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D4.7: Strategies for alleviation of operational problems and potential for nutrient recovery through precipitation reactions

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Main contributors:

P. Pavan [a]
C. Cavinato [a]
D. Bolzonella [b]
F. Cecchi[b]

[a] University Ca' Foscari of Venice, Department of Environmental Sciences, Informatics and Statistics, Dorsoduro 2137, 30123 Venice, Italy
[b] University of Verona, Department of Biotechnology, Strada Le Grazie, 15, 37134 Verona, Italy

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1 INTRODUCTION

The removal of ammonia from digestate supernatant after separation of the liquid and solid fractions can be achieved by the formation of ammonium magnesium phosphate (struvite):

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4\,6H_2O$$

This technology has been reported as an effective method for N and P recovery in several anaerobically digested wastes such swine manure (Nelson et al. 2003, Miles and Ellis 2001), calf wastewater (Schuiling and Andrade 1999), landfill leachate (Ozturk et al. 2003), potato processing industry wastewaters (Moerman et al. 2009), dairy manure (Uludag-Demirer et al. 2005), and molasses (Celen et al., 2001 and Turker et al., 2007).

Struvite is a valuable slow-release source of nitrogen and phosphorus as plant nutrients. Its formation requires a stoichiometric molar ratio between $Mg:NH_4:PO_4$ of 1:1:1, or 1.7 kg of magnesium and 2.2 kg of phosphorus for each kg of ammonia nitrogen removed. Food waste digestates are usually rich in N and P, but it is necessary to dose Mg in the form of $MgCl_2$, $Mg(OH)_2$, MgO or 'bittern' (the residue obtained after NaCl extraction from sea water). Lee et al. (2003) showed 67% removal of ammonia after Mg^{2+} addition in food waste digestion, and 65-73% removal of phosphorus. The key process parameters are:

- pH between 7 and 11 with optimal values of 9.5-10.5;
- HRT of 1-2 hours;
- low temperature.

In the current work experiments by UNIVE were carried out to determine the degree of removal achievable by manipulation of the molar ratio, and the effect of ageing of the digestate on the process.

2 OVERVIEW OF THE RESEARCH

2.3 Struvite precipitation for removal of ammonia from food waste digestate supernatant

The experiments to evaluate ammonia removal via struvite/hydroxyapatite crystallisation were carried out at bench scale. The digestate used came from a pilot-scale 2-phase plant located in Treviso WWTP (pilot hall) fed with the organic fraction of MSW from separate collection (residential areas and canteens). Two stainless steel CSTR reactors (AISI 304) were employed for optimised H_2 and CH_4 production, respectively. The first reactor, dedicated to the fermentative step, had a 200 l working volume, while the second reactor dedicated to the methanogenic step had a 760 l working volume. Both the reactors were heated by a hot water recirculation system and maintained at 55°C using electrical heater controlled by a PT100-based thermostatic probe. The feeding system was semi-continuous, arranged once per day.

a) first phase reactor.   b) second phase reactor.

Figure 1. Pilot scale reactors

The ammonia removal by struvite precipitation was carried out using two different supernatants (S-A and S-B). The average characteristics of the supernatant A over the first and second experimental periods are shown in Table 1. The average macro pollutants amounts of the supernatants B, employed in the third experimental phase, are given in Table 2.

Table 1. S-A characterisation

Parameter	**Unit**	**Average**	**min**	**max**	**S.D.**
TS	g kg^{-1} WW	23.0	20.5	24.4	1.3
VS	g kg^{-1} WW	15.3	14.6	16.1	0.6
VS/TS	%	66.8	64.4	71.1	2.0
COD	g kg^{-1} WW	12.8	9.1	15.6	2.7
SCOD	g kg^{-1} WW	1.4	1.1	1.8	0.3
P tot	g kg^{-1} WW	0.13	0.11	0.17	0.06
Alkalinity pH 4	mg $CaCO_3$ l^{-1}	5173	4500	6120	674
Alkalinity pH 6	mg $CaCO_3$ l^{-1}	3160	2760	3700	374
pH		8.25	8.13	8.45	0.12
NH_3-N	mg N l^{-1}	997.5	805.0	1360.0	187.9
VFA	mg COD l^{-1}	89.9	14.0	344.0	109.0

Table 2. S-B characterisation

Parameter	Unit	Average
TS	g kg^{-1} WW	29.0
VS	g kg^{-1} WW	21.0
VS/TS	%	69.0
COD	g kg^{-1} WW	23.0
VFA	mg COD l^{-1}	89.9
P tot	g kg^{-1} WW	0.20
Alkalinity pH 4	mg $CaCO_3$ l^{-1}	5324
Alkalinity pH 6	mg $CaCO_3$ l^{-1}	2732
pH		8.1
NH_3-N	mg N l^{-1}	1079
PO_4-P	mg P l^{-1}	182
Mg^{++}	mg Mg l^{-1}	30
Cl^-	mg Cl l^{-1}	1514

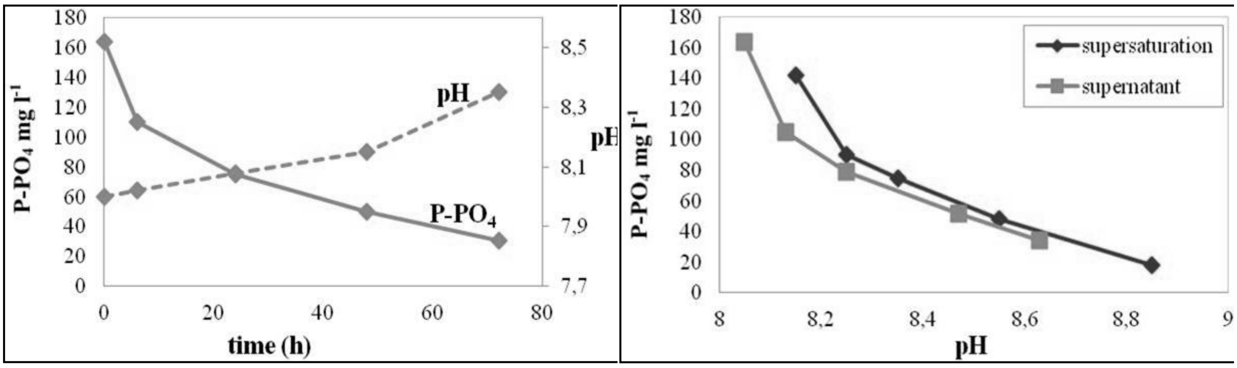
3 MATERIALS AND METHODS

In the struvite crystallisation test, the methods to characterize the TS, TVS and COD concentrations were in accordance with the Standard Method determination (APHA, 2005). The pH values were measured using a pH probe connected to a Titrino Plus 848 pH meter (Metron, CH). The pH meter was standardised using buffers of 4.0 and 7.0. Volatile fatty acids content was monitored using a gas chromatograph (Carlo Erba instruments) with hydrogen as the carrier gas, equipped with a Fused Silica Capillary Column (Supelco NUKOLTM, 15 0.53 0.5 lm film thickness) and with a flame ionisation detector (200 °C). The temperature during analysis started at 80 °C and reached 200 °C through two steps at 140 and 160 °C, at a rate of 10 °C min^{-1}. The analysed samples were centrifuged and filtered through a 0.45 µm membrane. Alkalinity at pH 6 and 4 was determined by titrating the sample to the defined pH values and recording the volume of titrant used (0.01 N hydrochloric acid).The ammonia concentration was defined using a Kjeldahl steam distillation unit according to the Standard Method procedure and with the manufacturer's instructions (Velp, IT). The soluble compounds, as anions and cations amounts, were measured by liquid chromatography system (Dionex, USA).

4 RESULTS AND DISCUSSION

4.1 First experimental phase: natural ageing tests

The first experiments were natural ageing tests to highlight the behaviour of phosphorus in relation to pH on supernatant A. During these tests the supernatant was slowly mixed and samples were taken and analysed daily. The results are shown in **Figure 2**.



a) Natural ageing curve.

b) Natural ageing in relation to super saturation.

Figure 2. Results of supernatant A ageing tests

The test showed the concentration of phosphate decreased over 3 days with a corresponding increase in pH. In order to evaluate the precipitation or crystalline nature of the solid obtained, a supersaturation curve was developed, with supersaturation reached by progressive addition of alkali. Figure 2 shows the natural evolution of the supernatant compared with the supersaturation limit and highlights that the metastable zone, indicated as the area under the supersaturation curve, is involved. This allows only magnesium ammonium phosphate (MAP) crystallisation.

4.2 Second experimental phase: precipitation tests on supernatants A

In the second set of experiments precipitation tests on supernatant A were carried out using added magnesium (as magnesium oxide) and phosphorus (as phosphoric acid) to achieve the correct molar ratio. An operating pH between 8 and 8.5 was chosen based on the results of the natural ageing experiment, and this was maintained using sodium hydroxide. Removal efficiencies and working parameters are shown in Table 3.

Table 3. Precipitation with MgO and H_3PO_4 on S-A

molar ratio	**pHm**	**T**	**NH_4-N in**	**NH_4-N (15')**	**E% NH_4-N (15')**	**PO_4-P in**	**PO_4-P (15')**	**E% PO_4-P (15')**
Mg : N : P		°C	mg l^{-1}	mg l^{-1}	%	mg l^{-1}	mg l^{-1}	%
1 : 1 : 1	8.38	26.1	1024	529	48	2203	1108	50
1.5 : 1 : 1	8.36	26.4	1079	473	56	2203	958	57
2 : 1 : 1	8.42	25.9	986	377	62	2203	785	64

The results showed that by working at unit molar ratio it was possible to achieve 50% removal of nutrients, while working with an excess of magnesium it was possible to increase the removal to above 60%. Additional tests using manure confirmed these results and showed it was possible to force nutrient removal, and in particular phosphorus removal, by manipulating the molar ratio to give an excess of magnesium.

4.3 Third experimental phase: precipitation tests on supernatants B

The third experimental phase was conducted using supernatant B, changing the following operative parameters:

- Molar ratio between Mg: N: P;
- Magnesium sources (industrial magnesium oxide (85% w/w) (RUN1) and magnesium chloride hexahydrate (RUN2));
- Precipitation test length (0.5 hour (RUN 1a) and 1 hour (RUN1b)).

4.3.1 Precipitation tests on supernatants B with industrial magnesium oxide

The first precipitation tests (RUN1a) on the supernatant B were executed using added magnesium (as magnesium oxide) and phosphorus (as phosphoric acid) to achieve the correct molar ratio. The molar ratio between Mg, N and P was changed from 1:1:1 up to 2:1:1 working with an excess of magnesium source (Table 4). An operating pH of about 8.5 was chosen for all the tests based on the results of the natural ageing experiment on S-A and this was maintained using sodium hydroxide.

Table 4. Precipitation with MgO and H_3PO_4 on S-B

	Influent (IN)		**molar ratio**	**MgO**	**Mg^{++}**	**H_3PO_4**	**PO_4-P**
	mg l^{-1}	**millimole**	**Mg:N:P**	**mg l^{-1}**	**mg l^{-1} (IN+Reagents)**	**mg l^{-1}**	**mg l^{-1} (IN+Reagents)**
Mg^{++}	30	1	1:1:1	3568	1850	6453	2389
NH_3-N	1079	77	1.5:1:1	5382	2775		
PO_4-P	182	6	2:1:1	7195	3699		

The effluent nutrients and magnesium concentrations and the performances obtained are reported in Table 5 and Figure 3, after 30 minutes of precipitation test length (RUN1a).

Table 5. Effluent characterisation of precipitation with MgO and H_3PO_4 on S-B

	Total Influent		
	mg l^{-1}		
	1:1:1	1.5:1:1	2:1:1
Mg^{++}	1850	2775	3699
NH_3-N	1079	1079	1079
PO_4-P	2389	2389	2389
	Total Effluent (time 30 min)		
	mg l^{-1}		
Mg^{++}	0	0	0
NH_3-N	518	453	345
PO_4-P	812	502	215

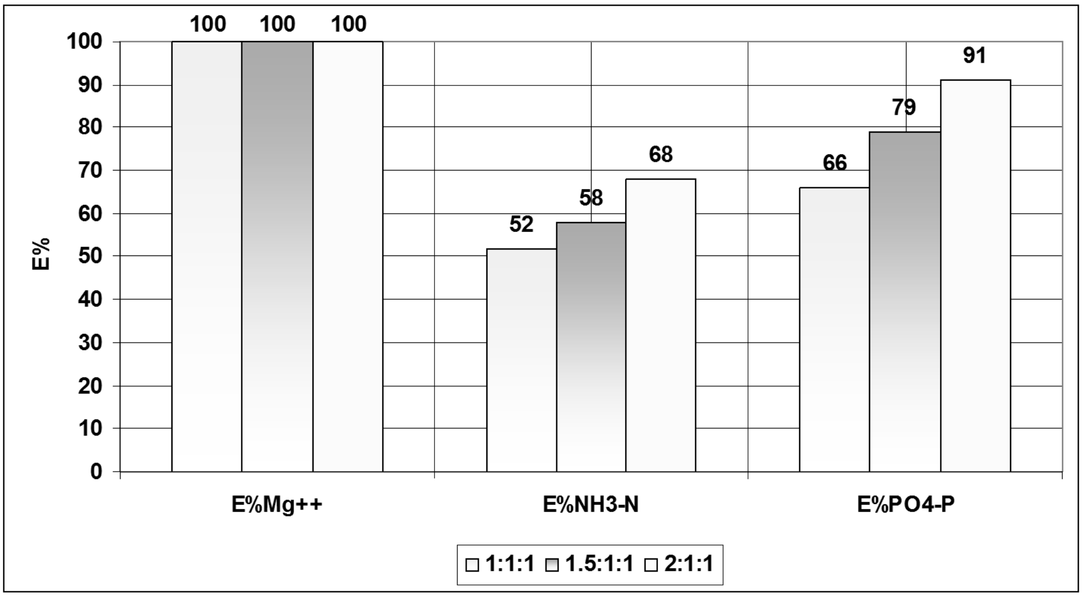


Figure 3. Performances of precipitation with MgO and H_3PO_4 on S-B (time 0.5 hours)

The results highlight that, using MgO as magnesium source, the phosphate performance increases from 66% (molar ratio 1:1:1) up to 91% (molar ratio 2:1:1) with a slow increment in the ammonia removal (from 52% (molar ratio 1:1:1) up to 68% (molar ratio 2:1:1)). No magnesium effluent was measured in solution at the end of the RUN1a for all the molar ratios tested.

In a second phase the S-B was used to defined the precipitation performance (RUN1b) using as in the previous tests magnesium oxide and phosphoric acid, incrementing the molar ratio (Mg:N:P) up to 3:1:1 and the time length of the tests to 1 hour (Table 6). An operating pH of about 8.5 was chosen for all the tests based on the results of the natural ageing experiment on S-A and this was maintained using sodium hydroxide.

Table 6. Precipitation with MgO and H_3PO_4 on S-B

	Influent (IN)		**molar ratio**	**MgO**	**Mg^{++}**	**H_3PO_4**	**PO_4-P**
	mg l^{-1}	**millimole**	**Mg:N:P**	**mg l^{-1}**	**mg l^{-1} (IN+Reagents)**	**mg l^{-1}**	**mg l^{-1} (IN+Reagents)**
Mg^{++}	30	1	1:1:1	3568	1850	6453	2389
NH_3-N	1079	77	1.5:1:1	5382	2775		
PO_4-P	182	6	2:1:1	7195	3699		
			3:1:1	10822	5549		

The effluent nutrient and magnesium performances obtained after 1 hour for all the molar ratios tested are reported Figure 4 (RUN1b).

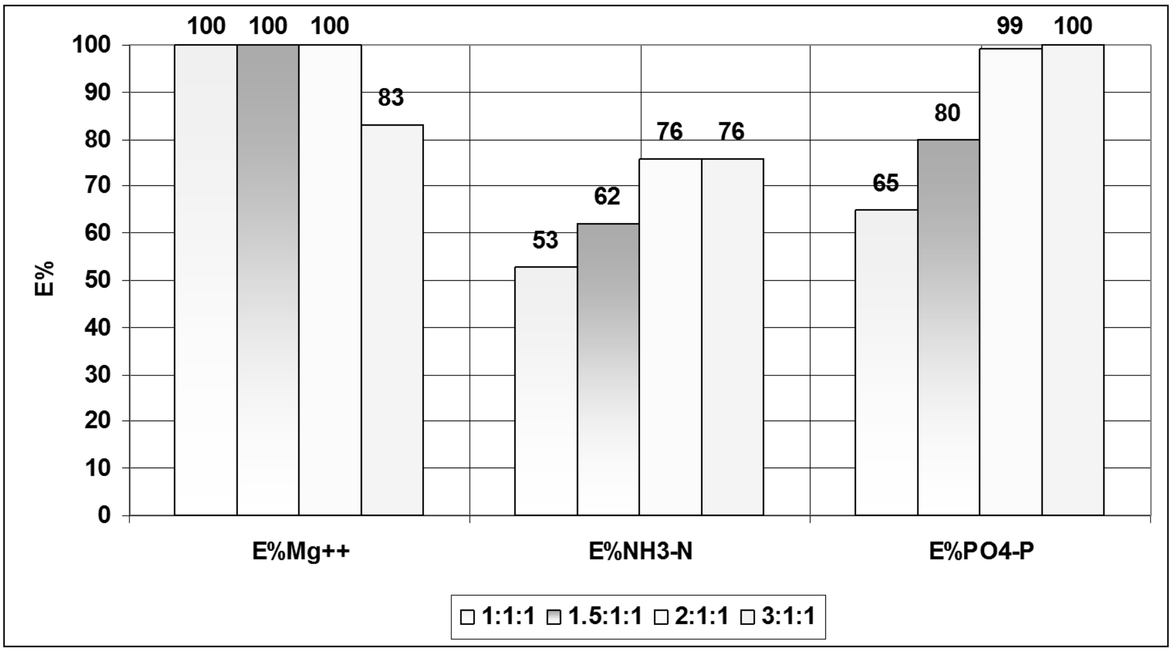


Figure 4. Performances of precipitation with MgO and H_3PO_4 on S-B (time 1 h)

The performances obtained, for all the molar ratio analysed indicated that increasing the reaction time up to 1 hour did not lead to a significant growth in the removal percentages compared with the results achieved at 30 minutes of reaction time (Figure 3 and Figure 4). Only for ammonia at the same molar ratio (2:1:1) a longer reaction time gave a performance of 76% (Figure 4) compared with 68% obtained after 30 minutes (Figure 3). Moreover, the increment of the molar ratio up to 3:1:1 (Figure 4), with a higher addition of magnesium oxide, showed a similar removal percentage for Ammonia and Phosphorous. In this last situation, the saturation condition determines that not all the added magnesium reacts in the solution creating a remaining Mg^{++} effluent concentration of about 900 mg l^{-1} (performance of 83% -Figure 4).

4.3.2 Precipitation tests on supernatants B with magnesium chloride hexahydrate

The third precipitation tests (RUN2) on the supernatant B were executed using added magnesium (as magnesium chloride hexahydrate) and phosphorus (as phosphoric acid) to achieve the correct molar ratio. The molar ratio, between Mg, N and P, was changed from 1:1:1 up to 2:1:1 working with an excess of magnesium source (
The effluent nutrient and magnesium concentrations and the performances obtained are reported in Table 8 and Figure 5, after 30 minutes of precipitation test length (RUN2).

Table 7). An operating pH from 8.3 (1:1:1) to 8.4 (2:1:1), was chosen for all the tests based on the results of the natural ageing experiment on S-A, and this was maintained using sodium hydroxide.

The effluent nutrient and magnesium concentrations and the performances obtained are reported in Table 8 and Figure 5, after 30 minutes of precipitation test length (RUN2).

Table 7 . Precipitation with $MgCl_2$*$6H_2O$ and H_3PO_4 on S-B

	Influent (IN)		**molar ratio**	**$MgCl_2$*$6H_20$**	**Mg^{++}**	**H_3PO_4**	**PO_4-P**
	mg l^{-1}	**millmole**	**Mg:N:P**	**mg l^{-1}**	**mg l^{-1} (IN+Reagents)**	**mg l^{-1}**	**mg l^{-1} (IN+Reagents)**
Mg^{++}	30	1	1:1:1	15392	1850	6453	2389
NH_3-N	1079	77	1.5:1:1	23215	2775		
PO_4-P	182	6	2:1:1	31037	3699		

Table 8. Effluent characterisation of precipitation with $MgCl_2$*$6H_2O$ and H_3PO_4 on S-B

	Total Influent		
	mg l^{-1}		
	1:1:1	**1.5:1:1**	**2:1:1**
Mg^{++}	1850	2775	3699
NH_3-N	1079	1079	1079
PO_4-P	2389	2389	2389
	Total Effluent (time 30 min)		
	mg l^{-1}		
Mg^{++}	0	0	0
NH_3-N	237	205	140
PO_4-P	24	0	0

The results from the tests conducted with magnesium chloride defined optimal performances for both the nutrients (Ammonia and Phosphorous) achieving complete removal for P (Figure 5). In this case, the increment of the molar ratio and the excess magnesium conditions did not cause a significant improvement in performance compared with the remarkable increment due to the reagents used (Figure 5). Despite the very high removal percentages, it is necessary to highlight that the $MgCl_2$*$6H_2O$ releases a high amount of chloride in the solution. The final effluent chloride concentration from 1,514 mg l^{-1} of the influent supernatant B (Table 2) increases up to 4,203 mg l^{-1}, 5,570 mg l^{-1} and 6,937 mg l^{-1} respectively for molar ratios of 1:1:1, 1.5:1:1 and 2:1:1.

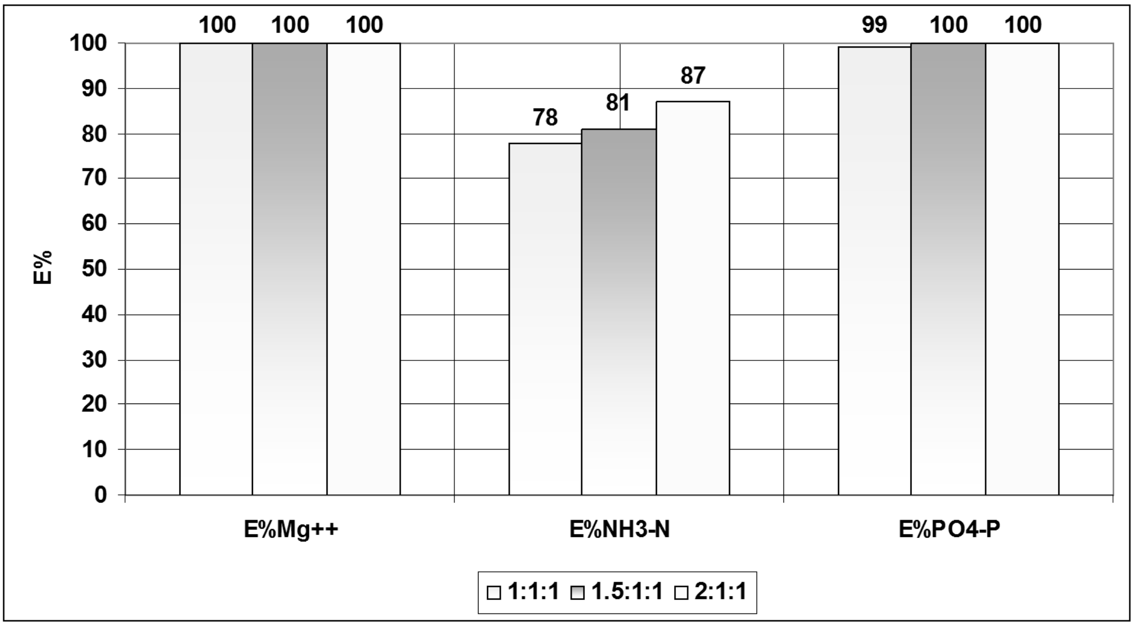


Figure 5. Performances of precipitation with $MgCl_2$*$6H_2O$ and H_3PO_4 on S-B (time 30')

4.4 Comparison of the results and optimal operative conditions

From the experimental bench scale tests conducted to evaluate the nutrient removal efficiencies by precipitation it was possible to define the following considerations. The performances for ammonia and phosphorus are remarkable and the process could be considered as suitable for a high removal with recovery of the nutrients. The use of MgO as magnesium source needs, at the minimum molar ratio a higher reaction time (from 15 minutes of S-A to 30 minutes of S-B) to obtain elevated efficiencies (66% for P and 52% for N). The excess magnesium condition (2:1:1), using MgO, gives removal percentages up to 68% and 91% at 30 minutes of reaction time; the increment of the ratio up to 3:1:1 does not lead to a considerable improvement in performance compared with the remarkable increment due to the reagents used. The magnesium chloride improves the effluent quality and the possible struvite recovery, achieving at minimum ratio 1:1:1 removal percentages of 78% for the ammonia and 99% for phosphorous. Against these last significant results, the $MgCl_2$*$6H_2O$ causes and increase of the chloride in the final effluent of 180% (molar ratio of 1:1:1) compared with the initial supernatant concentration. Finally, the specific sodium hydroxide consumption to maintain the correct operative pH was evaluated as equal to 0.3 kg NaOH kg^{-1} H_3PO_4 using MgO and 1.2 kg NaOH kg^{-1} H_3PO_4 using $MgCl_2$*$6H_2O$ characterised by water acid hydrolysis.

5 CONCLUSIONS

The work on struvite precipitation has shown its feasibility, but the molar ratio requirement for magnesium is high when magnesium oxide is added as a magnesium source. The performances could be optimised using magnesium chloride to remove and recover more than ~80% of the nutrients at the minimum molar ratio, at the expense, however, of an increased content chloride in the effluent flow. The use of magnesium oxide eliminates this operative problem and, moreover, allows a decrease in sodium hydroxide dosage.

Interesting future evaluations could be related to the results obtainable by incrementing the reaction time to improve the performance of the precipitation tests using MgO working at lower molar ratios. Moreover, indirect reagent dosage could be tested to enhance MgO solubility, as a pure and an industrial reagent, by mixing MgO in the phosphoric acid before the dosage. The optimisation of the dosing modality for the reagents is a key point to be evaluated. In fact, after the confirmation of the removal ammonia performances and of the molar ratios needed and the reaction times, the study of a different MgO dosing method could be the solution to improve the reliability of the struvite precipitation and to determine the scale-up demonstration phase.

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