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STRUVITE PRECIPITATION FROM SEWAGE SLUDGE ASH

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Abstract

The recovery of nutrients from sewage sludge ash, especial phosphorus, is one of the most important alternative in sewage sludge management. Phosphorus is an essential element for all living organisms and very important for agriculture and industry, as well as. Because the phosphorus is a non-regenerative resource, its recovery plays an important role for society. Phosphorus capitalization as struvite ($NH_4MgPO_4 \cdot 6H_2O$) from sewage sludge has attracted considerable attention due to its potential to be re-used as fertilizer through phosphorus recovery.
The aim of this paper is the recovery of phosphorus as struvite from the ash resulted after the sewage sludge incineration. The optimal conditions chosen were: L:S=5:1 and 5% sulfuric acid solution, obtaining in this case a phosphorus extraction eficieny of 92% and having a phosphorus content in of 8.2 g/L. The precipitation process was studied for two values of the Mg:P ratio of 1.5 and 1.2 for pH ranging between 8.5 and 10. For struvite precipitation, magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) and ammonium chloride (NH_4Cl) were used as the magnesium and nitrogen sources in alkaline media using 4M NaOH solution. The precipitates were characterized chemically and morpho-structurally. The optimum pH for the struvite formation is pH=9. The XRD pattern for the sample precipitated at pH of 9 shows the struvite as the only detectable crystalline phase with the highest intensity compared with other precipitates.
The proposed method for struvite obtaining represents a green and less expensive technology presenting advantages from both economic and environmental point of view.

Key words: phosphorus recovery; sewage sludge ash management; fertilizer

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1. Introduction

Phosphorus is one of the most important elements for biological growth (Jalali and Jalali, 2016; Metaxa et al., 2019; Yuanyao et al., 2017). The global population will grow from 7.2 billion individuals to 9.6 billion by the year 2050 (UN, 2014). Also, the food consumption rate will increase at a rate of 3.1% every year (Heffer and Prud'homme, 2014) and therefore the sustainable intensification of agricultural production will need to be implemented globally with the agricultural production growing by 60% (Kataki et al., 2016). Fertile soils play an important role for the intensification of agriculture production, which are highly dependent of commercial fertilizer. Commercial fertilizers also depend upon the availability of phosphorus (Kataki et al., 2016). On the other hand, it is predicted that the rock phosphate reserves will run out in the next 70-100 years (Łukawska, 2014). From this reasons the recovery of phosphorus from secondary sources is a global concern and is in agreement with the sustainable development and the "principle of natural sources protection".

The European Parliament has reviewed the list of critical raw material (CRM) for the European Union, which phosphate is an important rock due to the risks of a shortage of supply (COM, 2014). Europe has no important P mines and depends on the import of ore. Therefore, it is really important to implement at the level of the European Union a sustainable method for recycling and conserving the phosphorus

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resource (Lederer et al., 2014). Recovery of phosphorus through efficient and economically viable processes from waste and resides sources rich in phosphorus is a priority for sustainable development (Kataki et al., 2016).

In the European Union there is only one country where phosphates are produced from apatite deposits: Finland. Most of the countries which own large deposits of phosphate rock use these resource for their own needs or are politically unstable (Adam et al., 2009). Thus, there is a high potential in European Union to recover phosphorus from secondary source: waste streams, such as: wastewater (Zhang et al., 2013), sludge (Jeyakumar et al., 2019; Millier and Hooda, 2011), meat and bone meal (Darwish et al., 2016) and biomass.

Struvite precipitation ($MgNH_4PO_4 \cdot 6H_2O$) is one of the best ways to recover phosphorus from different types of wastewaters: swine wastewater (Rahman et al., 2011), calf manure wasterwater (Schuiling and Andrade, 1999), leather tanning wastewater (Tunay et al., 1997), sewage sludge (Munch and Barr, 2001), wasted sludge (Jaffer et al., 2002), digested supernatant (Pastor et al., 2010), industrial wastewater (Diwani et al., 2007), agro-industrial wastewater (Barreto dos Santos et al., 2016; Hidalgo et al., 2014; Moerman et al., 2009), and fertilizer plant wastewater (Yu et al., 2013). Precipitation of struvite has also been studied experimental using chemical reagents (Huang et al., 2019; Le Corre et al., 2005; Li et al., 2016; Polat and Sayan, 2019; Yan and Shih, 2016; Wei et al., 2019).

Sewage sludge ash also represents an important phosphorus source due to the high concentration of phosphorus. In this work is presented the recovery of phosphorus from a natural material (sewage sludge ash) using sulfuric acid as leaching solution studying the influence of different concentration of acid and different liquid: solid ratios upon the extraction efficiency. Struvite is obtained from the resulted extracted solution via chemical precipitation. Xu et al. (2012) investigated the possibilities of using the sewage sludge as secondary source for phosphorus precursor in order to obtain struvite precipitation. In this case they compared the phosphorus leaching efficiency using hydrochloric acid or sodium hydroxide solutions. The conclusion was that the acid was more effective than the alkaline solutions, but in their case the extraction of heavy metals (present in sewage sludge) was an inconvenient. In our case, using the sulfuric acid, the extraction of the heavy metals present in the sewage sludge is reduced due to the fact that the obtained metals sulfates have lower solubility. In other studies, phosphorus was extracted using sulfuric acid or citric acid, but in this cases, the phosphorus was recovered as iron phosphates, thus a further purification step using ion exchange to remove iron was required to increase the degree of P release (Shiba and Ntuli, 2017). Also, Franz and his co-workers (2007) used two methods to extract heavy metals from the extracted solution: ion exchange and sulfide precipitation. Another study presented a pretreatment method for heavy metals extraction using thermochemical treatment (Mattenberger et al., 2008). Therefore, the present study presents an efficient method of phosphorus recovery using sulfuric acid as leaching solution unlike the methods presented until now in the specialty literature. The direct precipitation of phosphorus from the resulted solution after the acid leaching process eliminate the need of extra purification, which minimize the production cost.

2. Experimental

2.1. Materials

The sewage sludge used throughout the present study was collected from a municipal wastewater treatment plant from Timis county, Romania. The sewage sludge ash was obtained after drying the sewage sludge at 105°C for 20 hours and then calcinated at 850°C for 3 hours using Nabertherm B180 oven.

Sulfuric acid (H_2SO_4, 98%) of analytical reagent grade used for the extraction experiments was provided by Merck, Darmstadt, Germany. Magnesium sulfate heptahydrate and ammonium chloride of analytical reagent grade used for the precipitation process were supplied also by Merck, Darmstadt, Germany. Ultrapure water was used for the analytical method.

2.2. Sewage sludge ash characterization

The sewage sludge ash was digested with aqua regia in order to determine its composition. The initial phosphorus content was determined using a Hach Lange DR 3900 spectrometer in accordance with Standard Method EPA 4500-P C (American Public Health Association, 2005) and metal content was analyzed by atomic absorption spectroscopy.

The structural characteristics of the sewage sludge ash were determined by transmission electron microscopy. A Titan G2 80-200 electron microscope (FEI Company, Netherlands) was used to analyze sewage sludge ash samples deposited from ethanol on 200 mesh copper grids (3 mm) coated with holey carbon film at an acceleration voltage of 200kV. TEM images were recorded using Digital Micrograph software and elemental distribution maps were obtained using Esprit software.

2.3. Phosphorus extraction from sewage sludge ash

The phosphorus extraction from sewage sludge ash was carried out in batch mode batch at room temperature using sulfuric acid as extraction agent. The influence of acid concentration and of the liquid: solid (L:S) ratio upon the extraction efficiency were studied.

Therefore, a measured amount of sewage sludge ash sample was mixed with a measured volume of sulfuric acid to reach the values of liquid: solid ratios ranged from 5:1 to 20:1. The stirring rate was

400 rpm. In order to determine the influence of the acid concentration upon the extraction efficiency different sulfuric acid concentrations ranged from 5% to 15%, were used.

The samples were stirred magnetically at constant speed for 15 minutes and then the slurry was centrifuged at 3500 rpm for 10 minutes, analyzing the phosphorus content from supernatant.

The extraction efficiency was calculated based on the equation bellow (1):

$$\eta(\%) = \frac{C}{C_0} \cdot 100 \quad (1)$$

where: η represents the extraction efficiency (%), C is phosphorus concentration from extraction acidic sample (g/L), and C_0 is initial phosphorus concentration (g/L).

2.4. Phosphorus recovery as struvite

The phosphorus extracted from the sewage sludge ash was recovered and capitalized as struvite. For struvite precipitation, ammonium chloride (NH_4Cl) and magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) were used as the nitrogen and magnesium source. The pH adjustment was achieved by a 4M NaOH solution. The magnesium source was firstly poured into the optimal acidic extracted solution, followed by the addition of NaOH solution for pH adjustment (8.5, 9, 9.5, 10). Finally, the nitrogen source for struvite precipitation was added. The magnesium and nitrogen source were introduced in order to obtain a Mg: P ratio of 1.5 and a N: P ratio of 1.2. Afterwards, the mixture was stirred at constant speed for 15 minutes, the suspension was filtered, and the precipitate was dried at 35°C.

2.5. Characterization of the obtained struvite

In order to determine if the extracted phosphorus from the sewage sludge ash was recovered as struvite the precipitates obtained at various pH values were subjected to the chemical analysis, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM and EDAX).

The obtained precipitates were digested using hydrochloride acid (HCl, 37%) in order to determine the total amount of phosphorus, magnesium, nitrogen and other metals. The phosphorus and iron concentrations were determined through molecular absorption spectrometry using a Hach Lange DR 3900 and DR 2800 spectrometers. The phosphorus concentrations were determined in accordance with ISO 6878:2004 (ISO, 2004). The nitrogen and calcium concentrations were performed using an automated wet chemistry analyzer known as continuous flow analyzer San++ from Skalar. The magnesium, sodium and potassium were determined through atomic absorption spectrometry using a Perkin Elmer Analyst 800 spectrometer. The other elements (Al, Pb, Cr, Ni, Cu, Cd, Se, Mn) were determined through inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer NexION 350X spectrometer.

The obtained precipitates were ground into powder and examined by XRD to determine their crystalline phase compositions. The X-ray diffraction patterns were recorded by using a Rigaku Ultima IV X-ray diffractometer (40 kV, 40 mA) with CuKα radiation (λ = 0.15406 nm) to identify the crystalline phases using PDF 4+ databases.

The morphology of the synthetized samples (SEM images) were observed using a Quanta FEG 250 microscope, equipped with an EDAX/ZAF quantifier. The thermal behavior of the struvite obtained in optimum conditions was determined through thermogravimetric analysis using a Derivatograph TG 209 F1 Libra, DSC 204 F1 Phoenix NETZSCH in static air atmosphere between 25 °C and 1000 °C with the heating rate of 5°C/min.

3. Results and discussions

3.1. Sewage sludge ash characterization

From the chemical composition of the sewage sludge (Militaru et al., 2019), can be observed that Ca, Fe, P and Al are the main elements contained in the ash. The phosphorus content was 4.3% P (42991 ppm) and respective, 9.86% P_2O_5.

The mapping technique was used as a structural characterization method, which highlighted by different colorations the presence of phosphorus, oxygen, calcium, magnesium, iron and aluminum, and the results are presented in Fig. 1, which illustrates a STEM image acquired on chosen area of the ash sample. It can be observed that the main elements, resulted also from the chemical analysis, are uniform distributed in the structure of the sewage sludge ash. Due to its high present and uniform distribution in the sewage sludge ash, the purpose of this study is to capitalize the phosphorus ions under struvite form.

Table 1. Chemical composition of the resulted extracted solution

Parameter	*Concentration of the resulted extracted solution (g/L)*
P	8.12
Ca	1.09
Al	2.32
Fe	0.650
K	0.959
Cu	0.051
Mn	0.142
Zn	0.108
Pb	UDL*
Cr	0.002
Ni	0.002
Cd	UDL*
Na	1.16
Mg	2.08

**UDL - under detection limit*

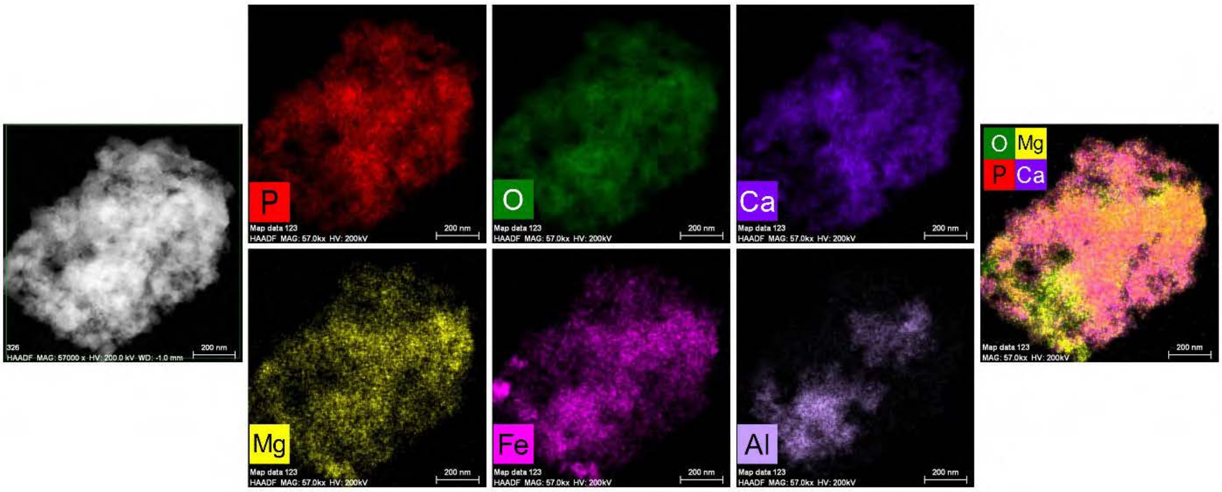

Fig. 1. STEM image of the studied sewage sludge ash

3.2. Extraction studies

In order to find the easiest way for phosphorus valorification as struvite, this study was conducted to find optimum conditions for its extraction in sulfuric acid as an intermediar step of the phosphorus recycling process. Fig. 2a shows the influence of liquid: solid (L:S) ratio upon the phosphorus extraction efficiency using three different concentration of sulfuric acid solution (5, 10 and 15%). Fig. 2b shows the evolution of the phosphorus concentration in the obtained exctracted solution.

It can be noticed that the phosphorus extraction efficiencies present a slow increasing with the L:S ratio increasing and with the increasing of the sulfuric acid concentration. For all the cases the obtained extraction efficiens were above 90%. In the same time, the increasing of the L:S ratio lead to a decreasing of the phosphorus concentration from the extracted solution. Therefore, from this reason and from economical point of view is not recomanded to use a higher L:S ratio and is not justified to use a higher concentration of sulfuric acid solution.

Based on these arguments the optimal conditions chosen in order to obtain the struvite were: L:S=5:1 and 5% sulfuric acid solution, obtaining in this case a phosphorus extraction eficieny of 92% and having a phosphorus content in the extracted solution of 8.12 g/L. In this case a higher extraction degree is obtained than the extraction degree reported in other reported studies (Ali and Kim, 2016, Sano et al., 2012, Shiba and Ntuli, 2017). Another important aspect is the presence of other impurities in the resulted extracted solution such as: heavy metals and other elements. In table 1 is presented the chemical composition of the resulted extracted solution parameters. It can be observed that the major elements extracted are P, Al, Mg, Mn, Na, K, Ca and Fe.

These elements are also used as micro and macro elements in different fertilizers, so their presence in the struvite will not be a problem. The heavy metals present in the sewage sludge which could raise a concern if will be present in the struvite were extracted in a very small quantity < 3 ppm, being in the range of the maximum admited levels (GD, 2004). Due to the fact that as leaching solutions is used the sulfuric acid, the extraction of the impurities is minimised compared with the resultes reported in literature when hydrocloric acid solution is used for extraction (Xu et al., 2012). Due to the highest content of phosphorus ion in the resulted extracted solutions, this could be capitalized as struvite.

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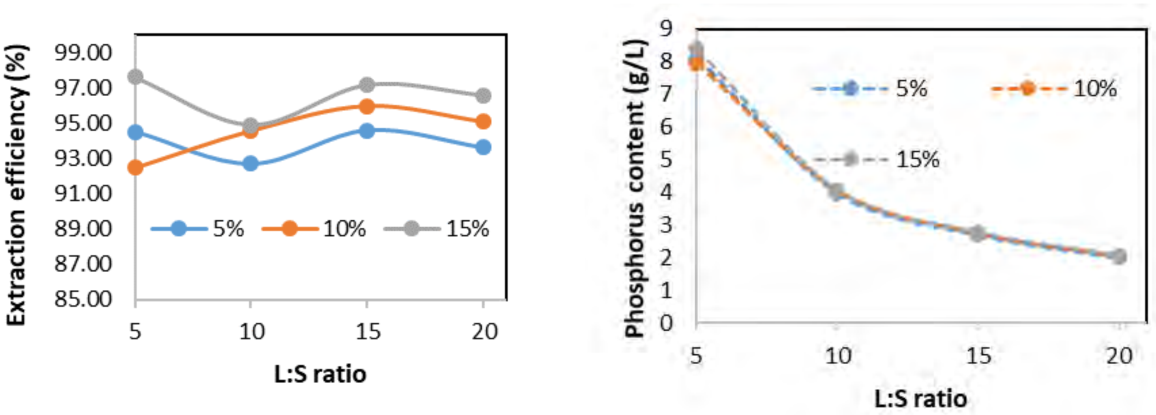
3.3. Recovery of phosphorus as struvite

Compared with other fertilizers, struvite ($MgNH_4PO_4 \cdot 6H_2O$) is an excellent slow release fertilizer with a high content in P (Xu et al., 2012). Struvite precipitation is a promising solution for P recovery technology (Jalali and Jalali, 2016).

The formation of struvite highly depends on the pH and the molar ratio of Mg:N:P. Previous studies also reported the influence of these factors (Xu et al., 2012). It was demonstrated that the struvite formation was highly pH dependent. The optimal parameters were observed at pH = 10, Mg: P = 1.6 and N: P = 1.6.

In the present study, for struvite obtaining the chosen parameters were: Mg: P = 1.5, N: P = 1.2 and pH ranged from 8.5 to 10. Struvite crystallization also depends by other factors such as the presence of impurities and the mixing speed (Bouropoulos and Koutsoukos, 2000, Li et al., 2016).



(a) **(b)**

Fig 2. Influence of L:S ratio upon the extraction efficiency (a) and the phosphorus content in the extracted solution (b)

The presence of impurities from the acid extraction solution affects struvite product morphology and purity. In Table 2 is presented the chemical composition for each precipitate obtained from the resulted extracted solution. It can be noticed that the concentration of P, N, Al, Mn, Cu, Zn, Fe, K and Ca decreases as the pH increases. On the other hand, the concentration of Mg and Na increases as the pH increases. The concentration of other elements remains almost constant during the precipitation. During phosphorus precipitation from resulted extracted solution heavy metals inevitably co-precipitated and further contaminated the precipitates. Even if, in the obtained struvite are present a lot of impurities from the sewage sludge ash (Table 3), these do not exceed the limits of fertilizer ordinance (GD, 2004). Table 3 shows the theoretical molar ratio in order to obtain the struvite and the molar ratios calculated for each precipitate.

It can be concluded that the optimum pH for struvite obtaining through precipitation is pH=9. At this pH the experimental molar ratio is closed to the theoretical one, and in this case are obtained the smallest quantity of impurities from the resulted struvite.

Table 3. Theoretical and experimental molar ratio

Element	*P*	*Mg*	*N*
Theoretical molar ratio	1	1	1
Molar ratio pH 8.5	1	0.76	0.76
Molar ratio pH 9	1	0.97	0.83
Molar ratio pH 9.5	1	1.10	0.83
Molar ratio pH 10	1	1.14	0.86

SEM pictures of the precipitates for each pH value (8.5, 9, 9.5, 10) are shown in Fig. 3. It can be observed the struvite crystalline rectangular particles formed during the precipitation. On the other hand, the surfaces of the struvite particles were covered with small amorphous particles. Li and co-workers observed similar SEM pictures for struvite obtained from pure reagents (Li et al., 2016).

Table 2. Chemical composition for precipitates

Element (%)	*pH = 8.5*	*pH = 9.0*	*pH = 9.5*	*pH = 10.0*
P	10.4	9.44	9.17	8.69
N	3.05	2.96	2.99	2.83
Mg	6.14	7.02	7.93	7.75
Ca	0.494	0.491	0.197	0.266
Al	3.21	3.20	2.84	2.46
Fe	1.31	1.21	1.07	0.885
K	0.203	0.417	0.171	0.129
Cu	0.061	0.058	0.055	0.048
Mn	0.138	0.155	0.135	0.117
Zn	0.121	0.195	0.113	0.098
Pb	0.002	0.005	0.007	0.001
Cr	0.003	0.012	0.005	0.003
Ni	0.002	0.002	0.003	0.002
Cd	UDL	UDL	UDL	UDL
Na	6.20	6.41	7.16	7.24

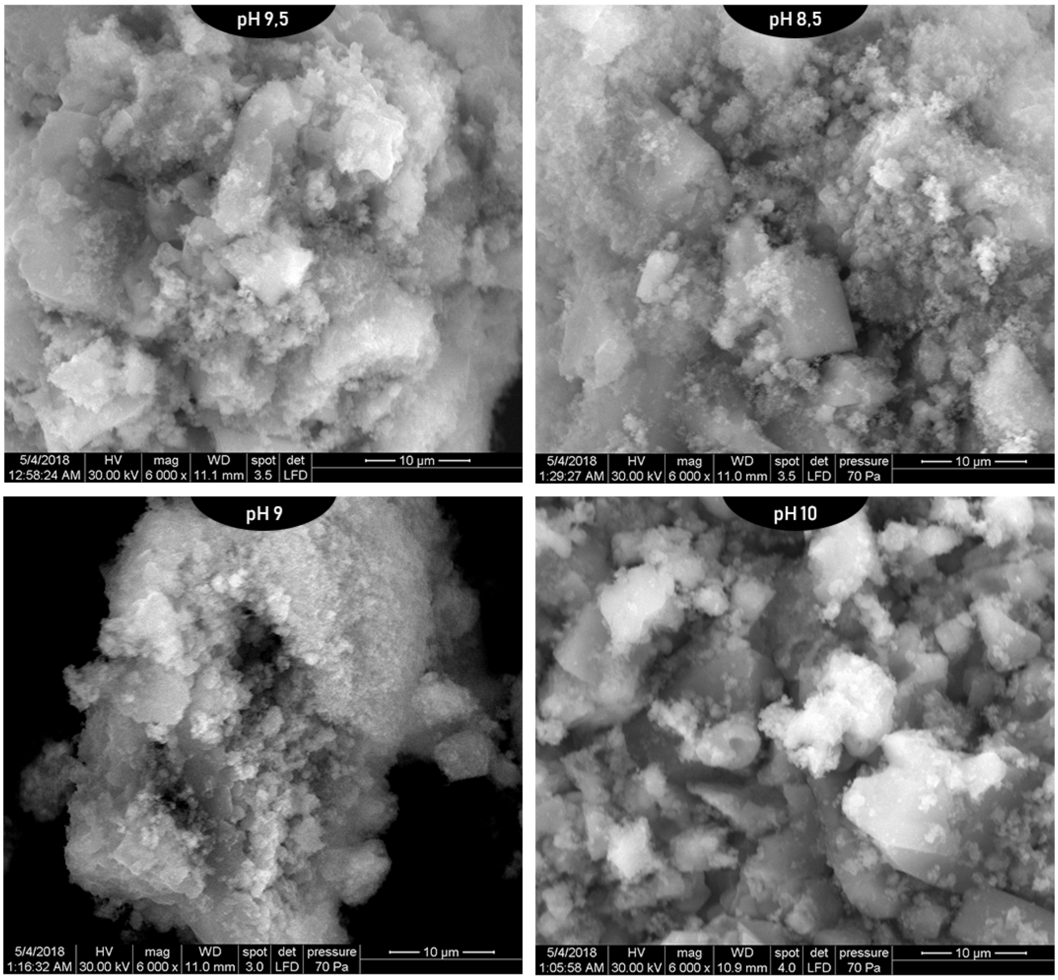


Fig. 3. SEM images of the precipitates for different pH values

The XRD pattern of the obtained struvite at different pH are presented in Fig. 4. The XRD pattern for the sample precipitated at pH of 9 shows the struvite as the only detectable crystalline phase with the highest intensity compared with other precipitates. The obtained RX in this case is similar with other RX difractograms presented for struvite in the specialty literature (Le Corre et al., 2005, Li et al., 2016, Xu et al., 2012). At pH=8.5 the P:Mg:N molar ratio is 1:0.76:0.76, which indicates an excess of P with the possible formation of other chemical compounds. The XRD pattern revealed the presence of the secondary crystalline phase: apatite.

As the pH increases, besides the presence of the struvite as the main phase, the XRD pattern reveals two more crystalline phases: sodium sulfate and magnesium sulfate. P:Mg molar ratio is 1:1.10 and 1:1.14 for pH=9.5 and pH=10, respectively, which indicates an excess of Mg and therefore formation of magnesium sulfate can take place. Correlating the results from the chemical analysis with the XRD patterns of samples it can be concluded that the optimum precipitation pH is 9. The best P:Mg:N molar ratio is for pH=9 (1:0.97:0.83) which indicates the formation of struvite as only crystalline phase.

The plot of thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) of the obtained struvite in optimum conditions are presented in Fig. 5.

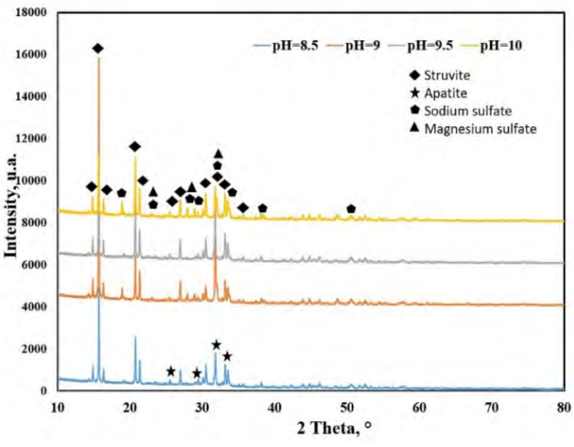


Fig. 4. RX spectrum of the precipitates obtained at pH=8.5,9, 9.5 10: ◆ $Mg(NH_4)(PO_4)(H_2O)_6$ – COD ID: 2106462, ★ $Ca_5(PO_4)_3(OH)$ – COD ID: 9010051, ⬟ Na_2SO_4 – COD ID: 9004092, ▲ $MgSO_4$ – COD ID: 9015317.

From the DSC curve can be observed an endothermic pic (at 112°C) corresponding to the main mass loss (~36%), which correspond to the ammonium decomposition and the loss of 5 molecules of water of crystallization (Chetan and Mihirkumar, 20140; Heraldy et al., 2017; Iovi et al., 2004).

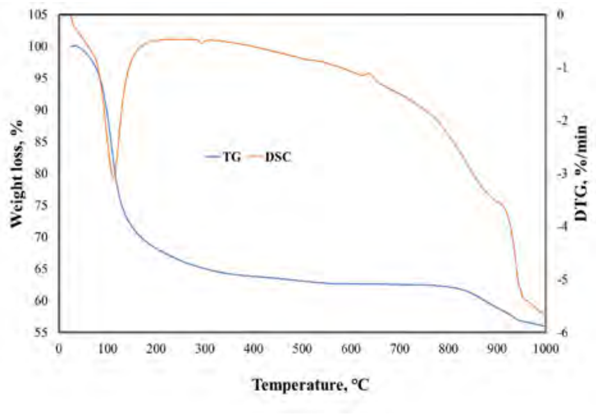


Fig. 5. Thermal analysis of the precipitate obtained at pH=9

At 294°C can be observed another endothermic effect due to the decomposition of the last moll of water (Iovi et al., 2004). The release of ammonium take place gradually (Frost et al., 2004). At 637°C can be observed an exothermic effect which correspond to the transformation of struvite in pyrophosphate (Paul et al., 2002). The water resulted in this reaction is loss at higher temperature, as can be seen the two-endothermic effect at 875°C and 950°C.

4. Conclusions

The sewage sludge ash resulted from the calcination of sewage sludge can be used as a phosphorus source due to the content of phosphorus (4.3% P, 9.86% P_2O_5). The presence of phosphorus was also confirmed by the STEM image using mapping technique.

The phosphorus extraction was performed using sulfuric acid as an extraction agent at high concentrations and lower liquid: solid ratios. The phosphorus extraction efficiencies present a slow increasing with the L:S ratio increasing and with the increasing of the sulfuric acid concentration. The optimal conditions chosen were: L:S=5:1 and 5% sulfuric acid solution, obtaining in this case a phosphorus extraction eficieny of 92% and having a phosphorus content in of 8.2 g/L.

To obtain the struvite, the chosen parameters were: Mg: P = 1.5, N: P = 1.2 and pH ranged from 8.5 to 10. The optimum pH for the struvite formation is pH=9. At this pH, the experimental molar ratio is closed to the theoretical one, are obtained the smallest quantity of impurities from the resulted struvite and also The XRD pattern for the sample precipitated at pH of 9 shows the struvite as the only detectable crystalline phase with the highest intensity compared with other precipitates.

The proposed method for struvite obtaining represents a green and less expensive technology presenting advantages from both economic and environmental point of view.

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References

Adam C., Peplinski B., Michaelis M., Kley G., Simon F.G., (2009), Thermochemical treatment of sewage sludge ashes for phosphorus recovery, *Waste Management*, **29**, 1122-1128.

Ali U.T., Kim D.J., (2016), Phosphorus extraction and sludge dissolution by acid and alkali treatments of polyaluminum chloride (PAC) treated wastewater sludge, *Bioresource Technology*, **217**, 233-238.

American Public Health Association, (2005), *Standard methods for the examination of water and wastewater*, 21st Edition, American Public Health Association/American Water Works Association, Water Environment Federation, Washington DC.

Barreto dos Santos W.R., Foletto E.L., Mazutti M.A., Cancelier A., Jahn S.L., (2016), Removal of phosphorus from waste of a beverage industry by struvite precipitation, *Environmental Engineering and Management Journal*, **15**, 2505-2509.

Bouropoulos N.C., Koutsoukos P.G., (2000), Spontaneous precipitation of struvite from aqueous solutions, *Journal of Crystal Growth*, **213**, 381–388.

Chetan K.C., Mihirkumar J.J., (2014), Growth and characterization of struvite-Na crystals, *Journal of Crystal Growth*, **401**, 221-226.

COM 297, (2014), Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the Review of the List of Critical Raw Materials for the EU and the Implementation of the Raw Materials Initiative, European Commission, Brussels, On line at: https://ec.europa.eu/transparency/regdoc/rep/1/2014/EN/1-2014-297-EN-F1-1.Pdf

Darwish M., Aris A., Puteh M.H., Jusoh M.N.H., Kadir A.A., (2016), Waste bones ash as an alternative source of P for struvite precipitation, *Journal of Environmental Management,* **203**, 861-866.

Diwani G.E., Rafie S.E., Ibiari N.N.E., El-Aila H.I., (2007), Recovery of ammonia nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer, *Desalination*, **214**, 200–214.

Franz M., (2008), Phosphate fertilizer from sewage sludge ash (SSA), *Waste Management*, **28**, 1809-1818.

Frost R.L., Weier M.L., Erickson K.L., (2004), Thermal decomposition of struvite, *Journal of Thermal Analysis and Calorimetry*, **76**, 1025-1033.

GD, (2004), Governmental Decision No.344/708 regarding the approval of technical standards on environmental protection and especially of soils when sewage sludge is used in agriculture, published in *Romanian Official Monitor*, No. 344 from 16th of August 2004, Bucharest, Romania.

Heffer P., Prud'homme M., (2014), *Fertilizer Outlook 2014–2018*. 82nd Annual Conf. Int. Fertilizer Industry Association, Sydney, Australia May 2014, 1-9.

Heraldy E., Rahmawatui F., Heyyanto H., Poernama P., (2017), Preparation of Struvite from desalination waste, *Journal of Environmental Chemical Engineering*, **5**, 1666-1675.

Hidalgo D., Corona F., Gomez M., Aguado A., Antolin G., (2014), Integrated and sustainable system for multi-waste valorization, *Environmental Engineering and Management Journal*, **13**, 2467-2475.

Huang H., Li B., Li J., Zhang P., Yu W., Zhao N., Guo G., Young B., (2019), Influence of process parameters on the heavy metal (Zn^{2+}, Cu^{2+} and Cr^{3+}) content of struvite obtained from synthetic swine wastewater, *Environmental Pollution*, **245**, 658-665.

Iovi A., Iovi C., (2004), *Ecological Technologies. Chemistry and Technology of Technique Phosphates*, Politehnica Publishing House, Bucharest, Romania.

ISO 6878, (2004), Water quality. Determination of phosphorus. Ammonium molybdate spectrometric method, On line at: https://www.iso.org/standard/36917.html

Jaffer Y., Clark T.A., Pearce P., Parsons S.A., (2002), Potential phosphorus recovery by struvite formation, *Water Research,* **36**, 1834– 1842.

Jalali M., Jalali M., (2016), Relation between various soil phosphorus extraction methods and sorption parameters in calcareous soils with different texture*, Science of the Total Environment*, **566**, 1080-1093.

Jeyakumar L., Zhao Y.Q., Hu Y.S., Babatunde A., Zhao X.H., (2019), Modelling high rate p-removal in a two-stage pilot scale alum sludge based constructed wetland system, *Environmental Engineering and Management Journal*, **18**, 359-366.

Kataki S., West H., Clarke M., Baruah D., (2016), Phosphorus recovery as struvite from farm, municipal and industrial waste: Feedstock suitability, methods and pre-treatments, *Waste Management*, **49**, 437–454

Le Corre K., Jones E., Hobbs P., Parsons S.A., (2005), Impact of calcium on struvite crystal size, shape and purity, *Journal of Crystal Growth*, **283**, 514-522.

Lederer J., Laner D., Fellner J., (2014), A framework for the evaluation of anthropogenic resources: the case study of phosphorus stocks in Austria, *Journal of Cleaner Production*, **84**, 368-381.

Li B., Boiarkina I., Young B., Yu W., (2016), Quantification and mitigation of the negative impact of calcium on struvite purity, *Advanced Powder Technology*, **27**, 2354-2362.

Łukawska M., (2014), Speciation analysis of phosphorus in sewage sludge after thermal utilization of sludge, *Inzynieria i Ochrona Srodowiska*, **17**, 433-439.

Mattenberger H., Fraissler G., Brunner T., Herk P., Hermann L., Obernberger I., (2008), Sewage sludge ash to phosphorus fertiliser: Variables influencing heavy metal removal during thermochemical treatment, *Waste Management*, **28**, 2709-2722.

Metaxa I., Petrea S.M., Mogodan A., (2019), Balance of phosphorus in two different types of cyprinids polyculture ponds, *Environmental Engineering and Management Journal*, **18**, 1821-1832.

Militaru B.A., Pode R., Manea F., Linul P.A., (2019), Simple and combined acidic extraction of phosphorus from sewage sludge ash, *Revista de Chimie (București)*, **70**, 133-139.

Millier H.K., Hooda P.S., (2011), Phosphorus species and fractionation. Why sewage derived phosphorus is a problem, *Journal of Environmental Management*, **92**, 1210-1214.

Moerman W., Carballa M., Wandekerckhove A., Derycke D., Werstraete W., (2009), Phosphate removal in agro-industry: pilot and full-scale operational considerations of struvite crystallization, *Water Research,* **43**, 1887-1892.

Munch E.V., Barr K., (2001), Controlled struvite crystallization for removing phosphorus from anaerobic digester side streams, *Water Research*, **35**, 151-159.

Pastor L., Mangin D., Ferrer J., Seco A., (2010), Struvite formation from the supernatants of an anaerobic digestion pilot plant, *Bioresource Technology,* **101**, 118-125.

Paul I., Varghese G., Ittyachem M.A., (2002), Thermal decomposition studies of struvite, *Indian Journal of Pure and Applied Physics*, **40**, 664-669.

Polat S., Sayan P., (2019), Application of response surface methodology with a Box–Behnken design for struvite precipitation, *Advanced Powder Technology,* **30**, 2396-2407.

Rahman M.M., Liu Y.H., Kwag, J.H., Ra C.S., (2011), Recovery of struvite from animal wastewater and its nutrient leaching loss in soil, *Journal of Hazardous Materials*, **186**, 2026–2030.

Ryu H.D., Kim D., Lee S.I., (2008), Application of struvite precipitation in treating ammonium nitrogen from semiconductor wastewater, *Journal of Hazardous Materials*, **156**, 163–169.

Sano A., Kanomata M., Inoue H., Sugiura N., Xu K., Inamori Y., (2012), Extraction of raw sewage sludge containing iron phosphate for phosphorus recovery, *Chemosphere*, **89**, 1243-1247.

Shiba N.C., Ntuli F., (2017), Extraction and precipitation of phosphorus from sewage sludge, *Waste Management*, **60**, 191-200.

Smol M., Kulczycka J., Kowalski Z., (2016), Sewage sludge ash (SSA) from large and small incineration plants as a potential source of phosphorus - Polish case study, *Journal of Environmental Management*, **184**, 617-628.

Schuiling R.D., Andrade A., (1999), Recovery of struvite from calf manure*, Environmental Technology*, **20**, 765-768.

Tunay O., Kabdasli, I., Orhon, D., Kolcak, S., (1997), Ammonia removal by magnesium ammonium phosphate precipitation in industrial wastewaters, *Water Science Technology*, **36**, 225-228.

UN, (2014), Concise Report on the World Population Situation in 2014, Department of Economic and Social Affairs, Population Division, United Nations.

Wei L., Hong T., Cui K., Chen T., Zhou Y., Zhao Y., Yin Y., Wang J., Zhang Q., (2019), Probing the effect of humic acid on the nucleation and growth kinetics of struvite by constant composition technique, *Chemical Engineering Journal*, **378**, 122-130.

Xu H., He P., Gu W., Wang G., Shao L., (2012), Recovery of phosphorus as struvite from sewage sludge ash, *Journal of Environmental Sciences*, **24**, 1533-1538.

Yan H., Shih K., (2016), Effects of calcium and ferric ions on struvite precipitation: A new assesment based on quantitative X-ray diffraction analysis, *Water Research*, **95**, 310-318.

Yu R., Geng J., Ren H., Wang Y., Xu K., (2013), Struvite pyrolysate recycling combined with dry pyrolysis for ammonium removal from wastewater, *Bioresource Technology,* **132**, 154–159.

Yuanyao Y., Huu Hao N., Wenshan G., Yiwen L., Jixiang L., Yi L., Xinbo Z., Hui J., (2017), Insight into chemical phosphate recovery from municipal wastewater, *Science of the Total Environment*, **576**, 159-171.

Zhang, X., Spanjers H., van Lier J.B., (2013), Potentials and limitations of biomethane and phosphorus recovery from sludges of brackish/marine aquaculture recirculation systems: a review, *Journal of Environmental Management*, **131**, 44-54.