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# ANAEROBIC DIGESTION OF WASTEWATER WITH HIGH SULFATE CONCENTRATION USING MICRO-AERATION AND NATURAL ZEOLITES

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**Abstract -** The behavior of anaerobic digestion in batch and UASB reactors using a microaerobic process and natural zeolites was studied. Laboratory assays were carried out across 4 sets of variables: different $COD/SO_4^{2-}$ ratios, different airflow levels, with and without natural zeolites and room and mesophilic controlled temperatures. The microaerobic process demonstrated hydrogen sulfide removal levels exceeding 90% in most cases, while maintaining the flammable condition of the generated biogas. The level of COD removal exceeded 75% in UASB reactors despite their operation under very low hydraulic retention times (2.8–4.8 hours). The effectiveness of natural zeolites in accelerating UASB reactor startup was demonstrated. Results showing the positive influence of zeolites on the granulation process in UASB reactors were also achieved.

*Keywords*: Granulation process; Micro-aeration; Sulfate; Sulfide; Temperature; UASB; Zeolite.

## INTRODUCTION

The advantages of anaerobic technology in organic matter removal from wastewater have been fully demonstrated in multiple studies and full-scale implementations (Pabón *et al*., 2013; Kothari *et al*., 2014; Zhang *et al*., 2014). However, the successful establishment of the chemical processes involved and the usefulness of the biogas generated therein are significantly affected by the presence of hydrogen sulfide ($H_2S$). $H_2S$ is toxic to methanogenic archea (MA) at relatively low concentrations in aqueous media (more than 50 mg/l) and is very odorous, corrosive and toxic in trace concentrations in its gaseous phase (Omil *et al*., 1996; Peu *et al*., 2012; Ramos and Fernández-Polanco, 2014). The generation of reduced sulfur compounds in the anaerobic process is mainly due to the action of sulfate-reducing bacteria (SRB), which are competing with the microorganisms responsible for the generation of methane in the process.

Due to the previously mentioned problems caused by the presence of hydrogen sulfide in biogas, different technologies have been applied to biogas purification (Cirne *et al*., 2008). For this application, a wide range of physical, chemical and biological methods exist (Abatzoglou and Boivin, 2009; Kobayashi *et al*., 2012; Lin *et al*., 2013). However, it is known that sulfide in the liquid phase can be toxic to MA at certain concentration values depending on several factors such as wastewater characteristics, temperature, pH and others (Cohen *et al*., 1982; Iza *et al*., 1986; Rinzema and Lettinga, 1988; Nanqi *et al*., 2002). For this reason it is more convenient to remove the sulfides in the liquid phase. The most im-

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portant physico-chemical method for hydrogen sulfide removal during the liquid phase in the anaerobic process has been precipitation with metals, mainly $Fe^{3+}$ (McFarland and Jewell, 1989). However, this practice has several important limitations because it is expensive, operationally complicated and generates sludge that may contain iron that complicates its final disposal.

In contrast, biological methods have low operational costs with little or no utilization of added chemicals (Syed *et al.* 2006; Mahmood *et al.* 2007). Several biological methods have been studied for sulfide removal from the aqueous phase in anaerobic digesters, but in the last 8 years research on micro-aerobic anaerobic processes has increased significantly (van der Zee *et al.*, 2007; Jenicek *et al.*, 2008). This is based on the use of microorganisms capable of oxidizing hydrogen sulfide to elemental sulfur, which becomes the main process byproduct.

However, there are still some aspects remaining to be clarified because the aeration rate and method of adding oxygen, among others, depend heavily on the characteristics of the wastewater to be treated and the type of anaerobic process to be used. For example, van der Zee *et al.* (2007) introduced a low airflow of 0.7–0.9 $m^3/m^3$.d (air volume/reactor volume. day) to an anaerobic fluidized bed reactor fed with low-sulfate vinasse, which was sufficient to reduce the biogas $H_2S$ content to an undetectable level. But Ramos and Fernández-Polanco (2013) applied hydraulic overload to a well-functioning pilot reactor treating sewage sludge with approximately 4.4 $Nl/m^3/d$ of oxygen and 18 days hydraulic retention time and noted that the process operated properly. The results achieved in other studies on the Micro-aerobic Anaerobic Process (MAP) have been highly satisfactory (Díaz *et al.*, 2011; Krayzelova *et al.*, 2014).

UASB reactors operating with natural zeolites have proven to be highly effective for biological wastewater treatment while working with low hydraulic retention times and under various operational conditions. Montalvo *et al.* (2014a) evaluated the behavior of a UASB reactor modified with natural zeolites operating at high nitrogen concentrations (0.5, 0.7 and 1.0 g/l), room temperatures ranging between 18 ºC and 21 ºC (using laboratory bioreactors), and with up-flow velocities of 0.25–0.75 m/h and hydraulic retention times ranging from 1.33 to 4 hours. It was observed that COD removal was 50% higher in the zeolite-modified UASB reactor than in the reactor without zeolite. The granulation process was also better when operating with zeolite. In other work, Montalvo *et al.* (2014b) also observed improved nitrogen removal behavior of a biological denitrification process when a UASB reactor with zeolite was applied to the process. In the batch startup period, 100% nitrate reduction was achieved in the UASB reactors with and without zeolite on the 7th and 11th days, respectively. UASB reactors operating in continuous mode at a high organic loading rate (44 kg $COD/m^3d$) and a very low HRT (2.5 h) revealed that the reactor with zeolite achieved a nitrate removal efficiency of 92.4% at a nitrogen load of 6.42 kg $NO_3^-/(m^3d)$.

Given these prior results, this paper evaluates the performance of the anaerobic process operating at different airflow levels and $COD/SO_4^{2-}$ ratios$^-$, with and without the presence of natural zeolites and at both room and mesophilic controlled (35 ºC) temperatures.

## MATERIALS AND METHODS

Three experimental series were performed. The first series, Experimental Series 1, was carried out in batch reactors, and consisted of three experimental runs. The first two runs (I and II) were aerated using pulse aeration wherein the reactors were injected with the same amount of air, once per day, throughout the duration of each run. In the third run (III) aeration was continuous throughout the duration of the run (Table 1).

As mentioned previously, the amount of air to be supplied for hydrogen sulfide removal will depend on several factors. It is, therefore, not possible to estimate such a quantity considering only the simple stoichiometry of the biochemical reaction involved:

$$H_2S + ½\ O_2 \rightarrow S° + H_2O \qquad (1)$$

In addition to the factors of the wastewater characteristics and the anaerobic processor reactor type, it should be noted that the wastewater substrate present in anaerobic biological reactors is extremely complex and that there is a highly diverse microbial culture of various microorganisms, other than sulfur-oxidizing bacteria (SOB), which can also use oxygen to consume various substrates. For these reasons, the determination of the amount of oxygen to be used in this study, in the form of aeration rates, was based on previously reported results and some preliminary trial and error tests (data not shown).

In the anaerobic process, sulfur from sulfate becomes mainly gaseous and dissolved sulfide. At the same time a very small proportion of the sulfur is incorporated into the microbial cells. On the other hand, when micro-aeration is applied, several additional processes and reactions take place at the same time. Reactions between oxygen, added as air, and dissolved sulfide can remove the gaseous $H_2S$ by stripping or reoxidizing it to elemental sulfur, and to sulfate as well.

**Table 1: Experimental Series 1 (discontinuous runs).**

| Experimental Run I | Experimental Run II | Experimental Run III |
|---|---|---|
| $COD/SO_4^{2-}$= 5, 10 and 15<br>Pulse aeration<br>Airflow: 0.6, 0.8 and 1.0 mL/d | $COD/SO_4^{2-}$= 5, 10 and 15<br>Pulse aeration<br>Airflow: 0, 0.2 and 0.4 mL/d | $COD/SO_4^{2-}$= 1, 5, 10 and 15<br>Continuous aeration<br>Airflow: 5, 7.5 and 10 mL/min |

The reactors had a capacity of 1 liter and were kept at a constant temperature of 35 ºC. The duration of each discontinuous run was 30 days with samples taken every three days. Each experimental condition was performed twice, and each sample was analyzed twice, such that each experimental point had four sampled values over which the average was calculated. This average was then taken as the single value for each parameter. Variations between each of the four sampled values were no more than 3%.

Table 2 shows the synthetic wastewater composition, which was prepared using glucose, ammonium sulfate, ammonium phosphate and sodium bicarbonate. The initial inoculum (10 g/L volatile suspended solids, VSS) came from anaerobic digester sewage sludge (La Farfana, Santiago de Chile) and was used to generate an initial COD/VSS = 0.1 in all reactors.

In Experimental Series 2, four UASB reactors of similar dimensions were used (Table 3). This experimental series aimed to evaluate the effect of the application of natural zeolite on MAP operating at both room and controlled mesophilic (35 °C) temperatures. Table 4 shows the operating conditions for the reactors used in Experimental Series 2. The natural zeolite used was of the clinoptilolite type, whose main characteristics are shown in Table 5. The initial COD concentration was 1000 mg $O_2$/L. The initial inoculum (15 g/L VSS) came from anaerobic digester sewage sludge (La Farfana, Santiago de Chile).

**Table 2: Synthetic Wastewater Composition.**

| $COD/SO_4^{2-}$ | Glucose (mg/L) | Sodium bicarbonate (mg/L) | Ammonium sulfate (mg/L) | Ammonium phosphate (mg/L) | Total sulfate (mg/L) |
|---|---|---|---|---|---|
| 15.1 | 937.5 | 1000 | 91.7 | 17.8 | 68 |
| 10:1 | 937.5 | 1000 | 137.6 | 27 | 100 |
| 5:1 | 937.5 | 1000 | 275 | 53 | 200 |
| 1:1 | 937.5 | 1000 | 1375 | 267 | 1000 |

**Table 3: UASB Reactor Specifications.**

| Parameter | Value |
|---|---|
| Reactor Height (H) | 1.22 m |
| Internal Diameter (D) | 0.1 m |
| Reactor Volume (V) | $9.42\times10^{-3}$ $m^3$ or 9.42 L |
| Material | Acrylic |

The main objective of Experimental Series 3 was to observe behavior of MAP operating with zeolites at low hydraulic retention times (HRT) ranging from 2.8 to 4.8 hours and low $COD/SO_4^{2-}$ ratio ranging from 2.5 to 4.2. The initial inoculum (14 g/L VSS) came from anaerobic digester sewage sludge (La Farfana, Santiago de Chile). As in Experimental Series 2, the MAP startup was carried out with an inoculum:zeolite mixture that filled 30% of the reactor volume. In this series the reactors operated at 35 ºC.

**Table 4: Operating conditions for the reactors used in Experimental Series 2.**

| Reactor | Zeolite (L) | Inoculum (L) | Initial $SO_4^{2-}$ (mg/L) | Temperature (ºC) | Days (Airflow in mL/min) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| R1 | 0 | 2.8 | 325 | 35 | 1–8<br>(0) | 9–14<br>(10) | 15–20<br>(14) | 21–29<br>(150) | 30–38<br>(200) |
| R2 | 0 | 2.8 | 325 | 19–23 | 1–8<br>(0) | 9–14<br>(10) | 15–20<br>(14) | 21–29<br>(150) | 30–38<br>(200) |
| R3 | 1.4 | 1.4 | 400 | 35 | 1–5<br>(0) | 6–14<br>(100) | 15–20<br>(150) | 21–36<br>(200) | |
| R4 | 1.4 | 1.4 | 400 | 10–14 | 1–5<br>(0) | 6–14<br>(100) | 15–20<br>(150) | 21–36<br>(200) | |

**Table 5: Composition and main features of the Chilean natural zeolite used (Clinoptilolite type)*.**

| Component | Composition (%) |
|---|---|
| $SiO_2$ | 67.00 |
| $Al_2O_3$ | 13.01 |
| $Fe_2O_3$ | 3.60 |
| CaO | 3.46 |
| $Na_2O$ | 1.32 |
| $TiO_2$ | 0.28 |
| MgO | 0.78 |
| $K_2O$ | 0.53 |

* Particle size: 1 mm. $SiO_2/Al_2O_3$ ratio: 5.15. Average pore diameter: 170.7 Å (0.017 μm).

The synthetic wastewater for Experimental Series 2 and 3 was prepared as previously described for Experimental Series 1. All parameters (COD, solids, nitrogen, pH, sulfides, sulfates, dissolved oxygen) were determined according to Standard Methods for Water and Wastewater Examination (2012).

## RESULTS

### Experimental Series 1

The assays carried out for Experimental Series 1, Experimental Runs I and II, showed negative results with respect to sulfide removal because the aeration pulse was insufficient. However, in Experimental Run III, positive results were achieved as shown in Table 6.

**Table 6: Sulfide removal* in Experimental Series 1.**

| Micro-aeration (mL/min) | Micro-aeration (vvm)** | $COD/SO_4^{2-}$ 1 | $COD/SO_4^{2-}$ 5 | $COD/SO_4^{2-}$ 10 | $COD/SO_4^{2-}$ 15 |
|---|---|---|---|---|---|
| | | Sulfide removal (%) | Sulfide removal (%) | Sulfide removal (%) | Sulfide removal (%) |
| 5 | 0.005 | 98.21 | 81.62 | 93.50 | 88.67 |
| 7.5 | 0.0075 | 98.76 | 87.38 | 95.81 | 87.64 |
| 10 | 0.01 | 98.29 | 87.57 | 90.87 | 92.42 |
| 0 (Control) | 0 | 0 | 0 | 0 | 0 |

*Sulfide removal was calculated considering the initial sulfide concentration to be that present when aeration was started (12 days from the beginning of the anaerobic process).
**Air volume/reactor volume.minute.

Initial sulfate concentrations were 4266, 1123, 730 and 600 mg/l for the $COD/SO_4^{2-}$ ratios of 1, 5, 10 and 15, respectively. Aeration began on the 12th day of the anaerobic process when sulfate concentrations in the anaerobic reactors were 1800, 915, 52 and 0 mg/l (by sulfate conversion to sulfide) for the $COD/SO_4^{2-}$ ratios of 1, 5, 10 and 15, respectively. Sulfide concentrations at that moment were 915, 274, 194 and 148 mg/l for the $COD/SO_4^{2-}$ ratios of 1, 5, 10 and 15, respectively. On the 30th day of anaerobic digestion, sulfate values were between 150 mg/l (for the lowest $COD/SO_4^{2-}$ ratio) and 1700 mg/l (for the highest $COD/SO_4^{2-}$ ratio). This implies that there could have been excessive aeration, although in all cases the concentration of dissolved oxygen in the medium was less than 1 mg/l. Besides this, based on the characteristics of the synthetic wastewater, a low availability of electrons may have had a decisive influence on the existence of residual sulfate for the lower $COD/SO_4^{2-}$ ratio (Table 7). COD removal was nearly 100% after 30 days of anaerobic digestion for all $COD/SO_4^{2-}$ ratios. Another cause for the persistence of sulfates after the aeration phase may be that the SRB, which can be autotrophic or heterotrophic, requires substrates such as hydrogen, carbon dioxide, acetate, propionate, butyrate and ethanol, which are mainly generated in the anaerobic fermentative process step. These substrates may not be present in the amounts necessary to permit the SRB to carry out sulfogenesis. Although the methane content in the gas was not measured, the biogas generated in the microaerobic process was qualitatively verified to be flammable. In this sense, Porpatham *et al.* (2007) demonstrated that "dilute" biogas can be used in combustion engines because they found that a decrease in methane concentration from 70% to 50% only reduced the spark-ignition energetic performance by 0.9% for the same methane mass flow.

**Table 7: Dissolved sulfide removal* in Experimental Series 1, Run III.**

| Micro-aeration (mL/min) | Micro-aeration (vvm)** | $COD/SO_4^{2-}$ 1 | $COD/SO_4^{2-}$ 5 | $COD/SO_4^{2-}$ 10 | $COD/SO_4^{2-}$ 15 |
|---|---|---|---|---|---|
| | | Sulfide removal (%) | Sulfide removal (%) | Sulfide removal (%) | Sulfide removal (%) |
| 5 | 0.005 | 98.21 | 81.62 | 93.50 | 88.67 |
| 7.5 | 0.0075 | 98.76 | 87.38 | 95.81 | 87.64 |
| 10 | 0.01 | 98.29 | 87.57 | 90.87 | 92.42 |
| 0 (Control) | 0 | 0 | 0 | 0 | 0 |

*Dissolved sulfide removal was calculated considering the initial dissolved sulfide concentration to be that present when aeration was started (12 days from the beginning of the anaerobic process).
**Air volume/(reactor volume.minute).

### Experimental Series 2

Figures 1 and 2 show soluble COD removal for the different evaluated processes. Each value is an average of three measurements for each sample point. In all cases no significant variation more than 4% was observed between the three measurements for a given sample point.

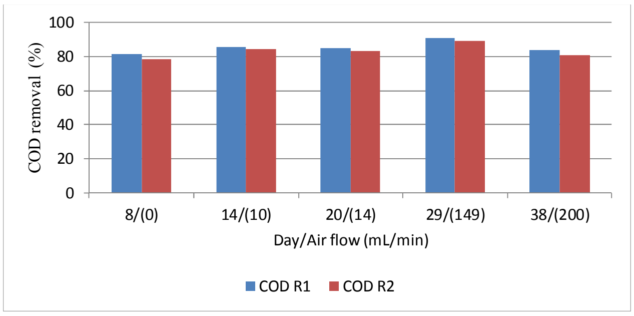

**Figure 1:** Soluble COD removal in reactors operating without zeolites at both controlled (R1) and room (R2) temperatures.

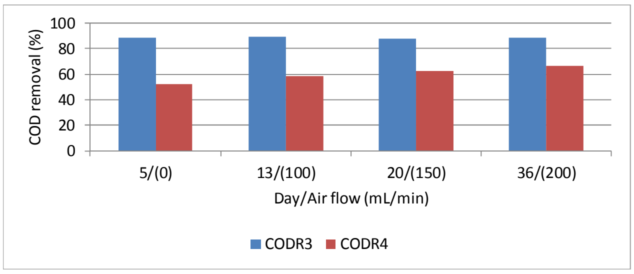

**Figure 2:** Soluble COD removal in reactors operating with zeolites at both controlled (R3) and room (R4) temperatures.

A statistical analysis of variance (ANOVA) was performed using the software GraphPad Prism, which resulted in the following findings (95% confidence, $p<0.05$):

1. There was no significant difference between reactors R1 and R2. This can be explained if one takes into account the fact that, although the room temperature operating condition was below the optimum value in the mesophilic range, 35–37 ºC (Rich, 1963; Chayovan, 1988; Arikan *et al.*, 2015), it was not excessively low.
2. There was a significant difference between reactors R3 and R4. This can be explained if one considers that, in this case, the operating condition of room temperature for reactor R4 was much lower than that for reactor R3.
3. There was a significant difference between reactors R1 and R3. There is significant evidence regarding the positive effect that zeolites have on the anaerobic process (Montalvo *et al.*, 2012). The feasibility of using natural zeolites as support media for the immobilization of microorganisms in different reactor configurations (UASB, fixed bed, fluidized bed, etc.) has been demonstrated (Tada *et al.*, 2005; Kotsopoulos *et al.*, 2008).
4. There was a significant difference between reactors R2 and R4, which is to be expected considering the operating temperatures that were present in both reactors. It is widely known that low temperatures, below 15 ºC, have negative effects on the anaerobic process (Seghezzo *et al.* 1998; Wei *et al.*, 2014). Also, the use of zeolites causes an increased colonization of microorganisms on the surface of the zeolites, which results in an increased process efficiency (Montalvo *et al.*, 2010; Wei *et al.*, 2011). Furthermore, there is evidence of the positive influence of certain inert solids on the granulation process in anaerobic reactors (Hulshoff Pol *et al.*, 2004; Rough *et al.*, 2005). However, if the temperature is very low, as turned out to be the case in reactor R4, the growth of methanogenic archaea is very limited, regardless of the existence of zeolites.

It is known that sulfate becomes sulfides, mainly hydrogen sulfide where SRB are involved, in the reducing conditions existing in the anaerobic reactors (Barrera *et al.*, 2015; Sijun *et al.*, 2015). Different investigations have shown that, when oxygen is supplied in small quantities, it allows sulfide-oxidizing bacteria (SOB) to convert the chemical species to elemental sulfur according to equation (1) (Fernández-Polanco *et al.*, 2010; Díaz and Fernández-Polanco, 2011).

Based on the previous discussion, it is better to assess the evolution of the main sulfur compounds ($SO_4{}^{2-}{}_e$ liquid effluent, dissolved $H_2S_e$ and gaseous $H_2S_g$), than it is to estimate or calculate sulfide removal in anaerobic reactors run in a continuous process. Table 8 shows the evolution of sulfur compounds in the reactors of Experimental Series 2.

It can be seen that the lowest hydrogen sulfide concentration, in both the liquid and gas phases, was achieved in reactor R3 that operated with zeolites and at 35 °C. The highest concentration of sulfides was obtained in reactor R1, which operated without zeolites and at room temperature (19–23 ºC).

The micro-aeration rate was increased beginning on day 5, for reactors R3 and R4, and day 8, for reactors R1 and R2 (see Table 4). As this aeration rate was increased, the sulfur concentration decreased in both the liquid and gaseous phases (data not shown). However, the sulfide concentration was reduced to extremely low levels with the application of the airflow of 200 ml/min, as shown in Table 8.

**Table 8: Evolution of sulfur compound concentrations in Experimental Series 2.**

| | **Concentrations for Aeration Rate = 0 mL/min** | | | **Concentrations for Aeration Rate = 200 mL/min** | | |
|---|---|---|---|---|---|---|
| **Reactor** | **$SO_4{}^{2-}{}_e$ (mg/L)** | **$H_2S_e$ (mg/L)** | **$H_2S_g$ (mg/L)** | **$SO_4{}^{2-}{}_e$ (mg/L)** | **$H_2S_e$ (mg/L)** | **$H_2S_g$ (mg/L)** |
| R1 | 150 | 64 | 18 | 185 | 26 | 4 |
| R2 | 165 | 58 | 15 | 200 | 43 | 10 |
| R3 | 164 | 56 | 14 | 163 | 2 | 0.1 |
| R4 | 335 | 14 | 11 | 359 | 14 | 2.4 |

## Experimental Series 3

The micro-aeration for this series was started when the stabilization process was completed (at 95 days) and used a flow rate of 0.08 vvm. At that moment the dissolved sulfide concentration was 100 mg of sulfide per liter. Table 9 shows the different reactor operational conditions (disturbances, P) applied in this experimental series. Table 10 shows average soluble COD removal achieved in each period or disturbance. Figure 3 and Figure 4 show the levels of sulfide and sulfate removal, respectively, achieved with continuous air supply.

**Table 9: Disturbances carried out in the reactor feed rate.**

| Up-flow velocity (m/h) | COD (mg $O_2$/L) | $SO_4^{2-}$ (mg/L) | COD/$SO_4^{2-}$ ratio | Organic Loading Rate (OLR) (kg COD/m$^3$.d) | HRT (hours) |
|---|---|---|---|---|---|
| 0.25 | 1000 | 400 | 2.5 | 5.0 | 4.8 |
| 0.25 (P2) | 1500 | 407 | 3.69 | 7.5 | 4.8 |
| 0.25 (P3) | 1798 | 408 | 4.42 | 9.0 | 4.8 |
| 0.29 (P4) | 1798 | 408 | 4.42 | 10.8 | 4.0 |
| 0.36 (P5) | 1798 | 408 | 4.42 | 12.9 | 3.3 |
| 0.36 (P6) | 1798 | 599 | 3.0 | 12.9 | 3.3 |
| 0.43 (P7) | 1798 | 599 | 3.0 | 15.5 | 2.8 |

**Table 10: Soluble COD removal for each disturbance of the process.**

| Disturbance | Average soluble COD removal (%) |
|---|---|
| Stabilization period | 76.92 ± 2.58 |
| P2 | 80.84 ± 3.65 |
| P3 | 78.62 ± 2.74 |
| P4 | 74.09 ± 2.76 |
| P5 | 72.79 ± 1.83 |
| P6 | 73.44 ± 2.85 |
| P7 | 68.26 ± 2.53 |
| P8 | 65.88 ± 3.05 |

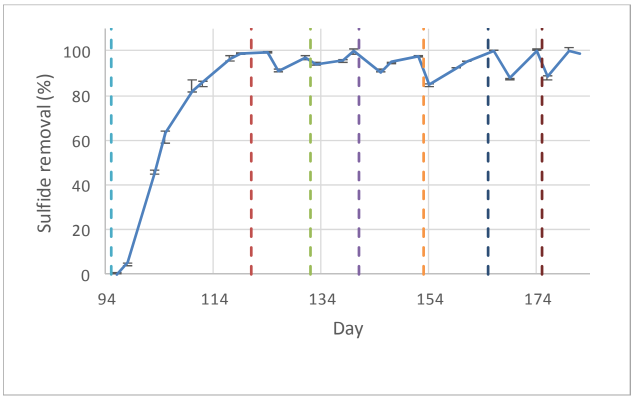

**Figure 3:** Sulfide removal in the UASB reactor during the operating period.

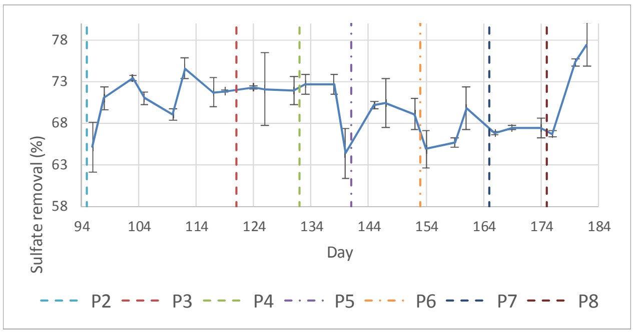

**Figure 4:** Sulfate removal in the UASB reactor during the operating period.

Figure 3 shows that dissolved sulfide removal (from the initial level of 100 mg/l) was 90–100% for all disturbances. Soluble COD removals were also high, until disturbance P6 was reached, if several conditions are taken into account that were very stressful for the process: low COD/$SO_4^{2-}$ ratio (3) and very low HRT (3.3 hours). Figure 4 shows that removal or conversion of sulfate (from the initial values shown in Table 4) was also significant under all operating conditions, given that results range between 63% and 78%.

## Granulation Process

According to the data presented in Figure 5, the sludge generated in the UASB reactor took on a granular shape where about 9% of the granules had a diameter greater than or equal to 2 mm and 10% of the granules had a diameter between 1 mm and 2 mm. These values are consistent with those reported in other studies for conventional UASB reactors (Yoda and Nishimura, 1997; Bhunia and Ghangrekar, 2007). Considering that most of the zeolites used in the investigation had a diameter less than 1/24th that of the larger granules generated in the reactor bed (Figure 6 shows granules up to 6 mm), it is possible to believe that the formation of these granules corresponds to those described by the inner-core model (Liu *et al*., 2003). This model states that, in the presence of inert particles, the anaerobic microorganisms present in a UASB reactor could adhere to the surface of the particles to form bio-layer-driven initialization of the granules, wherein the first step of granulation would be the surface fixation of microorganisms, thus forming the core to establish the bio-layers model.

Figure 5 shows that, as the diameter of the granules decreases, the VSS concentration increases. It can therefore be assumed that zeolites act as support for the formation of the granular core, which continues to grow with an increasing microorganism population on the zeolite surface. It has been found that this material has a very good surface for the colonization of anaerobic microorganisms (Fernández *et al.*, 2007; Mery *et al.*, 2012). This is why a greater quantity of VSS is found in smaller zeolite-granule particle diameters and there is 19% of VSS for the range of zeolite-granule diameters with greater presence in the reactor (from 0.6 to 0.212 mm) as shown in Figure 6. Figure 7 shows a photo of some samples of the granules developed in the reactor.

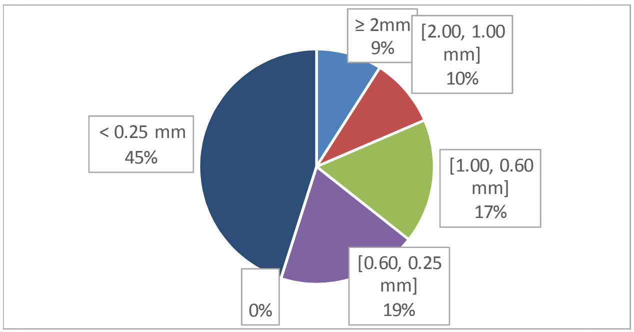

**Figure 5:** Volatile Suspended Solids (VSS) in granules of different sizes in the UASB reactor sludge bed.

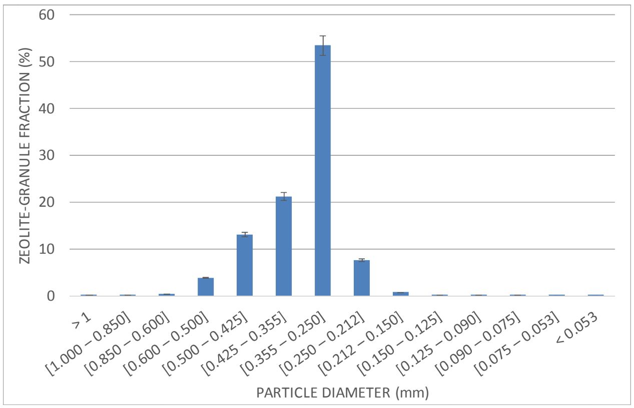

**Figure 6:** Distribution of zeolite-granule diameters produced in the UASB reactor.

**Figure 7:** Samples of granules generated in the UASB reactor bed.

## CONCLUSIONS

In general, for both pulse and continuous micro-aeration in batch reactors, good organic matter removal was achieved in all processes. However, higher percentages were observed for continuous micro-aeration, where a removal rate of over 90% was achieved for all operational airflows. It was also observed that reactors operating with lower sulfate concentrations in the wastewater, at the end of the micro-aeration process, generated a relatively high residual concentration of sulfate. This was caused by various factors including excess airflow, which indicates that, in these cases, for example for COD/$SO_4^{2-}$ ratios of 10 and 15, the planned airflows applied to the process must not be over-estimated.

It was demonstrated that natural zeolite has a positive effect on MAP in UASB reactors and in particular on the granulation process.

The behavior of the hydrogen sulfide removal process in the UASB reactor with natural zeolites and micro-aeration was not greatly affected by either very low HRT or high OLR, and achieved good sulfide removal in all cases.

The average sulfur removal was greater than 94.56% (±4.71%), which makes IT clear that the micro-aeration system is able to operate reliably under conditions in which the anaerobic process can suffer organic load shocks or high sulfate feed concentrations without decreasing organic matter removal efficiency.

## NOMENCLATURE

| | |
|---|---|
| (COD)/($SO_4^{2-}$) ratio | Chemical Oxygen Demand (g)/$SO_4^{-2}$ (g) |
| HRT | Hydraulic Retention Time (hours) |
| MA | Methanogenic Archea |
| MAP | Microaerobic Anaerobic Process |
| R1 | UASB reactor operated without natural zeolite at mesophilic temperature (35 ºC) |
| R2 | UASB reactor operated without natural zeolite at room temperature (19–23 ºC) |
| R3 | UASB reactor operated with natural zeolite at mesophilic temperature (35 ºC) |
| R4 | UASB reactor operated with natural zeolite at room temperature (10–14 ºC) |
| P | Disturbances of operational UASB reactor conditions |
| OLR | Organic Loading Rates |
| VSS | Volatile Suspended Solids (mg/L) |
| vvm | Air volume/minute.volume reactor (L/min.L) |

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