Lighting the anaerobic digestion process in rural areas: struvite from cattle manure digestate

Lighting the anaerobic digestion process in rural areas: struvite from cattle manure digestate

Liliana del Pilar Castro-Molano[*], *Kenia Paola Vecino-Gutiérrez*[**], *Luisa Jasbleidy Diaz- Moyano*[***], *Jaime Jaimes-Estévez*[****], *Humberto Escalante-Hernández*[*****]

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ABSTRACT

The aim of this research was recovery nutrients (PO_4^{3-} and NH_4^+ ions) in form of struvite, used cattle manure digestate from low cost anaerobic digester. In order to determinate operating variables (Mg_2^+: PO_4^{3-} molar ratio, reaction time and stirring speed) an experimental design was developed. Struvite crystal was identified by mean of petrographic microscopy and infrared radiation. The highest recovery rates of 55±4.94 % and 58±7.72 % for NH_4^+ and PO_4^{3-}, respectively was achieved at 1.5 molar ratio, 50 minutes reaction time and 450 rpm stirring speed. Struvite yield was 295.75 mg/L. These results show that the highest phosphate recovery is achieved with the magnesium concentration (153 mg/L) contained in the cattle manure digestate.

Key words: cattle manure, digestate; household digester; struvite.

RESUMEN

El objetivo de esta investigación fue obtener estruvita a partir del digerido de un digestor rural, alimentado con estiércol bovino. Con el fin de determinar las variables de operación para recuperar estruvita (iones PO_4^{3-} y NH_4^+), se desarrolló un diseño de experimentos, en el cual se evaluó el efecto combinado de la relación molar de Mg_2^+:PO_4^{3-} (1.5:1, 2.5:1 y 3.5:1), tiempo de reacción (10, 50 y 90 min) y velocidad de agitación (100, 450 y 800 rpm). Las condiciones determinadas como favorables fueron relación molar 1.5, tiempo de reacción 50 min y una velocidad de agitación de 450 rpm. Estos resultados muestran que la recuperación de fosfato más alta es alcanzada el contenido de Mg ya presente en el digerido de estiércol bovino (153 mg/L). Los porcentajes de recuperación obtenidos fueron 55 ± 4.94 % y 58 ± 7.72 % para NH_4^+ y PO_4^{3-} respectivamente. La formación y composición de cristales de estruvita se confirmó mediante microscopia petrografía, microscopía electrónica de barrido (SEM) y radiación infrarroja. El rendimiento de estruvita obteniendo fue 295.75 mg/L de digerido utilizado.

Palabras clave: digestor; digerido; estiércol bovino; estruvita.

[*] PhD. Ingeniería química, Universidad Industrial de Santander, Cra 27 Calle 9 Ciudad Universitaria, licasmol@uis.edu.co.
[**] Ingeniera Química, Universidad Industrial de Santander, Cra 27 Calle 9 Ciudad Universitaria, Kenia.vecino@gmail.com.
[***] Ingeniera Química, Universidad Industrial de Santander, Cra 27 Calle 9 Ciudad Universitaria, jasbleidy.1126@gmail.com.
[****] MSc Ingeniería Química, Universidad Industrial de Santander, Cra 27 Calle 9 Ciudad Universitaria, jaime.jaimes@correo.uis.edu.co.
[*****] PhD. Ingeniería química, Universidad Industrial de Santander, Cra 27 Calle 9 Ciudad Universitaria, escala@uis.edu.co.

RESUMO

O intuito desta investigação foi obter estruvita partindo do digerido de um digestor rural, alimentado com esterco bovino. A fim de determinar as variáveis de operação para recuperar a estruvita (íons PO_4^{3-} e NH_4^+), foi desenvolvido um delineamento experimental, no qual foi avaliado o efeito combinado da razão molar de Mg_2^+: PO_4^{3-} (1.5:1, 2.5:1 e 3.5: 1), tempo de reação (10, 50 e 90 min) e a velocidade de agitação (100, 450 e 800 rpm). A combinação de condições determinadas como favoráveis foram: relação molar de 1.5, tempo de reação de 50 minutos e velocidade de agitação de 450 rpm. Estes resultados indicam que a maior recuperação de fosfato é obtida com a concentração de magnésio (153 mg / L) contida no esterco bovino digerido. As porcentagens de recuperação obtidas foram de 55 ± 4.94% e 58 ± 7.72% para NH_4^+ e PO_4^{3-} respectivamente. A formação e composição de cristais de estruvita foram confirmadas por meio de microscopia de petrografia, microscopia eletrônica de varredura (SEM) e radiação infravermelha. O rendimento da estruvita obtida foi de 295.75 mg /L de digerido utilizado.

Palavras chave: digestor; esterco bovino; estruvita; matéria digerida.

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INTRODUCTION

Low-cost digesters are part of an attractive technology for anaerobic waste treatments in developing countries. There are a number of advantages to small-scale biogas production on farms, including savings on firewood or fossil fuels and reductions in odour and greenhouse gas emissions. Currently in Latin America, there are approximately 1.000 low cost digesters installed, with a capacity ranging from 2 to 100 m^3 (Martí-Herrero, *et al.*, 2016). These systems are mainly fed with cattle manure to produce biogas (a CH_4-CO_2 mixture) which is mainly used to cook (Kinyua, Ergas, & Rowse, 2016). Anaerobic digestion (AD) produces biogas (30% of the digestion product) and digestate or biogas sludge that corresponds to 70%. In the last decades, AD is energy focused contrasting with a low attention on nutrient recovery. The biogas sludge contains most of the nutrients (N and P) of the original substrate (Rivera *et al.*, 2012).

Nowadays, the use of digestate in developing countries has been focused on direct applications or using phase separation (liquid portion and solid portion). However, the agronomic uses previously described are limited because of pollution risks, storage and transport cost (Warnars & Oppenoorth, 2014). Pollution problems may be microbiological, physicochemical and agronomic. Among these inconveniences, the most highlighted are methane emissions, nutrient lixiviation, young seedling loss, phytotoxicity problems, salinization risks, nutrient competition and the presence of pathogenic agents (Moreno *et al.*, 2014).

In this sense, the continuous increase in fertilizer prices (mainly formed of N, P and K) has raised interest on nutrient recovery from digestate. The use of anaerobic digestates as organic fertilizer or soil conditioner seem to be the best option for nutrient recycling (Romero-Güiza *et al.,* 2015). Anaerobically digested cattle manure is rich in ammonium, orthophosphates, and magnesium (Castro *et al.*, 2017), indicating its high potential for struvite recovery.

Struvite precipitation is a useful process for both N and P recovery, where research is done to investigate the feasibility of using magnesium by-products as cost-effective Mg_2^+ source. The slower nutrient leaching loss and its fertilizer quality make struvite an eco-friendly fertilizer.

Struvite is formed based on an NH_4^+, Mg^{2+} and PO_4^{3-} equimolar concentration in accordance with the following reaction:

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

Struvite formation occurs in two stages: nucleation and crystal growth. Predicting or controlling these mechanisms is complex since they are controlled by a combination of physical–chemical parameters such as pH of the solution from which struvite precipitates, supersaturation, mixing energy, temperature, presence of foreign ions (Ca^{2+}), Mg^{2+}: PO_4^{3-} ratio and reaction time (Pastor *et al.,* 2010; Ariyanto, Sen, & Ang, 2014).

Production of struvite from digestates and its utilization as fertilizer provides benefit in several ways: (i) reduction of eutrophication hazard in the water bodies by removing nitrogen and phosphorus, (ii) mitigation of N_2O emission as compared to urea (1/3) due to slow releasing nature (Hussein, 2014), (iii) sustainable phosphorus recovery (production to replace increasingly scarce and more expensive phosphate rock) and reuse (Cordell *et al.,* 2011).

The Mg^{2+} is the limiting reagent for struvite formation, because this ion is related with the P recovery, since P is the most attractive nutrient to be recovered (higher cost). Struvite precipitation technique has been applied to several substrates (table 1). $MgCl_2$, Mg $(OH)_2$ and MgO are among the most used Mg^{2+} precursors at different degrees of purity (Battistoni *et al.*, 2002; Romero-Güiza *et al.*, 2015).

The small scale decentralised operations are emerging technologies to nutrients recovery, such as developments to precipitate struvite from source-separated urine from household digester in Sweden (Ganrot, Broberg, & Bydén, 2009) and Nepal (Neset & Cordell, 2010). Regarding to household biogas digesters in Latin America, knowledge about nutrient recovery through struvite precipitation from low cost digestate is limited. This is due to the lack of information about the benefits of struvite as a fertilizer, its value on the market, and problems related to the crystallization process such as the need to control the pH and the cost of reagents.

According to the scenario described above, it is necessary to adapt a nutrient recycling technology that can be implemented in rural zones to manage and valorise the digestate produced in rural digesters. The aim of this research was to determine the operating conditions to precipitate struvite from a real digestate obtained in a household digester.

METHODOLOGY

Description of the location and digester characteristics

This study was conducted at a farm named "Finca Marcella" (9 Hectares), located in Santander, Colombia, 9 km from the urban Zone, at a 959-m.a.s.l. altitude (Lat. N 7° 01 '0.07' Long. W 73°08' 13.3") with a 692-mm/m^2 of average precipitation and a 23±5°C room temperature. The farm has a tubular low-cost digester that uses cattle manure as substrate (figure 1). Table 2 summarizes the design parameters of the digester.

The digester reaches an average biogas production of 0.85 m^3/d with a CH_4 content of 65.6%. Additionally, the process generates 0.14 m^3/d of digestate, which its main nutrients content were Mg^{2+}: 153 mg/L; NH_4^+: 123 mg/L and PO_4^{3-}: 338 mg/L (Castro *et al.*, 2017).

Experimental design and statistical analysis

To evaluate struvite precipitation potential, digestate samples were collected weekly (for one month) and they were refrigerated at 4 °C.

Aiming to evaluate the effect of the variables that influence struvite precipitation, the study used a 2^3 factorial design with a central point. Each assay was carried out by triplicate. Three variables were co-related at high (+1) and low levels (-1): Reaction time (10; 90 min), stirring speed (100; 800 rpm) and a Mg^{2+}:PO_4^{3-} molar ratio (1.5:1; 3.5:1) (table 3 shows all experimental units). $MgCl_2$ was used as a source of Mg^{2+}. The molar ratio, stirring speed and reaction time used were chosen in accordance to what was reported in the literature (Ariyanto, Sen, & Ang, 2014; Barbosa *et al.*, 2016; Doyle & Parsons, 2002; Taddeo, Kolppo, & Lepistö, 2016). The experiments were conducted in 500 mL beakers (200 mL volume of work).

From the results obtained in the experimental design, a new assay (batch experiment by triplicate) was conducted in order to validate nutrient recovery percentages (PO_4^{3-} and NH_4^+) at a higher scale. This validation was performed in a 0.002 m^3 polypropylene reactor (1 L volume of work with a 0.130 m diameter).

Response surface and statistical analyses were conducted using a trial version of Stat graphics Software for Windows 7. The performance of the model suggested was evaluated based on PO_4^{3-} recovery percentage.

Description of struvite precipitation process

First, the phosphorus sedimentation was estimated: a test was conducted (blank) which was not stirred and Mg^{2+} was not added. Some samples were analyzed at different times (0.5, 1 and 24 h) in order to estimate the PO_4^{3-} recovery. Secondly, the effect of the variables defined in the experimental design was evaluated: digested matter samples were filtered (0.1 mm mesh sieve) and the liquid phase was stored to future analysis. As a pre-treatment, the study followed the methodology proposed by Zhao *et al.*, (2010). In this case, a pH treatment was conducted to protonate the phosphate ions found in the sample. Then, $MgCl_2$ was added to the different Mg^{2+}: PO_4^{3-} molar ratio and increased the pH to 9. The Mg^{2+} dose was calculated based on the starting PO_4^{3-} concentration. After that, the solution was stirred during the reaction time established in the experimental design and it was allowed to sediment during 30 minutes (Barbosa *et al.*, 2016).

Once the sedimentation time finished, crystals were separated from the liquid (residual digestate). The liquid was poured into another recipient and the precipitated crystals remained in the recipient used at the beginning. The crystals were collected in Petri dishes and finally dried in an incubator at 36±1°C, for further analysis.

Phosphate has a lower concentration in digestate, compared to the Mg^{2+} and NH_4^+ ions concentrations. Therefore, PO_4^{3-} acts as a limiting reagent and indicated the maximum amount of struvite that could be formed

Table 1. Struvite precipitation from different substrates.

Substrate	Mg^{2+} sources	Mg^{2+} to PO_4^{3-} molar ratio	Type of reactor and process conditions	% of PO_4^{3-} recovery	Reference
Municipal wasatewater	LG-MgO	3.6	1 L beaker with stirring at 120 rpm and 240 minutes	96	Quintana *et al*., (2005)
Digested Swine manure	$MgCl_2$	1	Conical bottom reactor with 750 rpm magnetic stirring, during 30-minutes.	>90	Quintana *et al*., (2008)
Cochineal insects processing	**LG-MgO	3.7	0.45 L beaker with stirring	100	Uysal, Yilmazel, & Demirer, (2010)
Digested cattle manure	*	1.02	Batch reactor with magnetic stirring, addition of Ethylenediamine-tetra-acetic acid (EDTA) and pH adjustment	62	Zhao, *et al*., (2010)
Waste Waters	MgO	1.6	CSTR Reactor with magnetic stirring at 120 rpm (1 hour) and airing system to increase pH	90	Etter *et al.,* (2011)
Digested Swine manure	Mg Anode	*	CSTR Reactor with a pH measuring system and a pair of electrodes, 70 minutes of magnetic stirring (150 rpm).	93	Huang *et al.*, (2016)
Piggery wastewater	Struvite pyrolysate	2.5	Jar with an airtight lid and stirring during 10 minutes.	96	Huang, Xu, & Zhang, (2016)
Human urine	MgO	1.1	Cylindrical propylene reactor with a conical bottom and an external filtering system. 10-minute manual stirring (60 rpm).	90	Taddeo, Kolppo, & Lepistö (2016)

Table 2. Design parameters of the digester studied.

Parameters		Unit	Value
Ditch dimensions	top width	m	1
	bottom width	m	0.8
	length	m	7.5
	depth	m	1
Diameter		m	1.3
Length		m	7.5
Digester Volume		m^3	9.5
Reservoir		m^3	5.1
Operating time		24	months

Table 3. Experimental design matrix to recover struvite.

Mg^{2+}: PO_4^{3-} molar ratio (mol/mol)	stirring speed (rpm)	reaction time (min)
1.5	800	10
1.5	100	90
1.5	450	50
1.5	800	90
1.5	100	10
2.5	800	50
2.5	450	90
2.5	450	10
2.5	100	50
2.5	450	50
3.5	100	90
3.5	100	10
3.5	800	10
3.5	450	50
3.5	800	90

(Escalante *et al.*, 2018). Thus, phosphate recovery percentage was taken as response variable in the experimental design and in the blank test.

The percentage of nutrient recovery (PO_4^{3-} and NH_4^+) was calculated having into account the initial and final PO_4^{3-} and NH_4^+ concentrations during the struvite precipitation process (photometric methods: APHA 4500-NH_3 y APHA 4500-P E (APHA, 2005). To calculate the percentage of nutrients recovery, equation (1) was proposed:

$$(1) \quad Recovery\ \% = \frac{[concentration]_{\text{starting}} - [concentration]_{final}}{[concentraion]_{\text{starting}}} * 100$$

It is important to mention that NH_4^+ content was determined only in the experiment with the most favorable conditions, because it is one of the main nutrients in struvite precipitation. The experiments were conducted at room temperature and at atmospheric pressure.

Qualitative and Quantitative Analysis of Struvite Crystals

Qualitative and quantitative analyses were carried out for the precipitated obtained from the most favorable conditions. This precipitate is a measurement of the nutritional potential that digestate has for struvite precipitation. Whereby crystals were determined using qualitative analysis. The petrographic analysis was the description of the samples collected using a petrographic microscope with polarized light (LEICA DM750). Crystals were also characterized using infrared radiation with an FTIR-8400S infrared using Fourier Transform. Quantitative analysis corresponds to determining the struvite potential (SP). This estimate was made based on the following equation (Equation 2).

$$(2) \quad SP = \frac{Mass_{precipitated}}{Volume_{digestate}}$$

Where $Mass_{Struvite}$ is the struvite mass and $Volume_{digestate}$ corresponds to digestate volume.

Economic potential of struvite precipitation

Based on the experimental results and theoretical yields of struvite precipitation reached in this study, an economic analysis was performed. Struvite would be precipitated without using stirring and a magnesium source, and pH adjustment with HCl and NaOH according to the methodology described by Zhao *et al.,* (2010). The cost of equipment for capital expenditures (CAPEX) calculation was considered based on the Colombian market for 2018 (personal communication). The other assumptions for operating expenses (OPEX) calculation were based on the data reported by Yetilmezsoy *et al.,* (2017) and Tao *et al.*, (2016). The economic components used in the calculation of the total investment costs are presented in Table 4. Economic aspects included the biogas supply for cooking food.

RESULTS

PO_4^{3-} and NH_4^+ recovery as struvite from biogas digestate

The digestate from the cattle manure studied contained dissolved ion concentrations of Mg_2^+(6 mM), PO_4^{3-} (4 mM), NH_4^+ (7 mM) and Ca^{+2} (22 mM) and Mg^{2+}:PO_4^{3-} molar ratio equal to 1.5 with a pH around 7.37 ± 0.23. These characteristics promoted phosphorus sedimentation, reflected in the percentage removal of PO_4^{3-}without adding chemical reactive and with 0 rpm (figure 2). Digestate pretreatment was not necessary due to total solids were 9.93 g/L. Previous studies suggest a pretreatment for digestates with total solids between 15-92 g/L (Tao, Fattah, & Huchzermeier, 2016).

In struvite precipitation processes, the highest recovery percentages can be seen from hour 16 to hour 25, about 80% to 93% and 88% to 93%for NH_4^+ and PO_4^{3-} respectively (Lee *et al*., 2015; Rahman, *et al*., 2014; Ryu & Lee, 2010). In this study after 24 hours, a 26% PO_4^{3-} recovery was obtained, figure 2. This percentage represented low process performance; therefore, it was recommended to increase precipitation time. Nonetheless, a technical-economic analysis must be conducted to decide if the spontaneous process is profitable and suitable to manage (Escalante *et al*., 2018).

Co-relation of the variables implicated in the Struvite Precipitation Process

The effects of the operating variables were modeled statistically with adjustment near to 95%, results of model are observed in figure 3. These results show favorable process conditions at Mg^{2+}:PO_4^{3-} molar ratio of 1.5, a 450 rpm stirring speed and a 50 minute reaction time.

The most influential variable in PO_4^{3-} recovery was a Mg^{2+}:PO_4^{3-} ratio (1.5) with a reliability of 95%. These results show that the highest phosphate recovery is achieved with the magnesium concentration (153 mg /L) contained in the cattle manure digestate. Based on above, a supplement $Mg^{2+}$was not necessary and the pH changes were the struvite promoter. Similar results were described by Tao, Fattah, & Huchzermeier (2016).

Using a stirring speed of 450 rpm, and reaction time of 50 min, the PO_4^{3-} and NH_4^+ recoveries were around

Figure 1. Tubular digester setup located on "Marcella" farm.

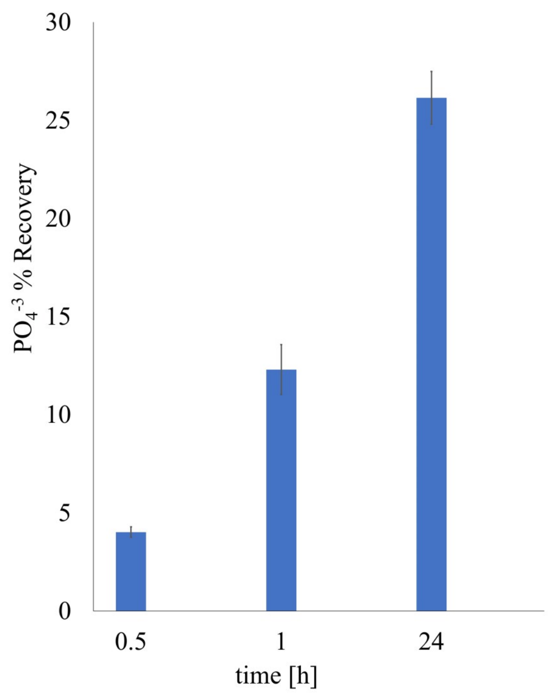

Figure 2. Phosphate ion recovery (as percentage) through spontaneous struvite precipitation. Bars represents standard deviation.

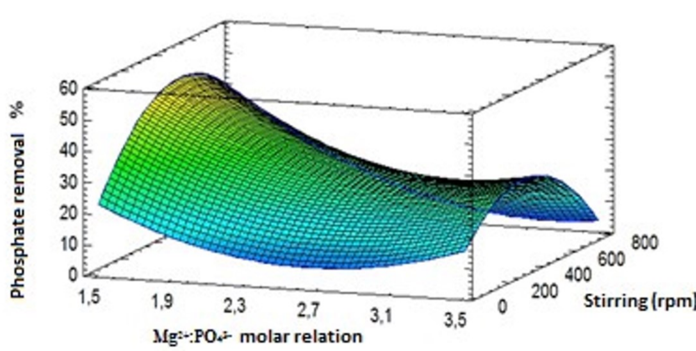

Figure 3. Surface response of the experimental PO_4^{3-} recovery design.

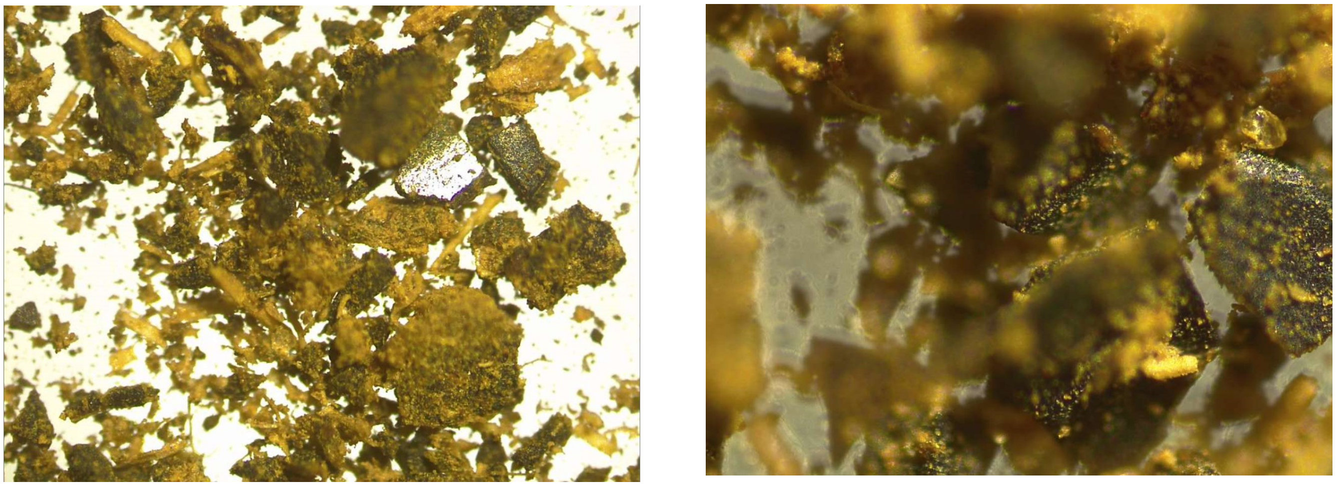

Figure 4. Micrographs of precipitate obtained from optimal conditions assay. **A:** Non-polarized light at 4x magnification; **B:** Non-polarized light at 10x magnification.

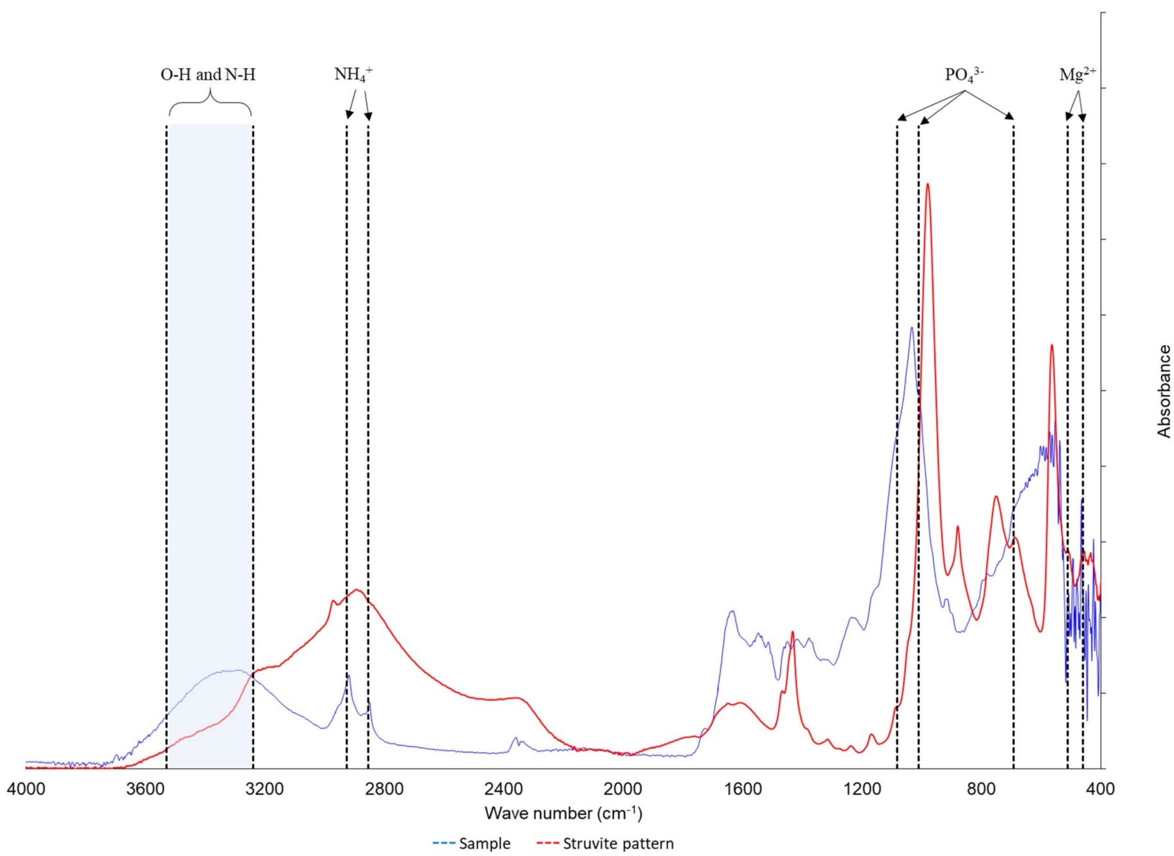

Figure 5. Infrared Radiation spectra of precipitate obtained of the optimal conditions assay (using FTIR-8400S infrared equipment).

Table 4. Economic parameters and assumptions for the economic study.

Parameter	Unit	Value
Assumptions for CAPEX calculation		
Equipment for struvite precipitation	US$	1000
Storage equipment	US$	1160
Assumptions for OPEX calculation		
Struvite	US$/kg	1.88
Biogas	US$/$m^3$	0.65
NaOH	US$/kg	0.503
HCl	US$/L	3.4
Assumptions for NPV calculation		
Equipment life	Year	7
Inflation	%	4
Discount rate i	%	6
Digestate flow	m^3/d	0.14
PPS	$g_{\text{struvite}}/L_{\text{digestate}}$	0.29

55±4.94 and 58±7.72 %, respectively. Calcium concentration is a hindered for struvite formation, hence phosphate precipitation could had been affected (Pastor *et al.,* 2010). Thus, the effect of the Mg^{2+}:PO_4^{3-} relation in the digestate allowed a magnesium-content supersaturation of the medium, and it was favorable to allow the first crystal seed (primary nucleation) (Mehta & Batstone, 2013). Literature reports PO_4^{3-} recoveries from 60% to 83% for cattle -manure digestate. Nevertheless, yields in these studies were reached as a result of pre-thermochemical treatments using microwaves and adding sources of Mg^{2+} and PO_4^{3-} (Jin, Hu, & Wen, 2009; Zeng & Li, 2006).

Precipitate Characterization and Identification

Petrographic microscopic analysis evidenced possible struvite formation (figure 4). 4A and 4B images correspond to the passing of non-polarized light at 4x and 10x magnification, respectively. With this preliminary assay is possible to observe crystal formation that could be struvite (figure 4) and some impurities that can be attributed to the type of substrate used and type of sampling. Because of the low availability of researches on struvite analysis using petrographic microscopy, results could not be compared.

Microscopic images showed that the form of the precipitate was not uniform. Chauhan & Joshi (2013) conducted a study on struvite growth. In that study, the authors stated that struvite could be found in different morphologies (drawer shaped, pyramidal, prismatic, needle-shaped, feather shaped, etc.) which strongly depend on growth parameters (Chauhan & Joshi, 2013). These images in figure 4 agree with the research studies on struvite crystallization (Heraldy *et al*., 2017; Barbosa *et al*., 2016).

Figure 5 shows an infrared spectrum of struvite crystals obtained under the favorable operating conditions (Mg^{2+}:PO_4^{3-}:1.5; 450 rpm; 50-min), compared to a struvite pattern (Stefov *et al.,* 2005). The spectrum shows the absorption bands corresponding to the different elements or components found in the crystal. The absorptions that take place in the range 3240 to 3529 cm^{-1} are due to vibrations resulting from O-H and N-H elongation. This also suggests the presence of hydration water. The absorptions produced in 2854±1 and 2925±1 cm^{-1} are due to the NH_4^+ ion. The observations that take place in 511±2, 1010±1 and 1083±2 cm^{-1} correspond to PO_4^{3-} ions and the peak produced at 461±1 y 691±1 cm^{-1} take part of Mg-oxygen bonds (Chauhan *et al*., 2008).

Previous struvite precipitation studies based on human urine presented absorptions that occurred in (2920.9, .2970 and 2889.26 cm^{-1}), (500, 1006 and 1064.5 cm^{-1}), (683.97 and 509.4 cm^{-1}), and (3276.9 to 3520.6) correspond to NH_4^+, PO_4^{3-}, Mg^{2+} and H_2O respectively (Kurtulus & Tas, 2011; Muryanto, Sutanti, & Kasmiyatun, 2016). The values obtained in literature are related to the ones obtained in the present study, proving the presence of these ions as struvite.

In addition, struvite was analyzed quantitatively. Struvite potential in this research was 297.75 mg struvite/L from the digestate used. Results confirm that cattle manure digestate has high nutritional potential for struvite precipitation thanks to its high nutrient content (PO_4^{3-} and NH_4^+). In comparison with the results obtained in the present study, Jaffer *et al.,* (2002), reported a struvite potential of 198 mg/L and 140 mg/L at a pH of 9, for mud digested matter and centrifuged wastewater liquor, respectively.

With the results previously obtained, the presence of struvite was proven. Therefore, it is possible to recycle nutrients (Mg^{2+}, PO_4^{3-} and NH_4^+) available in cattle manure digested matter. In this study, researchers adapted a low-cost struvite precipitation process (without adding Mg source, and with low energy use) so that it may be profitable and suitable for biogas digester users.

Economic consideration

The household digester is located in a rural area (difficult to access due to tertiary roads). This digester provides both biogas and digestate. The net present value (NPV) was USD $ 40/year. In this case, biogas is used for cooking with propane saving around USD $ 75/month (purchasing and transporting costs). Concerning to digestate, it could be used to precipitate struvite which represents fertilizing saving around USD $ 94/month (purchasing and transporting costs).

CONCLUSIONS

The optimal operation conditions to nutrients recovery from real digestate via struvite precipitation were determined by a composed central design. A statistical analysis revealed that the maximum phosphate recovery was obtained at a Mg^{2+}:PO_4^{3-} molar ratio of 1.5 (this ratio don't require external source of Mg^{2+}), with a 450 rpm stirring speed and a 50 minute reaction time. The results are quite promising, due to Mg^{2+} content in cattle digestate is favorable for phosphate recovery through struvite precipitation at the optimal settings. Under these conditions, the study reached a recovery of 55±4.94 and 58±7.72 % of PO_4^{3-} and NH_4^+ respectively. The petrography and infrared spectrum analyses confirmed that the precipitate formed was struvite with some impurities.

In agreement with the present research, household digester presents an integrative solution to cattle manure management. In this case, the low cost digester was fed with 50 kg/d of cattle manure to produced renewable energy in form of biogas (0.85 Nm^3 biogas/d with 65.6% methane), and to recycle nutrients as struvite, providing energy and fertilizer savings of 76% and 80% (using all digestate volume for crop irrigation), respectively.

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