

# Struvite Crystallization for Anaerobic Digested Supernatants: Influence on the Ammonia Efficiency of the Process Variables and the Chemicals Dosage Modality

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The treatment or recovery of nutrients (N and P) from anaerobically digested supernatants is now a central topic, related both to the zootechnical wastewaters and to the supernatants from the sludge lines of urban wastewater treatment plants (WWTP), applying codigestion of excess sludge and organic fraction of municipal solid waste (OFMSW). In both cases, the crystallization and precipitation of Struvite (Magnesium Ammonium Phosphate) is a hypothetical solution to reduce the high concentrations of ammonia nitrogen and to reuse the final product. This study shows the effects of the main variables of Struvite crystallization (pH, reaction time and dosage modality) applied in bench scale to anaerobic zootechnical and codigested urban supernatants. The matrices with initial concentrations of  $\text{NH}_4\text{-N}$  from 1000 to 2000  $\text{mgL}^{-1}$ , were added to phosphoric acid (source of P) and magnesium oxide (source of Mg), pure and of industrial origin, to achieve the correct molar ratios. Adjustment of the pH at 8.5 was provided through NaOH dosage. The experimental tests, at increasing ratios (Mg:N:P) from 1:1:1 to 2:1:1, have been carried out at reaction times from 0 to 60 minutes and at two distinct dosage modalities. Indeed, the dosing tests were firstly provided by direct addition of the different reagents and next by indirect addition, with the prior dilution of the magnesium source in the phosphoric acid. The results defined as the different sequence of reagents addition modifies the percentage of struvite formation and, consequently, the ammonia decrease. Specifically, compared to the obtained efficiencies range between 50 % and 70 % with direct dosage, the tests with indirect dosage allow the recovery of nitrogen greater than 20 %, at the same molar ratios and reaction times. The time factor does not affect the precipitation more than 10 %, regardless of the dosage carried out. Further, the use of a thermodynamic model allowed to assess and justify the transformation of other ions in solution ( $\text{K}^+$  and  $\text{Ca}^{++}$ ) highlighting the formation of other secondary compounds (k-struvite, hydroxyapatite).

## 1. Introduction

Anaerobic digested sludge represents an important resource in agricultural applications, defining a possible recycle of nutrients by soils assimilation. Indeed, the digestate spreading can enhance the land fertility, improving the contents of organic matter and microelements. Moreover there is increasing concern about the excessive manure spreading, which is related to the nutrients release in waterbodies and the consequent degradation of the water quality. Therefore, both the usage of sustainable and non-invasive agricultural and breeding techniques and the application of effective and feasible farming wastewater treatments are required. Concerning the diffusion of the anaerobic digestion process, codigestion of waste activated sludge and the organic fraction of municipal solid waste (OFMSW) has been widely applied (Bolzonella et al., 2006) as alternative to the disposal and for the production of good quality compost. Onsite treatment could represent a reliable solution to cope with the reduction of the nutrients pollution, as offsite handling is often economically unsustainable (Wang et al., 2005). In this scenario, the application of technologies to favour the energy production from zootechnical wastes and to enhance the fertilizers obtainment from digestate could be valuable for farming producers.

The phosphorous (P) recovery through struvite ( $\text{MgNH}_4\text{PO}_4$ ) precipitation represents, among the different P recovery techniques, a reliable method to supply to the demand of this limited and almost consumed resource (Shu et al., 2006) and to remove both ammonia ( $\text{NH}_4$ ) and phosphate ( $\text{PO}_4$ ) (Zeng et Li, 2006). Struvite precipitates has white orthorhombic crystals, which internal structure is composed by regular tetrahedrons of  $\text{PO}_4^{3-}$ , distorted octahedrons of  $\text{Mg}(\text{H}_2\text{O})_6^{2+}$  and  $\text{NH}_4$  groups, linked together through hydrogen bonds. The phases of nucleation and crystal growth have been deeply studied to determine the optimization of the solution conditions and the relations with the type of crystal formation. According to Battistoni et al. (2005), both the nucleation and growth occur simultaneously when the fines contents are scarce, while with higher particles concentrations the crystal accretion is the dominant phase. The increasing struvite precipitation is related to several factors as the supersaturation of the three ions magnesium, ammonia and phosphate. Also, another important aspect is related to the pH trend: each formation phase corresponds to the decrease of the pH values and to the enhancement of the phosphate solubility, with increment in P removal at greater pH. On the other hand, struvite solubility increases with pH values higher than 9 (Doyle et al., 2002). Another important issue is correlated to the presence of impurities in the reagents, as calcium (Nelson et al., 2003). In this sense, calcium as an impurity could inhibit the struvite formation because the precipitation of calcium-phosphorous compounds can occur (Le Corre et al., 2005)

Struvite formation requires ideal molar ratios between magnesium, ammonia and phosphorous. In most cases, especially when handling zootechnical digested manure, magnesium is present in limiting amount and struvite precipitation is reached by adding magnesium amendments. Among possible Mg correctives (Burns et al., 2001), the most common is magnesium chloride  $\text{MgCl}_2$ , which has been proved its efficiency due to high solubility in water ( $54.3 \text{ g } 100 \text{ mL}^{-1}$ ).  $\text{MgCl}_2$  dissolution in water always determines high residual chloride and an acid hydrolysis, requiring then higher dosage of chemicals to regulate the pH. Further,  $\text{MgCl}_2$  has a greater cost ( $\sim 17 \text{ €kg}^{-1}$ , purity w/w 96 %) if compared to other reagents. To deal with these aspects, the use of other Mg amendment can be considered as an alternative to  $\text{MgCl}_2$ , and magnesium hydroxide  $\text{Mg}(\text{OH})_2$  as well as magnesium oxide  $\text{MgO}$  are reliable options. Although both of them eliminate the risk of residual chloride and lower amounts of pH conditioners is usually required, the  $\text{Mg}(\text{OH})_2$  has an extremely low solubility, equal to  $9 \times 10^{-4} \text{ g } 100 \text{ mL}^{-1}$ , and this fact reduce its applicability. The use of  $\text{MgO}$ , which solubility value is  $0.209 \text{ g } 100 \text{ mL}^{-1}$ , is hence preferred and performances related to its addition are described in this paper. Also, this reagent has a reduced cost compared to the  $\text{MgCl}_2$ , of about  $3 \text{ €kg}^{-1}$ , with purity w/w of 95 %, and  $1 \text{ €kg}^{-1}$ , with purity w/w of 85 % and is easily commercially available.

Another predominant factor is represented by the method of reagents dosage to allow the precipitation. Experiments showed how the different addition of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  sources determined different percentages of struvite formation and hence the ammonia reduction (Harrison et al., 2011).

In this study, batch tests for the struvite precipitation were conducted on two different anaerobic supernatants, from the digestion of zootechnical manure and the codigestion of the OFMSW and urban sludge, by varying the  $\text{MgO}$  and  $\text{H}_3\text{PO}_4$  contents and the Mg:N:P molar ratios, the dosage modality and the reaction time, to evaluate P and N removal. The objective of this paper is to provide an overview on impacts in struvite precipitation and nutrient recovery at different operative conditions, aiming at obtaining products with agronomic properties.

## 2. Materials and Methods

Tests at laboratory scale were performed on two different anaerobic digested supernatants. The substrates derived both from full scale reactors. The first one was collected from the anaerobic digestate flow of an urban wastewater treatment plant, applying codigestion of the excess sludge and the organic fraction of municipal solid waste (A). The second substrate was obtained from an anaerobic digester treating cattle manure and agroindustrial residuals (B).

Batch tests to evaluate the precipitation of struvite were developed using a 1 L reactor, equipped with mixing and thermal conditioning systems. The pH and temperature values were monitored through online probes. All the tests were conducted at  $20 \text{ °C}$  temperature. Samples of 50 mL were collected and analyzed at the beginning and consequently after 2, 5, 15, 30 and 60 min, once filtered at  $20 \text{ }\mu\text{m}$  and  $0.45 \text{ }\mu\text{m}$ . The precipitation conditions were reached through the addition of pure and industrial magnesium oxide  $\text{MgO}$  (purity w/w 85 %), phosphoric acid  $\text{H}_3\text{PO}_4$  (purity w/w 75 %) and sodium hydroxide  $\text{NaOH}$  (solution 30 %w/w) to maintain the pH at 8.5. Further, the tests were conducted by varying the molar ratios of magnesium, nitrogen and phosphorous Mg:N:P at 1:1:1, 1.5:1:1 and 2:1:1. To determine the effect of different dosage modality of the reagents, direct and indirect addition of  $\text{MgO}$  and  $\text{H}_3\text{PO}_4$  was provided. In the first case (direct dosage),  $\text{MgO}$  was firstly dosed and next the  $\text{H}_3\text{PO}_4$  was separately added. The

reagents addition through indirect modality was afforded by mixing magnesium oxide in the phosphoric acid before the dosage, to reach a previous separate dissolution.

All the testing conditions and parameters, for both the supernatants, are summarized in Table 1.

Table 1: Testing conditions for the struvite precipitation

MgO-H <sub>3</sub> PO <sub>4</sub> Dosage	Supernatants	Molar ratios	MgO <sub>pure</sub>	MgO <sub>industrial</sub>	H <sub>3</sub> PO <sub>4</sub>	NaOH
		Mg:N:P	g	g	mL	mL
Direct	A	1:1:1	0.303	0.357	0.659	1.70
		1.5:1:1	0.463	0.545	0.659	1.70
		2:1:1	0.623	0.733	0.659	1.60
	B	1:1:1	0.498	1.200	1.014	1.75
		1.5:1:1	0.749	1.810	1.014	1.50
		2:1:1	2.000	2.400	2.040	3.50
Indirect	A	1:1:1	0.303	0.357	0.659	1.75
		1.5:1:1	0.463	0.659	0.659	1.40
		2:1:1	0.623	0.733	0.659	1.30
	B	1:1:1	1.140	0.578	2.330	5.00
		1.5:1:1	1.710	0.879	2.330	3.00
		2:1:1	2.000	1.177	2.340	2.05

The characterization of the influent matrices and the samples, collected at different reaction times, was carried out according to Standard Methods (APHA, 2005). Through the use of the thermodynamic model Visual Minteq ver. 3.0, the estimation of struvite precipitation and other compounds formation was assessed. The code was originally realized on MINTEQA<sub>2</sub> software by US EPA. Through an extensive database of the thermodynamic and chemical equilibrium equations, Visual Minteq allows the calculation of speciation, equilibrium of solid and dissolved phases and solubility of minerals in an aqueous solution (Gustafsson, 2005).

### 3. Results and Discussion

#### 3.1 Characterisation of the anaerobic supernatants

Through the characterisation of the two liquid fractions from the digestate dewatering, an estimation of the main parameters for the reagent dosage was conducted (Table 2). The first matrix A, from the codigestion of the excess sludge of an urban WWTP and the OFMSW, had average values of pH and alkalinity equal to 8.01 and 5811 mgL<sup>-1</sup>. The supernatants B, from the digestion of cattle manure and agroindustrial residuals, was characterized by higher values of pH and alkalinity, equal to 8.57 and 8929 mgL<sup>-1</sup> respectively. The main parameter for the evaluation of struvite precipitation is the ammonia nitrogen NH<sub>4</sub>-N, which amounts were of 1119 mgL<sup>-1</sup> (A) and 1797 mgL<sup>-1</sup> (B), while the concentration of Mg resulted higher in A (99 mgL<sup>-1</sup>) rather than in B (mgL<sup>-1</sup>). The PO<sub>4</sub>-P amount was almost absent for the first supernatants, with an average concentration of 8.6 mgL<sup>-1</sup>, while in B it assessed at a value of 61 mgL<sup>-1</sup>. Considering the sodium and calcium concentrations, the values were almost comparable for both the supernatants, equal to 684 mgL<sup>-1</sup> (A) and 867 mgL<sup>-1</sup> (B) for Na<sup>+</sup> and to 215 mgL<sup>-1</sup> (A) and 220 mgL<sup>-1</sup> (B) for Ca<sup>++</sup>, while a net difference was appreciable for the potassium. Indeed, the K<sup>+</sup> amount in A was equal to 457 mgL<sup>-1</sup> while in B the average values was of 1757 mgK<sup>+</sup>L<sup>-1</sup>.

Table 2: Supernatants characterization - excess sludge and OFMSW (A) and cattle manure (B)

Supernatants	pH	Alk	COD	NH <sub>4</sub> -N	P-PO <sub>4</sub>	Na	K	Mg	Ca
		mgL <sup>-1</sup>	mgL <sup>-1</sup>	mgL <sup>-1</sup>	mgL <sup>-1</sup>	mgL <sup>-1</sup>	mgL <sup>-1</sup>	mgL <sup>-1</sup>	mgL <sup>-1</sup>
A	8.08	5811	12653	1119	8.57	684	457	99	215
B	8.57	8929	8907	1797	61	867	1757	19	220

#### 3.2 Effects of increasing molar ratios and reagents dosage on removal performances

In this section, an evaluation of the dosage modality of H<sub>3</sub>PO<sub>4</sub> and MgO, both pure and of industrial origin, on the two different kind of supernatants is given. Further, this effect is linked with the performances due to

the molar ratio Mg:N:P increase, from minimum values of 1:1:1 to the maximum of 2:1:1. In particular, Figure 1 shows the NH<sub>4</sub>-N removal at the end of the precipitation test, after 1 h, by varying the molar ratios and the dosage of pure MgO. Concerning the sample A, added with MgO and next with H<sub>3</sub>PO<sub>4</sub> (Figure 1.A), a slight increase in NH<sub>4</sub>-N removal from 40 to 49 % corresponded to an excess condition of Mg source dosage, from 1:1:1 to 2:1:1. Indeed, when the molar ratio is 1.5:1:1, the increment in NH<sub>4</sub>-N reduction ( $\Delta=5\%$ ) has almost reached a constant value, determining a partial increment when increasing the MgO dosage until 2:1:1 (removal difference of 4 %). The same trend is appreciable when testing B (Figure 1.A), which increment in NH<sub>4</sub>-N removal from the first and second molar ratios conditions (from 1:1:1 to 1.5:1:1) is equal to 9 %, while a further MgO addition reveals only in 3 % of increment in NH<sub>4</sub>-N reduction (total removal of 12 %). This suggests that the reagent dosage is effective at initial condition (1:1:1), without increasing the molar ratios, and the further reagents addition is not sustainable if compared to the removal increase. On the other hand, when adding MgO and H<sub>3</sub>PO<sub>4</sub> mixed together (Figure 1.B), the increase in molar ratio determined a greater increment in NH<sub>4</sub>-N removal in B, with an average reduction of 20 % at maximum molar ratio of 2:1:1, compared to the 10 % decrease obtained at intermediate dosage of Mg:N:P equal to 1.5:1:1. Concerning the precipitation test carried out on the sample A, as previously evaluated, an increase in Mg source dosage corresponded to a modest NH<sub>4</sub>-N reduction percentage, varying from 57 % to 69 % as removal efficiencies (Figure 1.B). This aspect could be partially correlated to the presence of competitive salts, as calcium and potassium, dissolved in the matrix (Table 2).

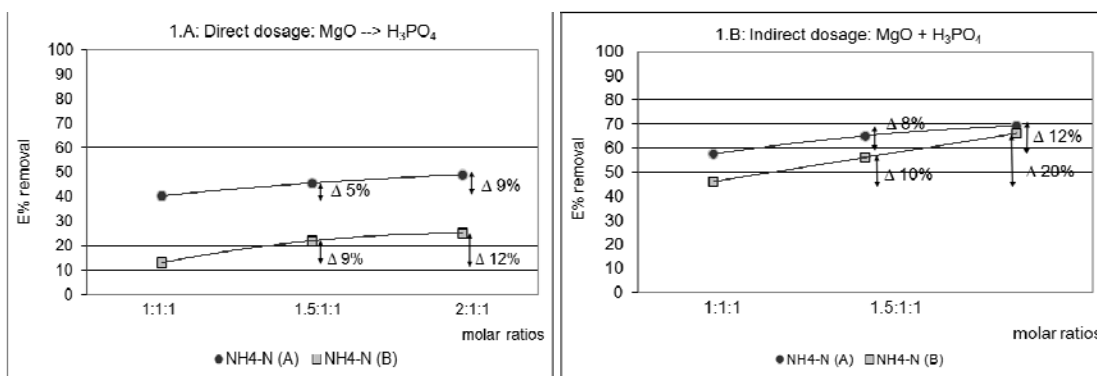


Figure 1: NH<sub>4</sub>-N removal with pure MgO – direct and indirect dosage

Precipitation test conducted by using the industrial magnesium oxide, which removal performances after 1 h are shown in Figure 2, highlighted greater overall NH<sub>4</sub>-N reduction than the ones obtained with pure MgO. Significant increases were detected when testing the supernatants B, at rising molar ratio conditions (Figure 2.A). Indeed, under direct reagents dosage in the matrix B, the removal efficiencies increased from 30 % (1:1:1) to 47 % (2:1:1). Similarly, the indirect dosage determined a variation in reduction percentage equal to 10 % for the sample B (Figure 2.B).

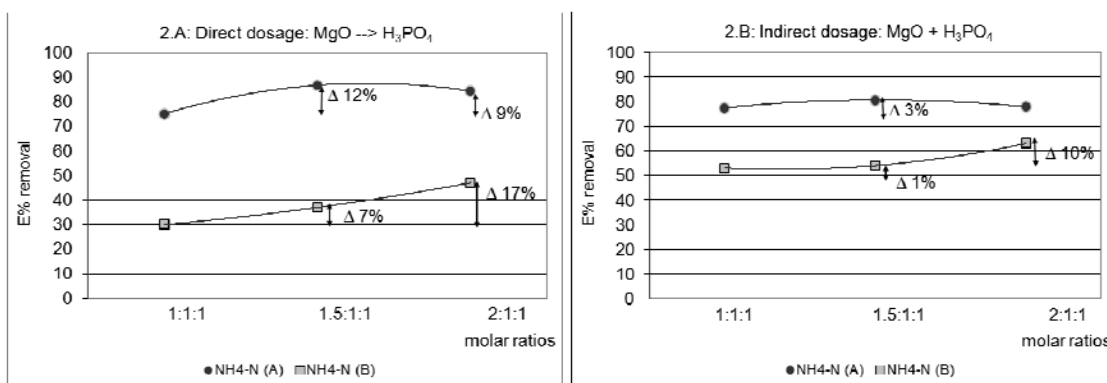


Figure 2: NH<sub>4</sub>-N removal with industrial MgO – direct and indirect dosage

Concerning the sample A, the MgO further addition until reaching the molar condition of 2:1:1, had no effect in NH<sub>4</sub>-N removal. Indeed, the indirect dosage for sample A revealed how the minor molar ratio condition was enough to obtain a NH<sub>4</sub>-N removal of 78 % (Figure 2.B). The best condition was reached with direct reagents dosage, at the intermediate molar ratio of 1.5:1:1, highlighting a general performance of 87 % (Figure 2.A). The use of industrial magnesium oxide permitted to obtain higher removal percentages if compared to the results related to the pure MgO dosage. Also, the effect linked to the indirect dosage was more appreciable in sample B, resulting in higher reduction percentages if compared with the results obtained when directly dosing the reagents (Figures 1 and 2).

### 3.3 Comparison between direct and indirect dosage modality

A direct comparison between the effect of dosages and molar ratios has been summarized below, in order to assess the impact of the MgO and H<sub>3</sub>PO<sub>4</sub> addition, if separately or earlier mixed, on ammonia removal. Further, in the following graphs, the effect of the magnesium oxide nature, if pure or of industrial origin, can be evaluated. Figure 3 shows the results obtained on the matrix A, if treated with pure (Figure 3.A) or industrial (Figure 3.B) magnesium oxide. The industrial magnesium font has a higher impact in ammonia removal, irrespective of the direct or indirect addition (Figure 3.B). The NH<sub>4</sub>-N removal with pure MgO at direct dosage assessed between 40-50 %, while the indirect addition of MgO and H<sub>3</sub>PO<sub>4</sub> determined removal percentages up to 70 % (Figure 3.A). The evaluation between direct and indirect pure MgO addition shows a net and constant improvement of about 20 % in NH<sub>4</sub>-N removal, as reported in Figure 3.A. On the other hand, the use of industrial MgO has an almost constant trend, revealing no differences in dissimilar test conditions in terms of molar ratios increase and direct-indirect dosages (Figure 3.B).

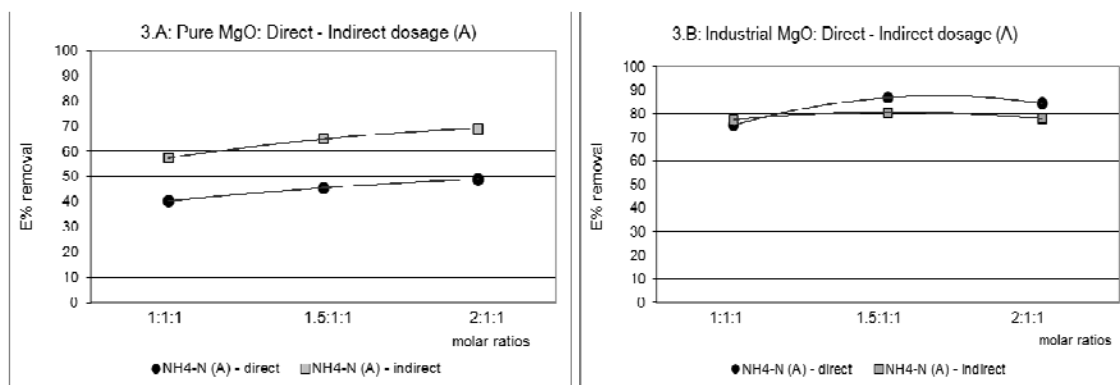


Figure 3: removal efficiencies sample A, comparison between direct and indirect dosage of pure and industrial MgO

As shown in Figure 3.B, the direct and indirect dosages has a similar effect on sample A, in terms of ammonia removal, equal to about 85 %. Hence, the pH was monitored according to the sampling time exposed in Section 2, for the three different molar ratios conditions. The results are shown in Figure 4.

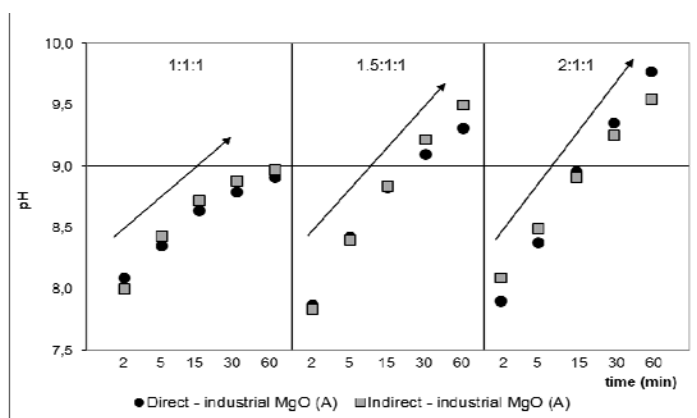


Figure 4: pH trend in sample A – effect of Industrial MgO direct and indirect dosage

The Figure 4 summarizes the pH trend at times of 2, 5, 15, 30 and 60 min, for the investigated molar ratios values of 1:1:1, 1.5:1:1 and 2:1:1, both for the direct and indirect industrial MgO addition. During time, an increase of the pH was detected for all the molar ratios conditions and for both the dosage modality. This, highlighted the similar behaviour of the testing environments and the sharp increment of pH up to values of 9.5 (1.5:1:1) and 9.8 (2:1:1), favouring the ammonia removal and the struvite formation. The pH has similar maximum values after 1 hour, both for the test at 1.5:1:1 and 2:1:1, indeed the removal efficiencies of ammonia for industrial direct and indirect dosage are similar and equal to 80 % and 85 % (Figure 3.B). The same evaluation has been carried out on the samples added with pure MgO and the results are exposed in figure 5. The pH, when directly dosing the MgO, increased from 7.9 reaching a stable value of 8.5, for all the molar ratios conditions. In case of indirect dosage, apart from the unitary molar sets 1:1:1, the pH has an increasing trend, reaching values up to 9 (1.5:1:1) and 9.8 (2:1:1). Concerning the almost constant pH trend for unitary molar ratios in Figure 5, it can be assessed that the improvement of 20 % in ammonia removal at molar condition of 1:1:1 (Figure 3.A) is related to the indirect dosage of the reagents. The increment of the NH<sub>4</sub>-N removal at molar ratios of 1.5:1:1 and 2:1:1 (Figure 3.A) could probably be correlated to the dosage modality but the pH increment showed in Figure 5 has to be considered in the ammonia reduction.

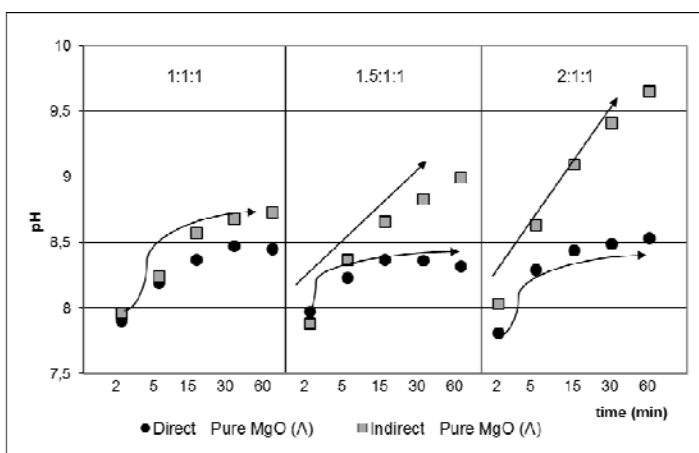


Figure 5: pH trend in sample A – effect of Pure MgO direct and indirect dosage

The same evaluation was conducted for the matrix B, from zootechnical and agroindustrial digestate, at the same conditions exposed above. As shown in Figure 6.A, the higher solubility of the MgO and H<sub>3</sub>PO<sub>4</sub>, previously mixed together and then added in the sludge, led up to higher NH<sub>4</sub>-N removal efficiencies from 46 % to 68 % at increasing molar ratios, in case of pure MgO. The ammonia reduction improvements linked to the indirect dosage were equal to 33 % (molar ratio of 1:1:1), 34 % (molar ratio of 1.5:1:1) and 41 % (molar ratio of 2:1:1).

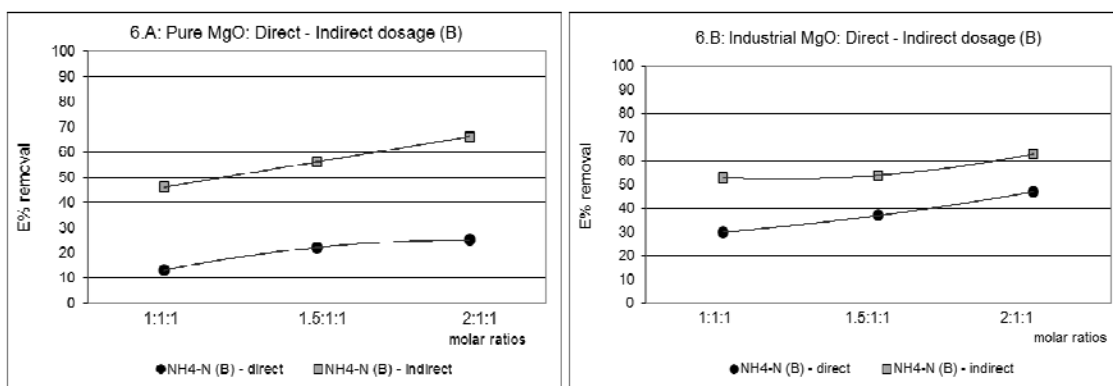


Figure 6: removal efficiencies sample B, comparison between direct and indirect dosage of pure and industrial MgO

Similarly the industrial magnesium font, indirectly dosed, had better performances than the direct addition (Figure 6.B). The percentages increase in ammonia removal with indirect dosage was equal to 23 % (molar ratio of 1:1:1), 17 % (molar ratio of 1.5:1:1) and 16 % (molar ratio of 2:1:1). The direct dosage, in both cases, revealed maximum  $\text{NH}_4\text{-N}$  removals up to 25 % with pure MgO (Figure 6.A) and about 45 % with industrial MgO (Figure 6.B). The low solubility of the reagents and the lower effect can further be correlated to the presence of competitive ions in this complex matrix. For example calcium and especially potassium (equal to  $1757 \text{ mgL}^{-1}$  in the matrix B, Table 2) can affect the struvite formation.

The pH was monitored as previously described and its trend (Figure 7), irrespective of the dosage modality and the molar ratios, maintained almost constant and on the average equal to 8.5, which is the proper value of the matrix. Further, it can be assessed that the stability of the pH results in the buffer capacity of the zootechnical supernatants, which alkalinity is on the average equal to  $9 \text{ gL}^{-1}$ .

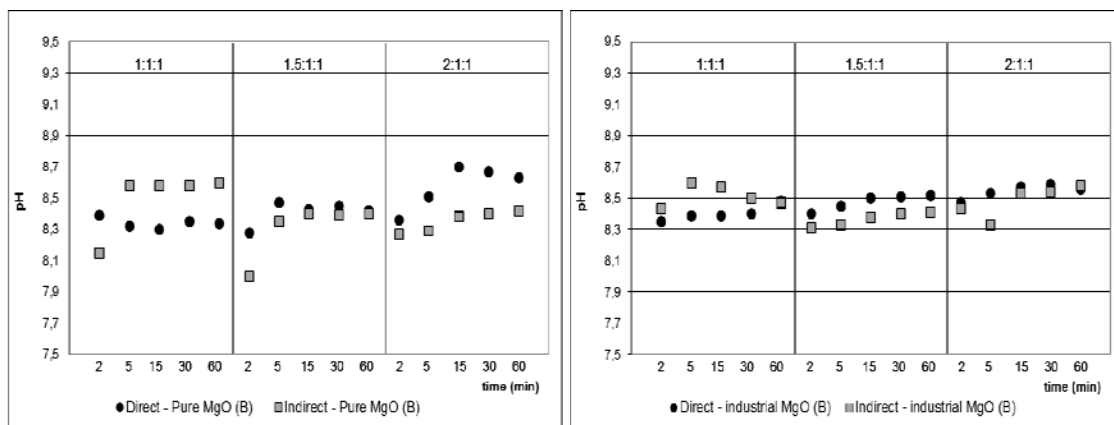


Figure 7: pH trend in sample B – effect of Pure MgO direct and indirect dosage

### 3.4 Ammonia removal at increasing reaction time

Struvite precipitation tests were developed on supernatant A, to evaluate the effect of the reaction time. It should be pointed out that the pH increment (Figures 4 and 5), when occurring, has to be considered as an important factor in the increase of ammonia removal. Tests were carried out using both the pure and industrial magnesium oxide, and the results are shown in Figure 8 and Figure 9 respectively. Samples collected at different intervals highlighted the elevated performances during the first minutes of the investigation, in both the dosage modality.

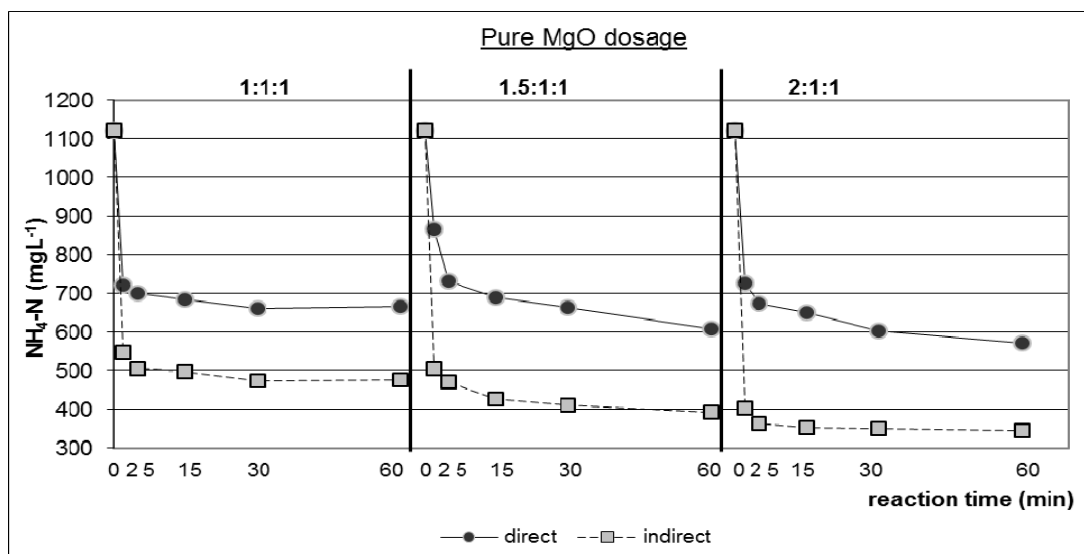


Figure 8:  $\text{NH}_4\text{-N}$  trends over reaction time – direct and indirect dosages using pure MgO

When dosing pure MgO and H<sub>3</sub>PO<sub>4</sub> separately (direct dosage), after 2 minutes the NH<sub>4</sub>-N concentration assessed at values on the average equal to 720 mgL<sup>-1</sup> with a removal of about 35 %. The increase in reaction time determined a further reduction of NH<sub>4</sub>-N only at increasing molar ratios. Indeed, when Mg:N:P was equal to 1:1:1, the reduction percentages reached values equal to 38 % and 39 % after 5 and 15 min, remaining constant and equal to 40 % at the end of the test (1 h). When increasing the MgO addition, the NH<sub>4</sub>-N concentrations decreased of 40 % (1.5:1:1) and 46 % (2:1:1) after 30 min, reaching further small reduction of 45 % (1.5:1:1) and 49 % (2:1:1) after 1 hour (Figure 8). In all these cases, the pH values remained almost constant and equal to 8.5 (Figure 5).

The effect related to short reaction times efficacy was more estimable when indirectly dosing the reagents, even if the pH value remained at 8.5 only in case of molar ratio equal to 1:1:1 (Figure 5). Indeed, after 5 min, the NH<sub>4</sub>-N removal percentages reached values equal to 56 % (1:1:1) and 69 % (2:1:1) and no significant reduction was obtained at the end of the experimental. When the molar ratio was equal to 2:1:1 at indirect dosage, although the pH reached the value of 9.7 at 1 h, the removal of ammonia did not increase after 5 min. At molar ration of 1.5:1:1, the asymptote condition was reached after 15 min, with a percentage of removal of 62 %. In this case, the pH was equal to 8.7 at 15 min and to 9 at the end of the test. The NH<sub>4</sub>-N concentrations after 1 h were equal to 476 mgL<sup>-1</sup> (1:1:1), 392 mgL<sup>-1</sup> (1.5:1:1) and 345 mgL<sup>-1</sup> (2:1:1).

Results on the ammonia removal performances at different reaction times and molar ratios, when directly and indirectly adding MgO of industrial origin are shown in Figure 9. The pH trend (Figure 4) for all the tests reached values greater than 9 after 1 h (molar ratio of 1:1:1), 30 min (molar ratio of 1.5:1:1) and 30 min (molar ratio of 2:1:1), and this influenced the ammonia removal. Concerning the direct reagents addition, the removal percentages of NH<sub>4</sub>-N after 2 min of testing were equal to 67 % (1:1:1), 76 % (1.5:1:1) and 74 % (2:1:1), with corresponding concentrations of 366 mgL<sup>-1</sup>, 269 mgL<sup>-1</sup> and 286 mgL<sup>-1</sup>. A further average reduction of 10 % was overall obtained when monitoring the ammonia amounts at the end of the tests, due to the pH increase. For the unitary molar ratio, the ammonia reduced to 279 mgL<sup>-1</sup> after 1 h, with a removal of 75 %. When increasing the Mg contents, the reduction percentages reached values of 87 % and 84 % at 1.5:1:1 and 2:1:1 after 30 min, with minimum concentration of 150 mgL<sup>-1</sup> and 180 mgL<sup>-1</sup> and no consistent decrease was observed at the end of the tests. At indirect dosage, the variation in removal percentages was on the average equal to 10 %, between 2 and 60 min reaction times, with the main difference that the higher reduction values were reached after few minutes testing. Indeed, the removal after 15 minutes was equal to 75 % (1:1:1), 77 % (1.5:1:1) and 75 % (2:1:1) while at the end of the tests the obtained values were of 77 %, 80 % and 78 % respectively. Hence the effect related to the reaction time increase was, in the last case, negligible, irrespective of the dosage modality.

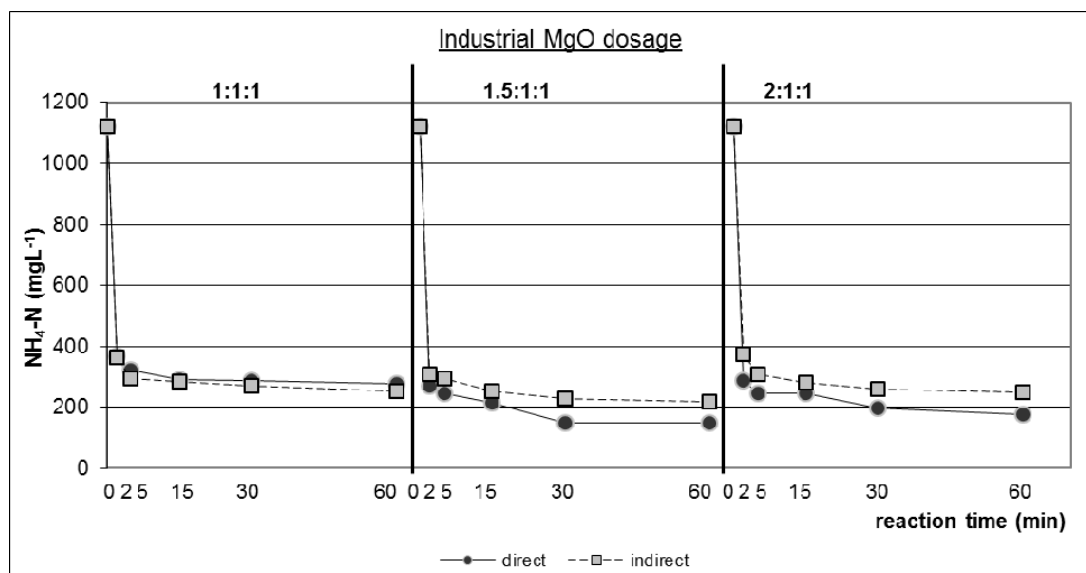


Figure 9: NH<sub>4</sub>-N trends over reaction time – direct and indirect dosages using industrial MgO



### 3.5 Simulation of the struvite, k-struvite and hydroxyapatite formation

An evaluation of the possible precipitation of possible compounds on the supernatants B was carried out at optimal pH value of 9, using the software Visual Minteq. Ions in solution, according to the characterisation reported in table 2, suggested the possibility of other precipitation products over struvite. Indeed, the presence of  $\text{Ca}^{++}$  and  $\text{K}^+$  can determine the formation of hydroxyapatite  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  or HAP (LogK -44.33), dicalcium phosphate  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  (LogK -19.27) or k-struvite  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  (LogK -10.61), besides the struvite (LogK -13.27) formation. The simulations were carried out by varying the Mg content and maintaining the N and P moles equal to 1. The magnesium moles were then defined equal to 0.01, 0.1, 0.2, 0.5, 1, 1.5 and 2. As expected, the k-struvite formation occurred. The HAP precipitation took place, instead of the other possible  $\text{Ca}^{++}$  compounds, due to its greater thermodynamic stability. The percentage of MAP on the total precipitated compounds reached up values of 98 % at molar ratio of 0.2:1:1, while 100 % MAP formation occurred when Mg:N:P was equal to 1:1:1. The higher HAP and k-struvite precipitation was reached at ratios of 0.01:1:1, with percentages of HAP and k-struvite moles on the total moles equal to 76 % and 24 % respectively. The k-struvite presence was null at increasing ratios, while the HAP progressively decreased.

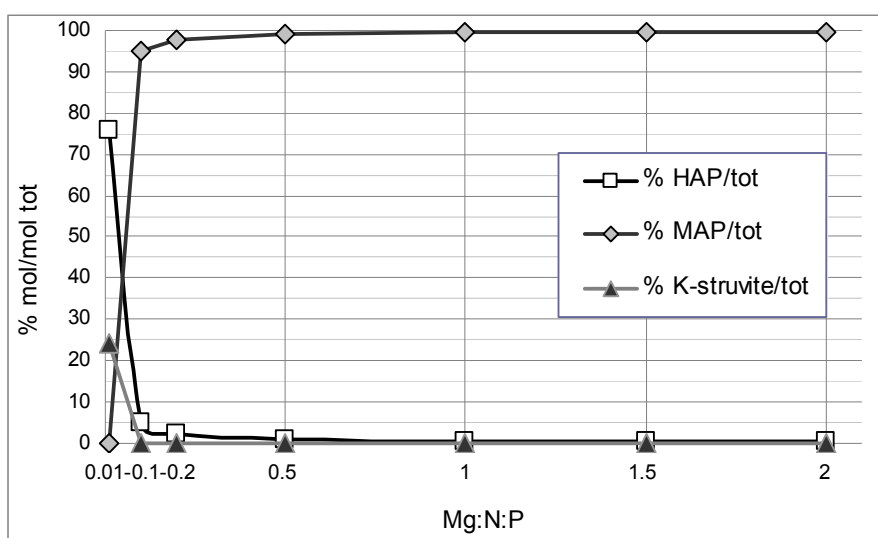


Figure 10: Visual Minteq simulation: precipitation of secondary compounds

## 4. Conclusions

Tests on anaerobic supernatants, from the codigestion of excess sludge plus the OFMSW and from cattle manure with agroindustrial residuals, were developed. The experimental was carried out by directly and indirectly adding pure and industrial  $\text{MgO}$  and  $\text{H}_3\text{PO}_4$  and the evaluating the effects of molar ratios and reaction time increases. The results highlighted how the indirect industrial  $\text{MgO}$  addition determined greater  $\text{NH}_4\text{-N}$  removals at the same molar ratios, when compared with the performances obtained at direct dosage. The indirect dosage of pure and industrial  $\text{MgO}$  resulted in a general improvement of 20 % of  $\text{NH}_4\text{-N}$  reduction, except when the presence of other ions in solution was consistent. The time factor determined differences in precipitation within 10 %, regardless of the dosage mode, as struvite precipitation occurred within the first minutes. Also, HAP and k-struvite formation was determined through the use of a thermodynamic model, defining amounts on the total precipitate compounds of 76 % and 24 % respectively at molar ratio lower than 1:1:1.

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