supersaturated solutions was investigated. The supersaturated solutions were prepared by the addition of either slurry of Mg(OH)<sub>2</sub> (brucite) obtained from the hydrothermal treatment of magnesium oxide (MgO) or using the aqueous solution equilibrated with brucite after separation from the solid. In both cases, in the supersaturated solutions prepared by the addition of ammonium dihydrogen phosphate, the Mg:NH<sub>4</sub>:P ratio was 1:1:1, pH 7.0–11.0. The apparent order for the precipitation suggested that the dominant mechanism was surface diffusion according to the polynuclear model. The apparent rate constant for struvite precipitation was two orders of magnitude smaller for the slurry prepared supersaturated solution in comparison with the respective prepared from the brucite-equilibrated solution. Simulated wastewater (SWW), was supersaturated with respect to struvite, by inoculation with brucite. The apparent rate constant was two orders of magnitude higher than that corresponding to the supersaturated solutions prepared by the addition of solution equilibrated with brucite. The P recovery from SWW reached 70%.

Keywords: municipal wastewater; phosphorus recovery; magnesium oxide; struvite

## 1. Introduction

Phosphorus (P) is a vital, unique element for all living organisms [1]. Most of the phosphorus required to cover industrial and domestic needs comes from the mining of phosphate rock, a limited mineral resource. It is estimated that almost 7000 million tons of phosphate rock exists as  $P_2O_5$  in reserves that could be mined, and about 80% of phosphate produced at present is used for fertilizers [2]. Global awareness of the need to save raw materials is increasing [3]. The development of sustainable methods to recycle and conserve P from P-rich residues is, therefore, of paramount importance [4].

Municipal, agricultural, and industrial wastewaters contain elevated concentrations of phosphorus and ammonia. These nutrients are responsible for water pollution and eutrophication. It is estimated that 20% of the raw phosphate ores used for P production could be saved from the respective P quantities recovered from municipal and/or agricultural wastewater [5]. Effective recovery of P and N from wastewater is very important for the circular economy. Nitrogen and phosphorus nutrient recovery processes can be classified into chemical, physical and biological [6–8]. Classical chemical methods include the precipitation of phosphate salts, including  $Ca_3(PO_4)_2$  and  $MgNH_4PO_4$ , by the addition of chemicals, which are often either expensive or not environmentally friendly. Physical methods based mainly on separation technologies using membranes (ion exchange, reverse osmosis) are gaining interest. The recovery of phosphorus and nitrogen in the form of



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). crystalline struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O, MAPH), which may be used as fertilizer, is very attractive and considerable research efforts are ongoing [9,10]. Struvite contains the necessary nutrients for plant growth, while it can be applied directly to soil. Compared to traditional fertilizers, the slow-release rate of struvite components and its low solubility make it an effective fertilizer that does not "burn" plant roots [2,11,12]. Struvite recovery from wastewater has been proven technically feasible and economically profitable [2]. P recovery as struvite has been applied in urine [13], wastewater [14] and anaerobic supernatant solutions [15]. Struvite may be directly precipitated out of wastewater, when ammonium, phosphate and magnesium ions exceed the struvite solubility limit. The precipitation of struvite is described by chemical Equation (1):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + H^+$$
 (1)

The low concentration of magnesium in wastewater calls for the addition of solutions to enrich the wastewater with the respective ions. For this purpose, magnesium salts are used often, e.g.,  $MgCl_2$ ,  $Mg(NO_3)_2$  or  $MgSO_4$ . The advantage of using readily soluble magnesium salts is that they dissolve in water rapidly, resulting in shorter reaction times. The slightly acidic pH of the magnesium soluble salts solutions and their relatively high costs are disadvantages, considering that struvite precipitation efficiency demands operational pH values during precipitation exceeding 8.50 [16]. Low-cost sources for magnesium for phosphorus recovery as MAPH include magnesia and seawater [17], which are both abundant in some countries (e.g., Greece) [18]. In Greece, GRECIAN MAGNESITE SA and TERNA MAG are producers of caustic calcined magnesia, deadburned (sintered) magnesia, magnesium carbonate (raw magnesite) and basic monolithic refractories, exporting their products all over the world. Calcined magnesia (MgO) obtained from the calcination of the raw magnesite can be converted into brucite  $(Mg(OH)_2)$ , which, besides serving as source for the supply of  $Mg^{2+}$  ions, raises the solution pH, increasing the supersaturation of solutions containing ammonia nitrogen and orthophosphate with respect to MAPH. It should be noted that the conversion of MgO to crystalline, multilayered Mg(OH)<sub>2</sub> (brucite) takes place by stepwise hydrolysis upon dispersion in water [19]. The conversion in this case, however, is not complete and the resulting solid is a mixed MgO and brucite solid. Complete conversion of magnesia to brucite is used for the production of environmentally friendly fire retardants. Brucite is poorly soluble in water, limiting the released magnesium in the respective solutions [20]. About 85% of magnesium oxide produced worldwide is of low reactivity, "deadburned" or fused, and only 15% is calcined [21,22].

In the present work, magnesium oxide was used as a source of magnesium ions for the precipitation of MAPH from supersaturated solutions. Magnesite ( $MgCO_3$ ) ores are abundant in Northern and Central Greece, and upon calcination, they are converted to MgO. The exploitation of use of MgO in wastewater treatment is an attractive option. Magnesiumcontaining minerals suspended in water partially undergo hydration, forming MgO, and  $Mg(OH)_2$ , among others, and have been successfully used for the removal of heavy metals in the form of the respective sparingly soluble metal hydroxides, or by adsorption, coprecipitation and co-crystallization products of hydration [23]. It is known that periclase (MgO), the main mineral component obtained from the calcination natural magnesite, hydrates rapidly to brucite, the most stable hydration phase. Besides its industrial use as refractory insulator, brucite has been reported to have antibacterial action as well [24]. In the present work, pure MgO was used, hydrothermally treated with acetic acid. The product of the treatment was used either as suspension of brucite or as the solution at equilibrium with the solid phase (brucite). The suspension of brucite obtained from the hydrothermal treatment or the solution obtained following the separation of this solid from the liquid phase were added in solutions containing ammonia and phosphorus, simulating N and P containing wastewater. The hydrothermal treatment was used to maximize conversion of MgO to brucite in aqueous suspensions as a model system. The method developed for phosphorus recovery was validated in simulated municipal wastewater containing organic and inorganic components.

## 2. Materials and Methods

The experimental procedure included two stages (Figure 1). In the first stage, crystalline magnesium oxide was converted hydrothermally into brucite. A suspension of 1 g of solid MgO (Merck Puriss.) in 200 mL of triply distilled water was introduced in a stirred reactor (PARR 4843 Parr Instruments Co., Moline, IL, USA, 450 mL). Upon dispersion of the MgO powder in 200 mL of water, the suspension pH reached very high values (13–14) within one hour of suspension under agitation to ensure homogenization. The pH of the suspension was adjusted to 9.0–11.5 with concentrated acetic acid (Merck Puriss). The temperature in the reactor was raised up to 190 °C over a period of 40 min., The suspension was kept at this temperature and pressure (13 bar) for one hour under stirring. Next, the reactor was cooled to room temperature and the suspension was collected. In the next stage, the suspension was either used as received (Method A) or the solid was separated from the liquid by filtration through membrane filters (0.2 µm, cellulose nitrate filters, Sartorius), the filtrate was saved and the concentration of magnesium was measured (Method B). Both the suspension of brucite and the filtrate were used for the preparation of the solutions supersaturated with respect to struvite. The supersaturated solutions, with a volume totaling 200 mL, were prepared by mixing ammonium phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) solutions with the brucite suspension or with the filtrate. The steps involved in the investigation of the precipitation of struvite are shown schematically in Figure 1. In the supersaturated solutions, the Total Mg: Total NH<sub>3</sub>: Total Phosphorus ratio was equal to 1:1:1. The relative struvite supersaturation,  $\sigma_s$ , is defined by Equation (2):





**Figure 1.** Schematic representation of the experimental methodology for the study of struvite precipitation in supersaturated solutions. For magnesium source, either brucite suspensions (obtained from hydrothermal treatment of MgO) or the supernatant of the suspension.

In Equation (2),  $\alpha$  is the activity of the subscripted ions and  $K_s^0$  is the thermodynamic solubility product of struvite. The activities of the free ions were calculated from the total concentrations of the main components of the solutions using PHREEQC<sup>®</sup> equilibrium calculations software, v. 3.3.12.12704 [25]. The relative supersaturation of the solutions in this work was in the range 0.30 to 36.60. The precipitation of struvite was done at constant temperature 25.0  $\pm$  0.5 °C in batch, magnetically stirred reactors.

During the precipitation of struvite, samples were withdrawn from the reactor and filtered through membrane filters (0.22  $\mu$ m), and the magnesium concentration in the

filtrates was measured by complexometric titrations with standard EDTA solution using a calmagite indicator.

The precipitation of struvite was also investigated from simulated domestic wastewater ter supersaturated with respect to struvite. The composition of the simulated wastewater is shown in Table 1. Glucose was added to make up COD to 100 ppm. For the struvite precipitation measurements, the artificial wastewater solutions were transferred in the reactor. Accurately weighted Mg(OH)<sub>2</sub> was obtained from the hydrothermal treatment of magnesium oxide with acetic acid, as already described. The Mg(OH)<sub>2</sub> was suspended in the reactor and was allowed to equilibrate with the solution under stirring for about an hour. Next, the pH of the suspension and of the ammonium phosphate solution to be added to make up for the artificial wastewater composition were both adjusted to the desired pH value. The ammonium phosphate solution was then added in the reactor and the final stoichiometry of (total) magnesium to total ammonia to total orthophosphate was the corresponding to MAPH solid, i.e., 1:1:1. During the course of precipitation, samples were withdrawn from the reactor and filtered through membrane filters, and the total magnesium and or phosphate were analysed in the filters by spectrophotometric methods.

Table 1. Composition of simulated aqueous wastewater (SWW).

Component	Concentration (/×10 <sup>-4</sup> mol·L <sup>-1</sup> )	
Glucose	5.17	
NaHCO <sub>3</sub>	176.8	
NaCl	100	
NaNO <sub>3</sub>	5.88	
Na <sub>2</sub> SO <sub>4</sub>	120	

When precipitation stopped, indicated from the macroscopically in variable solution composition, the solid precipitate was separated from the liquid by filtration. The solid on the filters was characterized by powder x-ray diffraction (XRD) (Siemens D-500, Siemens AG, Karlruhe, Germany, Cu K $\alpha$  radiation). The morphology of the precipitated solid was examined using scanning electron microscopy (SEM).

#### 3. Results

## 3.1. Stuvite Precipitation

Past the hydrothermal treatment of magnesium oxide solid, the XRD profile (Figure 2) showed extensive conversion of MgO to Mg(OH)<sub>2</sub> (brucite). The extent of conversion of MgO to brucite was calculated from the thermogravimetric analysis (TGA) of the solid. For the complete conversion of magnesium hydroxide to magnesium oxide, the mass loss due to water loss at the temperature interval between 350–400 °C is 31%, according to Equation (3):

$$Mg(OH)_2 \rightarrow MgO + H_2$$
 (3)

The mass loss measured from the controlled heating of the solid obtained from the hydrothermal treatment of MgO was 26.5%, as shown in Figure 2b, suggesting that the conversion of MgO to Mg(OH)<sub>2</sub> was ca.85%.

As shown in Figure 2a, all test samples of MgO (S1, S2 and S3) following hydrothermal treatment were converted into brucite, the characteristic reflections of which are exhibited in the powder XRD. The composition of the solid was confirmed by the thermographic analysis. TGA analysis for all three samples was identical and is shown in Figure 2b.

The first series of measurements of the kinetics of struvite precipitation, refer to the precipitation of struvite from supersaturated solutions, in which magnesium was supplied by the addition of the residual suspension of the hydrothermal treatment of MgO, to the solution of  $NH_4H_2PO_4$  (Method A). Both magnesium and solution pH decreased immediately as a function of time, reaching the plateau values shown in Figure 3.



**Figure 2.** (a) X-ray diffraction pattern and (b) Thermogravimetric analysis (TGA) of the solid obtained from the hydrothermal treatment of three magnesium oxide (MgO) samples S1, S2 and S3; B: Brucite; hydrothermal treatment conditions 190  $^{\circ}$ C, 13 bar, 1 h.



**Figure 3.** (a) Magnesium concentration as a function of time during the precipitation of struvite and (b) change in pH for struvite precipitation; the magnesium source was the suspension obtained for the hydrothermal treatment of MgO (Method A);  $25 \,^{\circ}$ C.

The initial rates of struvite precipitation were calculated from the magnesium concentration–time profiles. The experimental conditions and the results obtained are summarized in Table 2. It should be noted that the errors involved in pH measurements were  $\pm 0.005$  pH units, the errors in the analyses of magnesium and phosphorus were better than 1% (0.2–0.9%), and for the rates of precipitation, they were between 5–10%.

**Table 2.** Precipitation of struvite in its supersaturated solutions (Method A). Initial pH, magnesium concentration,  $C_{Mg}$ , relative supersaturation,  $\sigma_{struvite}$ , and initial precipitation rate, R<sub>s</sub>. 25 °C.

Exp.	pH <sub>initial</sub>	$[Mg]_{tot} = [N-NH_3]_{tot} = [P]_{tot}$ /×10 <sup>-2</sup> mol·L <sup>-1</sup>	σ <sub>struvite</sub>	Rate, $R_s$ /×10 <sup>-4</sup> mol·min <sup>-1</sup>
A18	10.25	7.39	34.61	9.74
A9	9.50	6.99	31.77	7.60
A14	10.50	5.77	27.37	5.38
A6	9.40	4.82	23.64	1.38
A7	10.8	3.95	18.68	0.66
A5	10.2	2.20	14.63	0.07

The dependence of the initial rates of struvite precipitation as a function of the relative supersaturation,  $\sigma_{\text{struvite}}$ , is shown in the plot shown in Figure 4. The parabolic dependence of the rate on the relative supersaturation suggested that the rate-determining step is surface diffusion of the growth units on the crystallites formed following a rapid nucleation first step.



**Figure 4.** Dependence of the rate of spontaneous precipitation of struvite from supersaturated solutions on the relative supersaturation with respect to struvite. Method A: Brucite suspension magnesium source; 25 °C.

The rate of struvite precipitation from supersaturated solutions, is a function of the solution supersaturation with respect to struvite and the relationship is described by the semiempirical law:

$$R_{s} = k_{s}\sigma_{struvite}^{n} \tag{4}$$

In Equation (4),  $k_s$  is the apparent rate constant and the exponent n, often referred as the apparent order of the precipitation process, has no fundamental meaning is indicative of the dominant mechanism [26]. Linear fitting of  $lnR_s$  as a function of  $ln\sigma_{struvite}$  yielded a value of  $n = 5.6 \pm 0.5$  for the apparent order, suggesting that the predominant mechanism is the birth and spread (polynuclear) model [27].

According to the second series of measurements of the kinetics of struvite precipitation, the process was done in supersaturated solutions prepared by the addition of the filtrate, separated from the brucite suspension. Immediately following the preparation of the supersaturated solutions, the magnesium concentration was measured in the aqueous phase. The solution pH was monitored until the end of precipitation, which was indicated by the constant magnesium concentration and pH values. The evolution of magnesium concentration and pH in the supersaturated solutions during the course of precipitation of struvite is shown in Figure 5.



**Figure 5.** Precipitation of struvite from supersaturated solutions prepared according to method B (filtrate of brucite suspension); (a) Magnesium concentration,  $C_{Mg}$  and (b) pH as a function of time; 25 °C. Error bars are included but they are too small to show off.

Magnesium concentration and pH values reached plateau values rather fast (within ca. 10 min), showing rapid precipitation of struvite at the selected supersaturation. The dependence of the rate of struvite precipitation on the initial relative supersaturation with respect to struvite is shown in the plot of Figure 6. Least squares polynomial fitting was applied to the data. The experimental conditions and the results obtained from the measurements during the precipitation of struvite from supersaturated solutions prepared according to method B are summarized in Table 3. The relative errors in the measurements are the same as those for Table 2.



**Figure 6.** Spontaneous precipitation of struvite from aqueous supersaturated solutions prepared according to method B. Dependence of the rate of precipitation on the relative supersaturation with respect to struvite.  $25 \,^{\circ}$ C.

**Table 3.** Precipitation of struvite in its supersaturated solutions prepared according to method B. Initial pH value, magnesium concentration, Mg, relative supersaturation,  $\sigma$  and the corresponding rates measured for the experiments of Method B. 25 °C.

Exp.	pH <sub>initial</sub>	$[Mg]_{tot} = [N-NH_3]_{tot} = [P]_{tot}$ /×10 <sup>-2</sup> mol·L <sup>-1</sup>	σ <sub>struvite</sub>	Rate, $R_s$ /×10 <sup>-6</sup> mol·min <sup>-1</sup>
B20	9.90	7.75	36.60	1030.0
B15	9.70	6.03	30.26	762.0
B16	9.45	5.48	26.54	790.0
B17	10.30	4.65	24.67	590.0
B26	9.10	0.40	18.25	53.0
B23	11.60	0.16	0.30	2.3

The apparent order calculated from the logRs-log $\sigma_{struvite}$  plots was 4.2 ± 1.2, suggesting that the predominant mechanism is again polynuclear, surface-diffusion controlled. The change in methodology of preparation of the supersaturated solutions did not change the mechanism of struvite precipitation. The apparent rate constant obtained was significantly higher in this case (5 × 10<sup>-10</sup>) in comparison with the preparation of the supersaturated solutions with method A (2.5 × 10<sup>-12</sup>). The precipitation of struvite in the supersaturated solutions prepared by both methods involves heterogeneous nucleation and crystal growth of struvite. In method A, the suspended brucite particles apparently retard struvite precipitation possibly because there is no crystallographic compatibility between brucite (trigonal with unit cell lattice parameters a = 3.142 Å, c = 4.766 Å) and struvite (orthorhombic a = 6.942Å, b = 6.317 Å, c = 11.199 Å). The suspended brucite particles apparently block the active sites on the supercritical nuclei, which grow further as macroscopic crystals. The rates of struvite precipitation in the present work were significantly higher in comparison with the rates of struvite precipitation in which the source of magnesium in the supersaturated solutions were either MgCl<sub>2</sub>·6H<sub>2</sub>O or MgSO<sub>4</sub>·7H<sub>2</sub>O [23,24]. Comparison of the recovery rate of phosphorus from supersaturated solutions with respect to struvite (Figure 7), using brucite (from hydrothermal treatment of MgO), magnesium chloride [28] and magnesium sulfate [29] as a magnesium source, showing that in the first case, the rates were quite higher for higher values of relative supersaturation, which could also lead to more efficient phosphorus recovery.



**Figure 7.** Comparison of precipitation rate of spontaneous struvite precipitation rates in its supersaturated solutions using as magnesium source: Mg(OH)<sub>2</sub> suspensions (•); MgCl<sub>2</sub> [23] ( $\blacktriangle$ );MgSO<sub>4</sub> [29] ( $\nu$ ); 25 °C.

The solid precipitated from the supersaturated solutions by both methods was struvite exclusively, as shown in the XRD diagrams shown in Figure 8.



**Figure 8.** XRD patterns for the solid obtained by precipitation of struvite from supersaturated solutions prepared according to methods A and B. S: Struvite.

The morphology of the precipitated struvite is shown in the SEM pictures presented in Figure 9.



**Figure 9.** Scanning electron microscopy (SEM) photographs of struvite spontaneously precipitated by Method A (**i–iii**) and Method B (**iv–vi**).

#### 3.2. Stuvite Precipitation in Simulated Wastewater

The precipitation of struvite was also investigated in solutions simulating wastewater (SWW), supersaturated with respect to struvite. The SWW was supersaturated by the addition of ammonium phosphate solution, followed by inoculation with 50 mg (0.05 g brucite/L) of brucite, prepared by hydrothermal treatment of MgO, as already described. The dissolution of brucite crystals supplied the necessary magnesium ions to achieve supersaturation of SWW with respect to struvite. Removal of magnesium during the precipitation of struvite, which followed attainment of a supersaturation threshold, was sustained by the concomitant dissolution of the brucite solid, which was in excess considering its respective solubility.

The progress of struvite precipitation was monitored by sampling and analysis of the fluid phase for inorganic orthophosphate and magnesium provided that the stoichiometry of the solid forming was  $Mg:NH_3:P = 1:1:1$ . The solution pH was also monitored. The magnesium concentration- time profile, from which the rates of precipitation were calculated, is shown in Figure 10. As may be seen, the relative supersaturation with respect to struvite were significantly low because of the presence of the rest of the ions of the SWW which form a number of complexes, which are taken into consideration all possible equilibria in the calculation of the supersaturation.

**Table 4.** Precipitation of struvite from synthetic wastewater supersaturated solutions. Initial pH value, magnesium concentration, Mg, relative supersaturation,  $\sigma$  and the corresponding rates measured for the experiments in synthetic wastewater (SWW) at 25 °C.

Exp.	pH <sub>initial</sub>	$[Mg]_{tot} = [N-NH_3]_{tot} = [P]_{tot}$ /×10 <sup>-2</sup> mol·L <sup>-1</sup>	σ <sub>struvite</sub>	Rate, R <sub>s</sub> ∕×10 <sup>-6</sup> mol∙min <sup>-1</sup>
SWW1	9.48	0.12	0.29	0.77
SWW2	9.47	1.07	4.45	2.41
SWW3	9.49	1.93	6.76	3.18
SWW4	9.34	3.26	8.26	3.62
SWW5	9.40	4.05	9.36	6.58



**Figure 10.** Precipitation of struvite from supersaturated synthetic wastewater. Magnesium concentration,  $C_{Mg}$  as a function of time. Initial pH ca. 9.50 (Table 4); 25 °C.

The conditions for the precipitation of struvite from synthetic wastewater (SWW) supersaturated with respect to this solid are summarized in Table 4. The plot of the measured rates of precipitation as a function of the relative supersaturation of SWW with respect to struvite are shown in Figure 11.



**Figure 11.** Rate of struvite precipitation in synthetic wastewater as a function of the relative struvite supersaturation.

From the plot of the rate of precipitation of struvite as a function of the relative supersaturation with respect to struvite, the apparent order, from Equation (4) was calculated equal to  $1.1 \pm 0.4$ , suggesting surface diffusion, a spiral growth mechanism. The apparent rate constant was  $4.0 \times 10^{-7}$ , which is significantly higher in comparison with the respective constants of the model solutions. The comparison of the rates of precipitation of struvite as a function of the relative supersaturation with respect to struvite, for the different cases studied in this work, is shown in the diagram of Figure 12. 1.2x10<sup>-3</sup>





Method A

**Figure 12.** Precipitation of struvite from supersaturated solutions: (■) Method A; (■) Method B; (■) synthetic wastewater; 25 °C.

The precipitate in SWW supersaturated with respect to struvite was identified as struvite (Figure 13). Brucite was also detected in the supersaturated SWW with relative supersaturations in the range between,  $\sigma_{\text{struvite}} = 0.29-9.36$ , however, the reflections are weak.



**Figure 13.** XRD patterns of the precipitate formed from SWW supersaturated with respect to struvite seeded with brucite; 25 °C. B: Brucite, S: Struvite.

The morphology of the precipitated solid (Figure 14) was characteristic of struvite, however, they were not well formed enough for an experiment in the absence of SWW.



**Figure 14.** Scanning electron microscopy (SEM) photographs of struvite spontaneously precipitated in presence of SWW. (**i**–**iii**)  $\sigma_{\text{struvite}} = 0.29$  (**iv–vi**)  $\sigma_{\text{struvite}} = 4.45$  and (**vii–ix**)  $\sigma_{\text{struvite}} = 6.76$ .

The fact that struvite crystals did not seem to be associated with brucite particles suggested that, besides acting as a source of magnesium, brucite also acted as a catalyst for heterogeneous secondary nucleation of struvite.

Phosphorus removal from supersaturated SWW inoculated with brucite crystals obtained from the hydrothermal treatment of MgO was calculated from the reduction of the phosphate concentration in the solution (Equation (5)) following the termination of the precipitation process.

Phosphorus removal (%) = 
$$\left| \frac{P_{\text{initial}} - P_{\text{final}}}{P_{\text{initial}}} \right| \times 100$$
 (5)

where P<sub>initial</sub> and P<sub>final</sub> are the initial and final phosphorus concentrations in the supersaturated solutions, respectively.

In Figure 15, phosphorus removal from the supersaturated SWW is presented. It is shown that the removal of phosphorus reached 70% corresponding to the SWW with the highest relative supersaturation with respect to struvite ( $\sigma_{struvite} = 9.36$ ).

Increasing supersaturation in SWW with respect to struvite resulted in higher P removal from the aqueous phase, and the recovery in the form of struvite was proportionally higher. Earlier reports of P removal in the form of struvite from model supersaturated solutions with respect to struvite in which MgSO<sub>4</sub> was the source of magnesium in the solutions yielded twice as high removal, as can be seen in Figure 16. The lower removal in SWW is probably due to the components of the solution which may have an inhibitory effect [24]. The significantly higher rate constant however of struvite precipitation in SWW shows that there is a relati





ve advantage, especially in case a continuous recovery process (e.g., fluidized bed) is used.



**Figure 16.** Phosphorus removal (%) from SWW supersaturated with respect to struvite; (■) inoculated with brucite obtained from hydrothermal treatment of MgO, (■) MgSO<sub>4</sub> as magnesium source [30].

#### 4. Conclusions

In the present work, the use of MgO, the main mineral obtained from the naturally abundant in Greece magnesite ores, was investigated as an alternative source of magnesium for the recovery of phosphorus from municipal wastewater. MgO, which, upon hydration, converts partially to brucite, was converted into brucite almost quantitatively by hydrothermal treatment. The solid obtained was stable and was used as a magnesium source to supersaturate aqueous media containing ammonia and phosphorus with respect to struvite. Brucite was used either in the form of suspension, obtained from the hydrothermal treatment of MgO, or in the form of the supernatant solution only, in equilibrium with the solid. In both cases, crystalline struvite was formed by a surface diffusion-controlled mechanism. Simulated wastewater with composition encountered in municipal wastewater (SWW) was inoculated either with the brucite suspension or with the saturated solution that resulted in the formation of crystalline struvite. The analysis of the rates of precipitation showed that the precipitation of struvite took place with the same mechanism, but the apparent rate constant was higher. The presence of brucite particles inhibited the growth of the supercritical nuclei of struvite, possibly through attachment on the supercritical struvite

crystallites, and blocking of the active sites. The rate constant of struvite precipitation upon inoculating SWW with brucite, which supplied the magnesium needed to make up the supersaturation to initiate spontaneous precipitation, was the highest, showing that brucite prepared by the hydrothermal treatment of MgO is promising as a magnesium source for the recovery of phosphorus from wastewater. Calculation of phosphorus recovery by this method increased with increasing solution supersaturation and reached 70%. The encouraging results obtained suggested that P recovery from municipal wastewater may be achieved using a low cost raw material through the appropriate pre-treatment.

Author Contributions: P.D.N. was involved with the experimental investigation, methodology, data curation and writing-original draft preparation. K.-A.G. undergraduate student was involved with the experimental investigation. P.G.K. was involved in conceptualization, supervision, ensuring resources and writing and editing of the work. All authors have read and agreed to the published version of the manuscript.

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