"Application of iron oxide powder for the reduction of hydrogen sulfide in the biogas from a dry anaerobic digester "

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Abstract

This work presents the results obtained in a case study on the application of powder iron oxide for the control of hydrogen sulphide in a dry anaerobic digester during the implementation of LIFE ANADRY project (ENV / ES / 000524). The test was carried out on a 20 m^3 anaerobic reactor with the capacity to treat up to 3 ton/day of dehydrated sludge of a sewage treatment plant. The reactor was equipped with a membrane gasometer on the top, electrical resistance and heating jacket for temperature control. It also has a biogas line with pressure sensor and biogas counter.

During the study, different doses of iron oxide powder were applied depending on the hydraulic retention time of the digester and the sulphide concentration in the biogas. The results obtained made it possible to determine that it is possible to keep the sulphide concentration in values below 500 ppm by adding between 2-3 kg /day for a TRH between 30 and 15 days. Also, the operational and environmental risks associated with the use of this material were found to decrease drastically compared to those of ferric chloride. During the study the amount of iron oxide was optimized and the time remained in the system in order to avoid dosing of iron powder was determined. During the test, the concentration of biogas was analyzed, noting that the values of methane (CH_4) and carbon dioxide (CO_2) in the biogas were not affected after the addition of this product.

Keywords: anaerobic digestion, sulphide, iron oxide, biogas

1. Introduction

The anaerobic processes used to treat the sludge generated in WWTP presents a number of technological challenges associated with the biogas quality, the sanitation and the stability of the digested sludge. Regarding biogas, there are several compounds that can cause partial or total inhibition of the biological process. This inhibition is mainly associated with high ammonia nitrogen concentrations in the form of free ammonia, hydrogen sulfide (H_2S) and other undesired compounds within the digester.

In the case of hydrogen sulfide (H_2S), this compound is formed by the action of Sulfate-Reducing Bacteria (SRB) present in the system that are very versatile, from several families and categories. They use sulfate or other sulfur oxidized compounds as final electron acceptor for H_2S production. They can grow heterotrophically using low molecular weight organic molecules and in an autotrophic way using hydrogen and carbon dioxide (Nagpal *et al.,* 2000; Lens & Kuenen, 2001). SRB are easily adapted to different environments, mainly those where oxygen has been depleted due to the anaerobic decomposition of organic matter. They are mainly found in anoxic or anaerobic environments rich in sulfates.

SRB are known to appear in groups of microorganisms involved in the anaerobic digestion process, widely used for wastewater treatment. During the high sulphate levels wastewater treatment, they compete with fermentative or acidogenic bacteria for the products of hydrolysis, with acetogenic bacteria for intermediate substrates such as volatile fatty acids and alcohols, and with methanogenic bacteria for less complex substrates such as hydrogen and acetate. The result of this competition is important because it determines the final mineralization products yield (sulfide and methane) (Lens *et al.,* 2000). The activity of the SRB depends mainly on the availability of sulfate (Espinosa-Chávez,2007).

In practice, many authors have observed that the result of competition between bacteria can be also affected by other factors, such as the ratio between organic matter and sulphate, the substrate type, the presence of trace metals and other nutrients, the inoculum type, the properties of immobilization, the duration of the test, environmental factors such as pH and temperature, and inhibition by sulfides (Patidar & Tare, 2005).

In the anaerobic treatment of wastewater or sludge with high levels of sulfate, it may be affected by the potential toxicity of sulfur as the end product of sulfate reduction to sulfide. Hydrogen sulfide is a toxic compound for almost any bacteria (Lettinga *et al.,* 1988). No dissociated specie (H_2S) is the most toxic sulfur kind because it is a neutral molecule that can break through the cell membrane (González-Silva, 2007). The right mechanism of toxicity has not been elucidated. One possible explanation is the denaturation of proteins by disulfide bridges formation between polypeptide chains.

Another important issue related to the presence of H_2S are odor and corrosion problems among others, which are perceived and observed in the wastewater treatment plants, which are quite recurring problems. In addition to the corrosion and odor problems generated by this compound, some literature (Sears *et al.,* 2004; Bejarano *et al.,* 2013) refer to the possible inhibition of some biological processes developed in WWTP in the presence of sulfides. This is an important point to take into account when developing technologies that combine various processes and where sulfur is present. Sulfur compounds use to appear in wastewater discharges from the petrochemical, textile, tannery, food and paper processing industries. In urban water discharges, sulfur is usually found in the form of sulfate, but in the collectors or during the treatment itself, sulfides can be generated from the reduction of sulfate and can finally cause an inhibition (Sánchez-Ramírez, 2016).

Sulfur concentration control in anaerobic processes is increasingly studied and has focused in recent years on: the oxidation of sulfur to sulfate by adding low concentrations of oxygen (micro-aeration), precipitation using iron salts , mainly ferric chloride, biological desulphurisation or the cleaning of biogas through physical-chemical processes before its recovery as an energy source.

This paper presents the results obtained in a case study where an iron oxide powder has been used to control the H_2S concentration inside a dry anaerobic digester that treats dehydrated wastewater treatment plants sludge. Results obtained show that it is possible to keep the levels of H_2S below 500 ppm dosing between 2-3 kg/day of iron oxide powder, considering the volume of the digester means a dose between 0.10 - 0.15 kg/day·m^3. The easy application of powdered iron oxide allows to minimize the construction of facilities for its dosage and minimizes environmental and health risks.

2. Materials and methods

The trial demonstration environment was carried out within the execution of the LIFE ANADRY project in the urban WWTP of Alguazas (Murcia) (Figure 1), which give coverage to a 60,000 equivalent inhabitants and get an average flow of 3,500 m^3/day urban wastewater. The main biological treatment by which wastewater is treated is prolonged aeration in two carousel-type reactors.

The dry anaerobic digestion prototype is fed from the hopper where the dehydrated sludge from the treatment plant is stored, which is obtained by a centrifugation system. Digester is fed semi-continuously ten times a day, to keep a constant sludge load. The digester gasometer allows monitoring the daily biogas production working at a constant pressure. The pre-industrial prototype has a 20 m^3 cylindrical shaped and horizontal digester, with capacity to treat up to 3 ton/day dehydrated sludge. It also has a dual boiler to make use of the biogas for heating and energy self-sufficiency purposes, and a stirring system that allows the complete mixing of the dehydrated sludge (Figure 1). Prototype has enough capacity to treat up to 25% of the dehydrated sludge produced in the Alguazas WWTP.

Figure 1. Prototype overview

2.1. Analytical monitoring

To evaluate the performance of the process, composition measurements of biogas (CH_4, CO_2, H_2S, O_2, N_2) has been made by gas chromatography once a week (GCTCD HP6890) and daily by portable probe (Biogas 5000 Geotec). Likewise, total solids, volatile solids, volatile fatty acids and alkalinity have been measured. The prototype project has been followed based on weekly measurements of parameters that, in combination with methane content, provide key information on the stability of the process and its metabolic state: pH, total nitrogen ammonia, sulfate (SO_4^{2-}) and total iron. These values and the total/volatile solids data have been determined by methods based on the Standard Methods (APHA, 2005).

2.2. Characteristics of iron oxide powder

Iron oxide powder used corresponds to the Micronox ON16 brand (PROMINDSA Company). It is a mix of iron oxide-hydroxides specially developed to be added directly to the anaerobic reactor. Reacts with hydrogen sulfide to generate iron sulfide and sulphur. Both elements are common components in fertilizers, giving them improved properties. The specific characteristics of the material are shown in table 1. The average content of iron hydroxide (FeOOH) is 72±5% and the size of the particles is less than 10 µm (Figure 3).

Minerales		Fórmula química	wt %	CAS No
Goethita/Hematites		α-FeOOH/ α-Fe_2O_3	> 73	1310-14-1/1317-60-8
Minerales de manganeso		*Óxidos de manganeso anhidros e hidratados*	4.5 (±2)	-
Minerales de arcilla	Illita	$K_{0.7}Al_2[Al_{0.7}Si_{3.3}O_{10}](OH)_2$	5.0 (±2)	12173-60-7
	Vermiculita	$Mg_3[Si_4O_{10}](OH)_2 \cdot 4H_2O$	3.5 (±1)	1318-00-9
	Caolinita	$Al_2Si_2O_5(OH)_4$	3.0 (±1)	1318-74-7
Cuarzo		α-SiO_2	6.0 (±2)	14808-60-7
Magnesita + Dolomita		$MgCO_3 + CaMg(CO_3)_2$	< 2.0	546-93-0 / 16389-88-1
Otros minerales		Minerales accesorios de Ti, P y Zr	< 1.0	-
Agua (humedad)		H_2O adsorbida	< 2.0	7732-18-5

Table 1. General characteristics of iron oxide powder

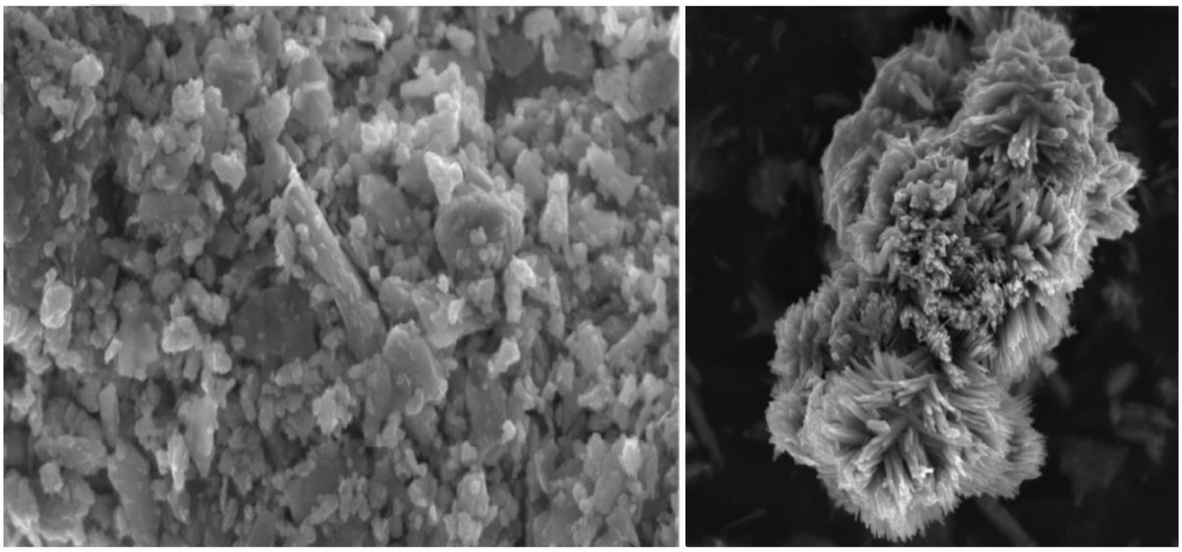

Figure 2. SEM images of powdered iron oxide (200nm -1µm)

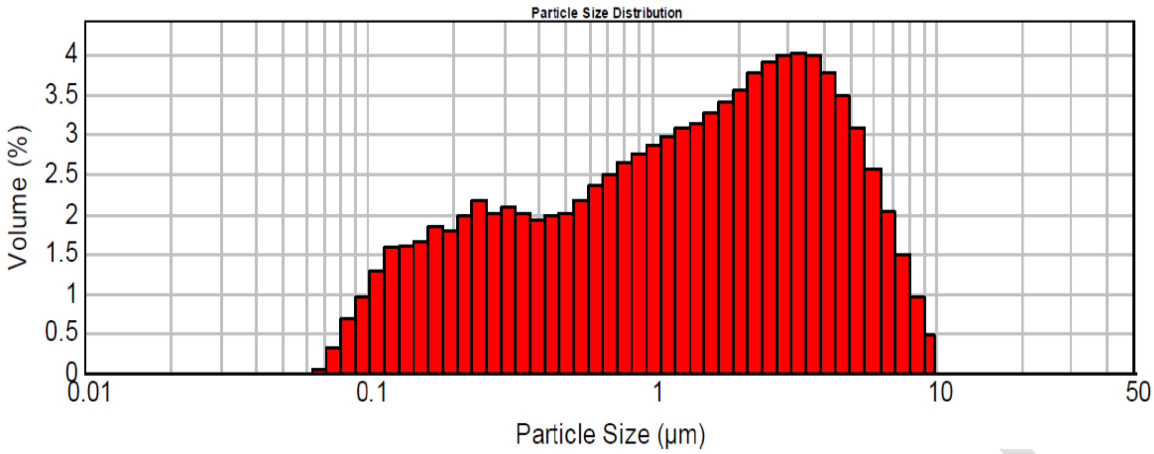

Figure 3. Particle size distribution of iron oxide powder

2.3. Anaerobic digester operation

The anaerobic digester used in this project was operated at two different temperature conditions, mesophilic (35ºC) and thermophilic (55ºC). During the operation, hydraulic retention time effect on the stability of the process in terms of biogas production, biogas quality, reduction of volatile solids and elimination of pathogens was studied. Retention time studied at both temperature conditions were 40, 30, 20, 15 and 10 days, which means working at organic loads between 3.1 and 12.4 kgSV/ m^3·day.

3. RESULTS AND DISCUSSION

3.1. Characterization of the dehydrated sludge

In the current scheme of the WWTP, sludge produced is thickened, dehydrated and then stored in a hopper. Once stored, it is fed to the digester for stabilization and sanitation. The characteristics of the sludge are shown in table 2. Dry matter content was kept between 14-16% throughout the study phase.

Fango deshidratado	
DQO t (mg·L^{-1})	70225 ± 64235
ST (%)	15.5 ± 1.2
SV (%)	76.5 ± 11.9
NT (%)	3.2 ± 2.6
NH4 (mg·L^{-1})	2808 ± 574.7
pH	7.1 ± 0.5
Salmonella sp..	Existente
E.coli (UFC)	7.5 x 10-3

Table 2. Characteristics of dehydrated sludge

3.2. Study of the process under mesophilic and thermophilic conditions

During the start-up of the process under thermophilic conditions, the digester was inoculated with 16 m^3 of thermophilic biomass from an anaerobic digester that treats the organic fraction of urban solid waste (FORSU). Once inoculated, the temperature was adjusted to thermophilic conditions (55 °C). The digester was not fed during the first days and just let it progress until reaching the set temperature.

Subsequently, a dehydrated sludge of 15.3 ± 1.4% ST and 11.7 ± 1.3% SV was fed, with a retention time of 20 days, which produced an increase in volatile fatty acids (VFAs), reaching concentrations of 34 gHAc/L and a decrease in pH to 7.5. In order to control the VFA concentration, retention time was adjusted to 40 days, reducing the load of the pilot digester to 3 kg SV m^3/day. However, the increase in retention time promoted the release of ammonia nitrogen, which reached values higher than 6,000 mgN/L (Figure 3a). This situation resulted in a significant increase in free ammonia, higher than 250 mg N-NH^3/L. H_2S concentration during this period was around 10 g/L, these values being high inside the digester. Some studies suggest (Gao *et al.,* 2015; Karthikeyan *et al.,* 2012) that high concentrations of ammonia nitrogen produced a partial inhibition of the digestion process under thermophilic conditions. Inhibition caused a low biogas production during the operation period with a retention time of 40 days (Image 3b), with values around 2.6 ± 0.5 m^3/day, with a methane concentration of 11.6 ± 7.0% and a mean volatile solids (VS) removal of 14.3 ± 8.0%. In order to solve the inhibition problem, the volumetric organic load was increased, reducing the retention time to 30, 20 and 15 days successively, which contributed to wash the ammonia nitrogen and increasing the methanogenic activity, reaching an average methane composition of 29.6 ± 4%, with a considerable increase in the maximum biogas production of 17 m^3/day (Figure 3b). Operating under thermophilic conditions guaranteed a complete sanitation of Alguazas sludge, with the absence of *Salmonella spp.* and with values of *Escherichia coli* less than 10 CFU/g guaranteeing complete sanitation of the sludge.

The start-up of the process under mesophilic conditions was carried out with inoculum from a mesophilic anaerobic digester from an urban WWTP near Alguazas, with a 1:1 mixture of dehydrated Alguazas sludge and inoculum, until completing 18 m^3 useful volume. Temperature was adjusted to 35ºC and the reactor start-up process consisted of increasing the volumetric organic load by one unit each week, until reaching 5 kg VS m^3/day and a retention time of 20 days.
During the mesophilic process, the reactor has been fed with sludge of 14.0 ± 0.9% of TS and 11.0 ± 0.9% of VS, values slightly lower than the previous process due to variability in the characteristics of wastewater incoming to WWTP Alguazas. pH value remained alkaline at 8.33±0.4, with an lower VFA than the previous process of 4000 ± 1108 mg HAc/L (Figure 3c). Due to the lower temperature used, the total ammonia nitrogen values have remained more stable below 4000 mg N/L. The sulfur concentration during this stage reached maximum values around 6000 mg/L.

During the operation period, with a retention time of 20 and 15 days, a maximum biogas production of around 30 m^3/day has been obtained and an average production of 25.0 ± 5 m^3/day, with a stable methane composition of 61.5 ± 2.7% (Figure 3d). Likewise, the elimination of VS has been much higher than the thermophilic process, with an average value of 30.2 ± 6.5%. It should be noted that there is no presence of *Salmonella spp.* in 25 g of samples, while the values of *Escherichia coli* have been less than 40 CFU/g, pathogens contemplated in Order AAA / 1072/2013.

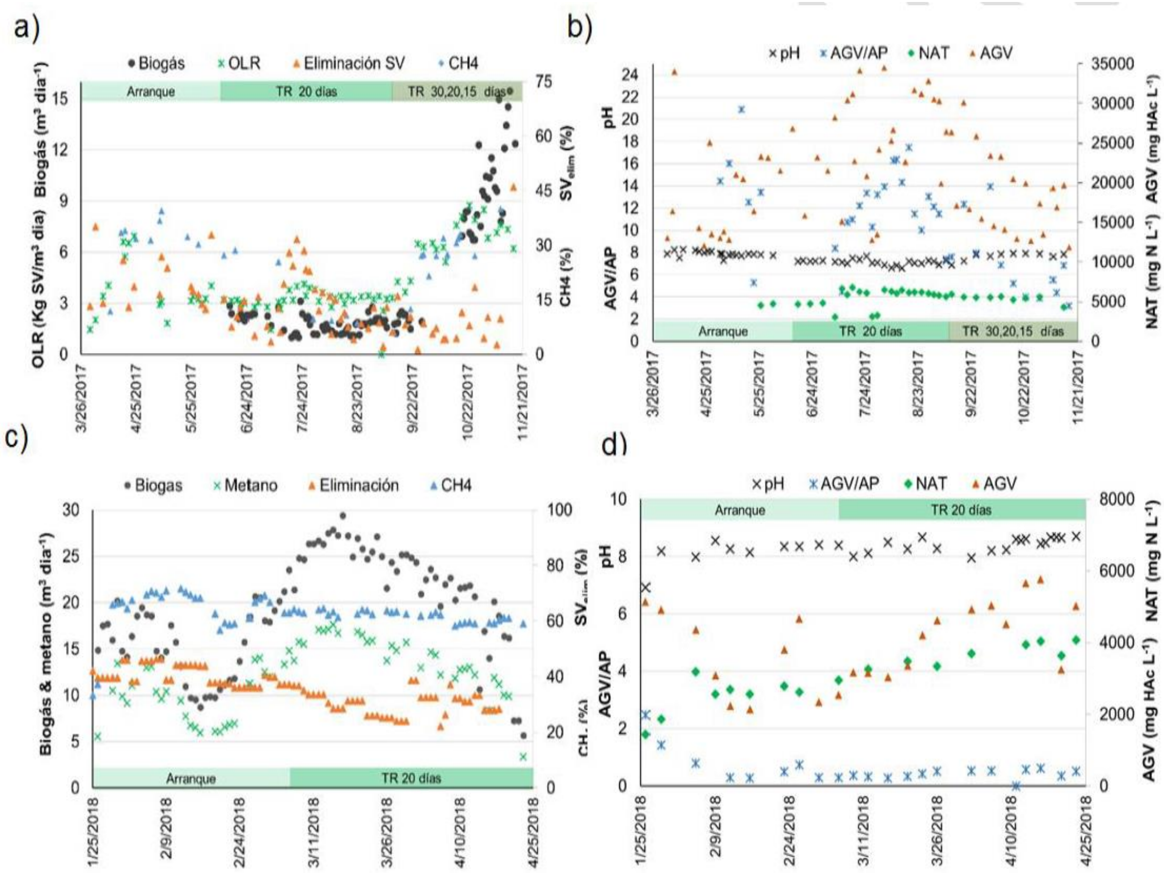

Figure 3. Results and monitoring of the main parameters in the mesophilic phase (a, b) and in the thermophilic phase (c, d).

3.2. Adding iron oxide powder for H_2S control

During the analytical monitoring of the process, an exhaustive analysis of the quality of the biogas obtained was carried out. The characteristics of the biogas before the addition of powdered iron oxide are shown in table 3. A high H_2S concentration in biogas was noted, reaching sometimes values close to 10,000ppm that could compromise the stability of the process. For this reason H_2S must be removed from biogas, in order to minimize the risks associated with corrosion and inhibition of the biological process.

Thermophilic		Mesophilic	
CH_4 (%)	38.7±2.9	**CH_4 (%)**	57.4±6.1
CO_2 (%)	42.5±3.4	**CO_2 (%)**	33.9±0.8
H_2S (ppm)	5400±1200	**H_2S (ppm)**	5578±1626
O_2 (ppm)	0.5±0.3	**O_2 (ppm)**	0.14±0.1

Table 3. Characteristics of the biogas generated in the prototype.

Before adding iron oxide into the system, tests were carried out in order to analyse the compatibility of the product with water and with digested sludge. Objective was to determine possible interferences or unwanted secondary reactions. First test was mixing a quantity of powdered iron oxide with water to check the behavior of this product (figure 4A). 5 grams of product were mixed with 300 ml of water in a beaker, stirred and allowed to precipitate for 30 minutes. As can be seen in figure 4B, the product settle quickly, not being completely miscible with water and leaving a slight reddish color characteristic of the presence of iron in the medium.

Second test carried was adding 5 g of powdered iron oxide to 125 ml of digested sludge (Figures 4 CD). Mixture was stirred with a magnetic stirrer for 15 minutes. The stirring speed applied was 500 rpm. Same test was performed using double (10g) and triple (15g) of iron oxide and the behavior is similar, concluding that iron oxide mixes perfectly with mud without forming any product side effect such as foams or unwanted reactions. Once the agitation is finished, settle of the sludge and the typical reddish coloration in the final mixture are observed.

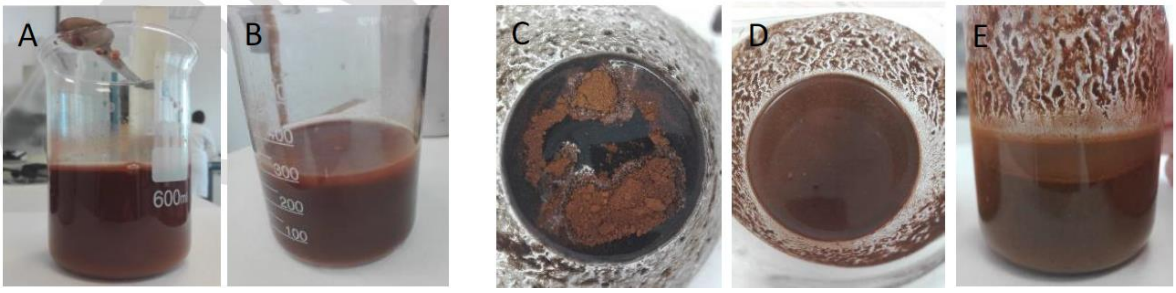

Figure 4. Compatibility tests with water (AB) and digested sludge (CDE).

After this, the product was incorporated into the dry anaerobic digester. According to the manufacturer's recommendations, the optimal dose depends on the retention time of digester and initial and final H_2S concentration. Table 4 shows the dose used in the digester as a function of retention time for both temperature conditions, initial concentration of H_2S remained between 5000-7000 ppm and final H_2S concentration was set at 500 ppm taking into account the requirements of the recovery unit and the usage recommendations from membrane gasometer manufacturer to avoid damage to the membrane.

Figure 5 shows the evolution of H_2S concentration for each retention time studied under mesophilic conditions. Addition of the product allows maintaining H_2S levels below 500 ppm. During retention time of 15 and 12 days, it was decided to decrease the dose of the product in order to evaluate the system response. It was observed that after 24 hours of operation H_2S concentration increased to values around 2000 ppm. However going back to dose recommended by the manufacturer, they quickly reached the values of final H_2S.

On the other hand, results obtained under thermophilic conditions were evaluated only during the 40 day test, observing that the addition of 2.0 kg/day (0.1 kg/day·m^3) of product allows removing more than 90% of the sulfur found in biogas, with final H_2S concentrations between 200 -500 ppm.

Tracking of the total iron content in the digested sludge shown a concentration around 14053 ± 2867 mgFe · KgSM, these values are common in this kind of sludge, which indicates that the addition of iron oxide does not significantly increase the concentration of this element in the digestate.

Iron oxide powder dosage		
Retention time (days)	Quantity (g/day)	Dose (Kg/day·m3)
20	1000	0.050
15	2000	0.100
12	3000	0.150
10	3500	0.175

Table 4. Dose of powdered iron oxide used in the digester.

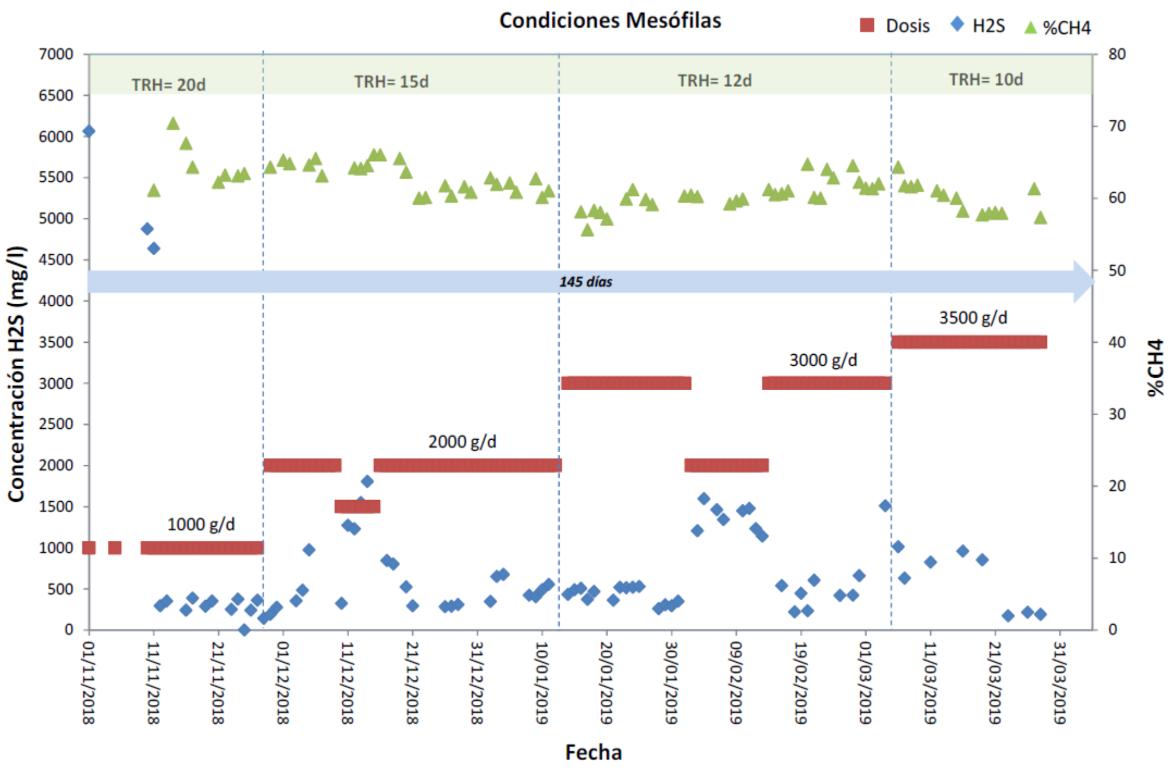

Figure 5. Evolution of H2S concentration under mesophilic conditions.

4. Conclusions

- The conclusions offered by this study allow us to say that the addition of 2.0-3.0 kg/day of iron oxide powder in a 20 m^3 reactor with a retention time between 30-10 days, allows the reduction and significant control of H_2S levels in biogas generated in a dry anaerobic digester. The final H_2S concentration was kept below 500 ppm.
- The addition of the product does not interfere with the anaerobic process and could be an interesting alternative to decrease H_2S in anaerobic digesters (both dry and wet way).
- The addition of the product offers significant improvements related to the infrastructure required for storage and reduces safety and health risks.
- It is necessary to carry out a comparative study between the use of iron oxide and ferric chloride, to determine the feasibility of implementation on a larger scale.

5. Acknowledgments

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