

EFFECT OF ELECTROCHEMICAL TREATMENT OF OLEIC ACID ON ANAEROBIC DIGESTION

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ABSTRACT

Electrochemical pre-treatment of oleate on anaerobic digestion was investigated using two anaerobic filters (AF and AFm) working, respectively, with increasing concentrations of electrochemically pre-treated oleate and oleate. Influent containing 25% and 50% of chemical oxygen demand (COD) of these substrates did not cause relevant alterations in either digester's performance. Comparatively, the pre-treated oleate unit (AF) showed a higher gas production but a lower COD removal than AFm (2.0 vs 1.5 m³ CH₄ m⁻³ d⁻¹; 76-85 vs 91-93% COD removal). The raised AFm COD removal together with the larger proportion of VSS in its effluent than in AF (5.69 vs 0.26 kg m⁻³) indicate that the biomass washout can be a consequence of the encapsulated solids by lipidic compounds that were not fairly degraded. Further increases of oleate in AFm feed (75 and 100% COD) led to decreases of biogas production to half and COD removal from values higher than 90% to 83-75%. The simultaneous increase of effluent VSS concentrations to 10-12 kg m⁻³ emphasizes the oleate negative effect. The use of pre-treated oleate as the only carbon source did not influence negatively the AF behaviour in terms of methane production. COD removal was maintained at values higher than 80% and the effluent VSS at low concentrations (0.15 kg m⁻³). The significantly higher methane yield achieved by AF than AFm indicates a higher accumulation of oleate than pre-treated oleate. Therefore, electrochemical process stands for a suitable pre-treatment for lipid rich effluents, allowing the application of higher organic loads keeping a higher methane yield.

Keywords: Electrooxidation of oleic acid, anaerobic treatment, lipids, oleate, anaerobic filter

INTRODUCTION

Lipids constitute an important part of effluents' organic matter and are a potential substrate of methane production. They are easily hydrolysed to long chain fatty acids (LCFA) [1] which are potentially inhibitory to the bacterial groups involved in LCFA mineralization, the acetogenic and the methanogenic bacteria [2-3]. Lipids also contribute to biomass flotation and reactor washout by forming a lipid layer around the bacterial aggregates [4-5].

Electrochemical methods have been successfully applied for the treatment of different organic compounds [6-10]. Under carefully chosen conditions the electrooxidation of such substances can be done without complete mineralization of the organic molecules with the formation of less harmful products than the reactants. Usually the complete mineralization is attained at high electrode potential (or current density) values which represent a high electric power consumption to achieve the complete degradation of a given compound. Under less drastic conditions (lower power consumption) the products of the electrooxidation process are intermediate species of the mineralization route with low toxicity and keeping the potential for anaerobic production of methane. Some batch experiments of oleate electrooxidation

have been carried out in our laboratory on a Dimensionally Stable Anode (DSA) type electrode based on RuO₂ [11-12]. The data obtained revealed that the product of the electrochemical transformation was biodegraded faster than oleate, suggesting that this methodology is an effective and promising pre-treatment for inhibitory effluents processing. The present work is part of a broader study aimed at evaluating of the biodegradation advantages by using an electrochemical process as a pre-treatment of anaerobic digestion of lipidic effluents. The objective of this work is to study the effect of the electrochemical oxidation of oleic acid-based effluent on the up-flow anaerobic filter performance operating in a continuous mode.

MATERIAL AND METHODS

Electrooxidation of Oleate

The electrolysis apparatus (Figure 1) consisted of a batch reactor of 10 dm³ working volume fitted with three electrodes kept parallel to each other by a distance of 10 cm to allow good convection by stirring the solution, and connected to an electrical DC power supply (Kikusui). The electrochemical oxidation of the oleate takes place over a

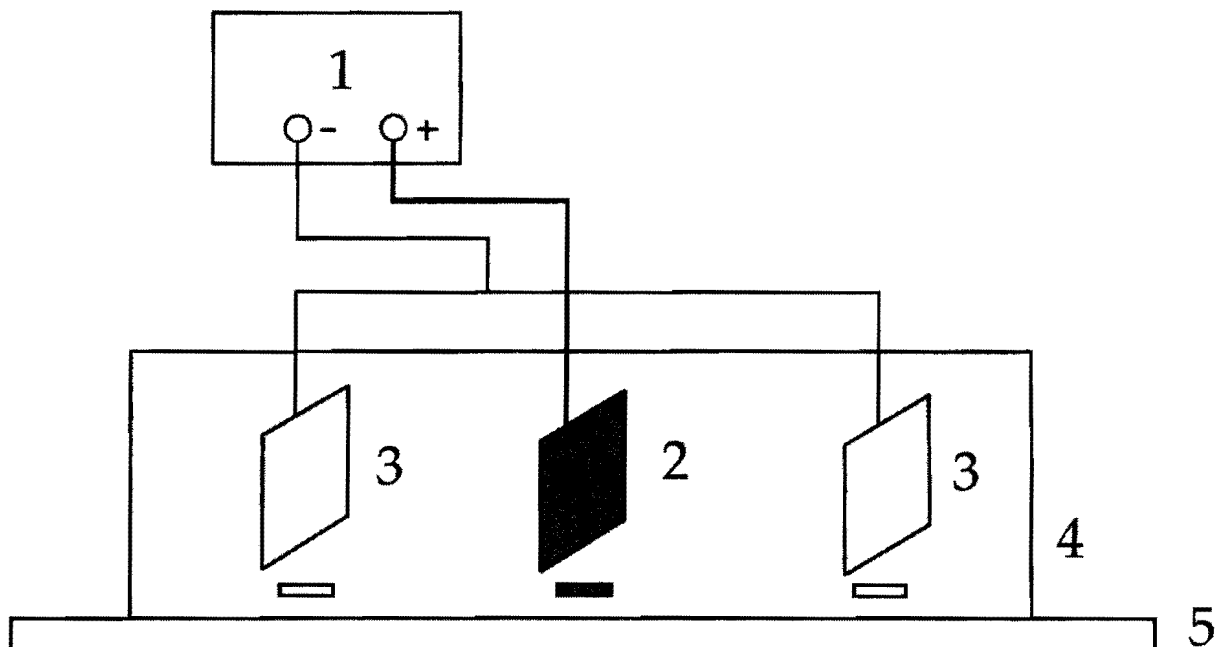


Figure 1. Schematic diagram of experimental electrooxidation set-up. 1- DC power supply, 2- anode, 3- cathode, 4- electrolytic cell, 5-magnetic stirrer.

RuO₂ type DSA plate (both sides active) provided by ELTECH Systems Corporation and used with a geometric working area of 3.67 dm² (2 x 20.4 x 9 cm). Two stainless steel plates were employed as cathodes (immersed geometric area of 7.34 dm²). A solution of 10 g dm⁻³ sodium oleate was used in the presence of NaOH 0.2 mol dm⁻³ as supporting electrolyte. The electrolysis was carried out under galvanostatic control at a current intensity of 10 A for a period of seven days. Under these conditions a cell potential of 9 ± 1 V was recorded being the anode potential of 1.2 ± 0.1 V vs. Saturated Calomel Electrode.

Anaerobic Digestion

Digesters

The anaerobic digestion experiments were performed in two up flow anaerobic filters (AF and AFm). AF was built out of polyvinyl chloride pipe, holds a total volume of 2.7 dm³ and a folded polyethylene net (bed porosity of 83%) as support matrix. AFm is a Plexiglas digester of 1 dm³ total volume and is packed with polyvinyl chloride Raschig rings (bed porosity of 92%). Both units were maintained at $37 \pm 1^\circ\text{C}$ using a water jacket and were continuously fed through a time controlled peristaltic pump. The feed tank temperature was kept at 4°C and the gas production was measured by a wet gas meter.

Inoculum and substrates

The digesters were inoculated with solids obtained

from another laboratory anaerobic filter fed with skim milk as substrate. The initial digesters feed was made by dilution of skim milk with tap water and supplemented with macro- and micronutrients [13]. Afterwards, the skim milk was replaced by the mixtures of skim milk and pre-treated oleate (AF) or skim milk and oleate (AFm). In the last operation period, pre-treated oleate and oleate were the sole organic carbon source feed of AF and AFm, respectively.

Analytical methods and (gas) chromatography

Total chemical oxygen demand (COD) and soluble COD were determined according to Standard Methods [14] (1998). Samples for soluble COD were centrifuged at 9,800 for 10 minutes (Janetzki, TH-12). Volatile suspended solids (VSS) were estimated by the difference between total and soluble COD, considering that 1 g of VSS corresponds to 1.42 g of COD. Gases were separated in a 1/8" x 3 m Porapak column (80-100 mesh) and determined with a thermal conductivity detector in a Varian 3800 chromatograph with column, injector and detector temperatures at 50, 60 and 100°C, respectively.

Start-up and reactor operation

AF was first filled with tap water and then two-thirds of it was displaced by pumping equal volumes of sludge and substrate. It was left without further feeding until methane (CH₄) content in the biogas reached more than 50% (Table 1. Period A). AFm was inoculated with 0.3 dm³ of solids (25 kg m⁻³ VSS) and fed with skim milk. During the Period B, a decrease in hydraulic retention time (HRT) and an increase in

Table 1. Operational conditions of anaerobic filters.

Experimental period	Influent	HRT d	La kg CQO m ⁻³ d ⁻¹
A			
B	skim milk	decrease 2.7-0.6 (AF) 3.1-0.6 (AFm) ↓	increase 1.9-7.6 (AF) 0.7-6.0 (AFm) ↓
C	skim milk + pre-treated oleate (AF) / / oleate (AFm)	0.6 (AF) 0.6 (AFm)	5.4-6.7 (AF) 6.0 (AFm)
D	pre-treated oleate (AF) / / oleate (AFm)	0.5-0.9 (AF) 0.6 (AFm)	1.9-4.5 (AF) 6.0, 12.5 (AFm)

HRT - hydraulic retention time, La - loading rate

loading rate (La) from 1.9 to 7.6 kg COD m⁻³ d⁻¹ and from 0.7 to 6.0 kg COD m⁻³ d⁻¹ were applied in AF and AFm digesters, respectively. After that, the mixtures of skim milk and pre-treated oleate/skim milk and oleate were successively altered by increasing the pre-treated oleate/oleate concentrations in influent (Table 1, Period C). At the end, only the pre-treated oleate and oleate-based influents were used (Table 1, Period D).

RESULTS AND DISCUSSION

The La increments performed in AF along Period B (Table 2) raised the biogas production and originated a decrease in methane content and COD removal. By increasing La from 1.9-4.0 to 7.0-7.6 kg COD m⁻³ d⁻¹ the gas evolved from 0.67-1.60 m³ m⁻³ d⁻¹ (72-75% CH₄) to 3.2-3.5 m³ m⁻³ d⁻¹

Table 2. Performance of anaerobic filter – AF.

Experimental period	Influent	Time d	HRT d	La kg COD m ⁻³ d ⁻¹	VSS ef. kg VSS m ⁻³	CODr %	Biogas m ³ m ⁻³ d ⁻¹	CH ₄ %	Y dm ³ CH ₄ Kg ⁻¹ CODr
A		0-17							
B	skim milk	18-33	2.73±0.19	2.3±0.18	0.17±0.00	60.0±0.00	0.41±0.05	77.1±0.00	226±0.02
		34-41	1.35±0.17	1.9±0.21	0.04±0.00	92.6±0.00	0.67±0.26	73.5±0.00	276±0.11
		76-111	0.55±0.06	3.5±0.45	0.05±0.02	93.4±1.40	1.39±0.38	72.1±1.88	308±0.07
		112-152	0.56±0.04	4.0±0.36	0.07±0.01	91.1±1.36	1.60±0.18	75.2±2.60	330±0.04
		153-182	0.54±0.02	7.4±0.33	0.12±0.02	93.0±1.71	3.45±0.26	71.1±4.26	356±0.03
		183-210	0.57±0.04	7.6±0.52	0.25±0.02	80.4±0.38	3.23±0.36	67.3±1.05	359±0.04
C	skim milk + pre-treated oleate	211-241	0.62±0.03	7.0±0.32	0.27±0.00	76.8±0.00	3.21±0.17	65.7±2.68	392±0.03
		242-246 (1)	0.66±0.03	6.4±0.33	0.26±0.00	75.7±0.00	2.87±0.28	70.4±0.00	417±0.06
		247-251 (2)	0.62±0.04	6.7±0.45	-	81.2±0.00	2.48±0.03	74.2±0.00	341±0.02
D	pre-treated oleate	252-260 (2)	0.65±0.07	5.4±0.46	0.19±0.00	85.2±0.00	2.22±0.09	74.2±0.00	359±0.04
		261--273	0.92±0.16	3.0±0.57	0.15±0.01	83.0±2.07	1.20±0.58	76.3±1.99	359±0.12
		274-284	0.52±0.06	4.5±0.44	0.14±0.00	81.2±0.00	1.34±0.17	78.0±0.00	288±0.03
		285-301	0.78±0.28	1.9±0.56	-	82.6±0.00	0.63±0.17	78.0±0.00	356±0.17

HRT - hydraulic retention time, La - loading rate, COD - total Chemical Oxygen Demand, CODr - total COD removal, VSS - volatile suspended solids, ef. - effluent, Y - methane yield.
Influent containing 25% (1) and 50% COD influent (2) of pre-treated oleate

(66-71% CH₄) and the COD reduction from 91-93% to values of 77-80%, respectively.

The main difference in the digesters behaviour during Period B concerns gas productions. The proportion of gas methane in AFm was significantly lower than that obtained in AF indicating a better performance of methanogenic bacterial population in this last unit. When La increased in AFm from 3.4 to 6.0 kg COD m⁻³ d⁻¹ the biogas production duplicated and reached 2.4 m³ m⁻³ d⁻¹ whereas the methane content and the COD removal were maintained at around 60% and 94%, respectively (Table 3).

The feed containing 25% and 50% COD influent of pre-treated oleate/oleate was well accepted by each of the digester systems (Tables 2 and 3, Period C). The values achieved in each unit under these operational conditions were comparable to the data already obtained in the absence of oleate as substrate. Nevertheless, the comparison of the digesters behaviour reveals that the presence of pre-treated oleate in the AF influent allowed a better methane content but a lower COD removal range (70-74 vs 56-66% CH₄ and 76-85 vs 91-93% COD removal: AF vs AFm). AFm effectively showed a good COD removal during Period C but it was not reflected in the resulting gas production and lower values of methane yield were obtained than AF. In compliance with these results, Sayed et al [15] also observed a poor methane yield during the operation of an effluent containing high lipid content. The AFm facts reflect a probable retention of influent compounds inside the digester that were not conveniently degraded as was previously evidenced by other works [16]. Simultaneously, the higher VSS concentrations obtained in the AFm effluent than in the AF one (AF: 0.19, 0.26 kg m⁻³ vs AFm: 1.77, 5.69 kg m⁻³) suggests that a larger promotion of biomass washout was occurring in the earliest unit. The biomass washout phenomenon is one of the problems associated with

biomass encapsulation by lipidic compounds when lipidic effluents are the bacterial substrate [17-19].

The implementation of oleate concentration into AFm feed to 75% and 100% COD influent originated a decrease in biogas production to half of the values recorded for lower contents of this substrate compound. Volumes of around 1 m³ biogas m⁻³ d⁻¹ with methane content that did not exceed 70% and a relevant decrease of methane yield parameter from the values of 276-323 to 88-149 dm³ kg⁻¹ COD removal were obtained. Simultaneously, the COD removal decreased from values higher than 90% to levels of 83-75% and the effluent VSS raised to concentrations of 10-12 kg m⁻³ (Table 3, Period D). Based on current data, the oleate as sole carbon source exerted an important negative effect on the AFm digester behaviour, especially concerning gas production.

In respect of AF, the use of pre-treated oleate in feed (Table 2, Period D) led to gas productions in agreement with the values already obtained in this unit without the presence of the pre-treated oleate (Table 2, Period B). The methane yield data (288-359 dm³ kg⁻¹ COD removal) reveals that the bacterial population kept its capacity of converting a relevant part of COD influent into methane. AF was neither affected in its COD removal capacity nor in its effluent quality when the pre-treated oleate was used as feed. The COD reduction was maintained at values higher than 80% and the effluent VSS in a low concentration range of 0.15 kg m⁻³. Nevertheless, it can be pointed out that AF had worked with lower La's than FAm ones due to operational limitations during the trial Period D (Table 1). This event compromises an effective comparison between two digesters behaviour of Period D but does not invalidate the observations already formulated by comparing the digester performance itself under feeding conditions with and without pre-treated oleate. So, it is possible to state that the pre-treated oleate as the only AF feed

Table 3. Performance of anaerobic filter – Afm.

Experimental period	Influent	Time d	HRT d	La kg COD m ⁻³ d ⁻¹	VSS ef. kg VSS m ⁻³	CODr %	Biogas m ³ m ⁻³ d ⁻¹	CH ₄ %	Y dm ³ CH ₄ Kg ⁻¹ CODr
B	skim milk	0-6	3.15±0.06	0.7±0.03	0.23±0.11	91±2.8	-	-	-
		6-29	1.54±0.02	1.43±0.05	0.12±0.06	93±2.7	-	48.9±11.9	-
		29-44	0.99±0.01	2.22±0.08	0.19±0.03	94±0.5	-	61.5±1.2	-
		44-80	0.64±0.01	3.44±0.13	0.65±0.15	94±0.9	1.22±0.10	60.7±2.8	229±33
		80-94	0.64±0.01	6.00±0.14	0.80±0.35	94±2.6	2.39±0.14	60.5±1.4	255±26
C	skim milk + oleate	94-105 (1)	0.64±0.01	6.00±0.14	1.77±0.35	93±1.0	2.57±0.11	60.1±1.3	276±21
		105-119 (2)	0.64±0.01	6.00±0.14	5.69±1.68	91±1.0	2.26±0.07	55.9±4.3	231±16
		119-150 (3)	0.64±0.01	6.00±0.14	12.02±1.80	92±0.7	1.04±0.05	65.5±3.0	123±11
D	oleate	150-205	0.64±0.01	6.00±0.14	11.46±1.29	83±2.3	1.05±0.09	70.5±2.7	149±20
		205-233	0.64±0.01	12.47±0.22	9.91±2.05	75±4.0	1.22±0.06	66.7±2.7	88±0.9

Influent containing 25% (1), 50% (2) and 75% COD influent (3) of oleate

did not exert a negative effect on the digester performance. The results obtained under this operating condition reinforce the results observed in Period C when the influent was partially constituted by pre-treated oleate (AF) or oleate (AFm) and the La 's of two digesters were within similar range. Figure 2 presents the daily methane productions registered along the trial periods in each digester against the operational La .

Effectively, the obtained AFm data indicate a detrimental effect of oleate on the anaerobic process in accordance with other authors' experiments [19] and underline the results previously reached in batch essays [20]. A usual practice to retrieve this operational limitation is to remove the lipidic matter from the substrate before the anaerobic treatment step. Nevertheless, this type of physical/physicochemical procedure is not effective as some

residual lipidic fraction remains in effluent which can still affect the anaerobic process [21-22]. On the other hand, lipids represent a greater potential of methane than proteins or carbohydrates, and the action of removing it from the substrate represents a waste of the methane production. Recently, Pereira et al. [23] proposed a sequencing batch operation with adsorption and degradation cycles in order to mineralize efficiently lipidic compounds and enhance the methane production. However, when concentrations are far above the optimal load defined by the authors, the time needed for the degradation phase can last a long time and therefore in these cases a pre-treatment should be appropriately applied. Taking into account the AF performance fed with and without pre-treated oleate, electrochemical oxidation can be advantageously associated with anaerobic digestion as a pre-treatment of lipidic

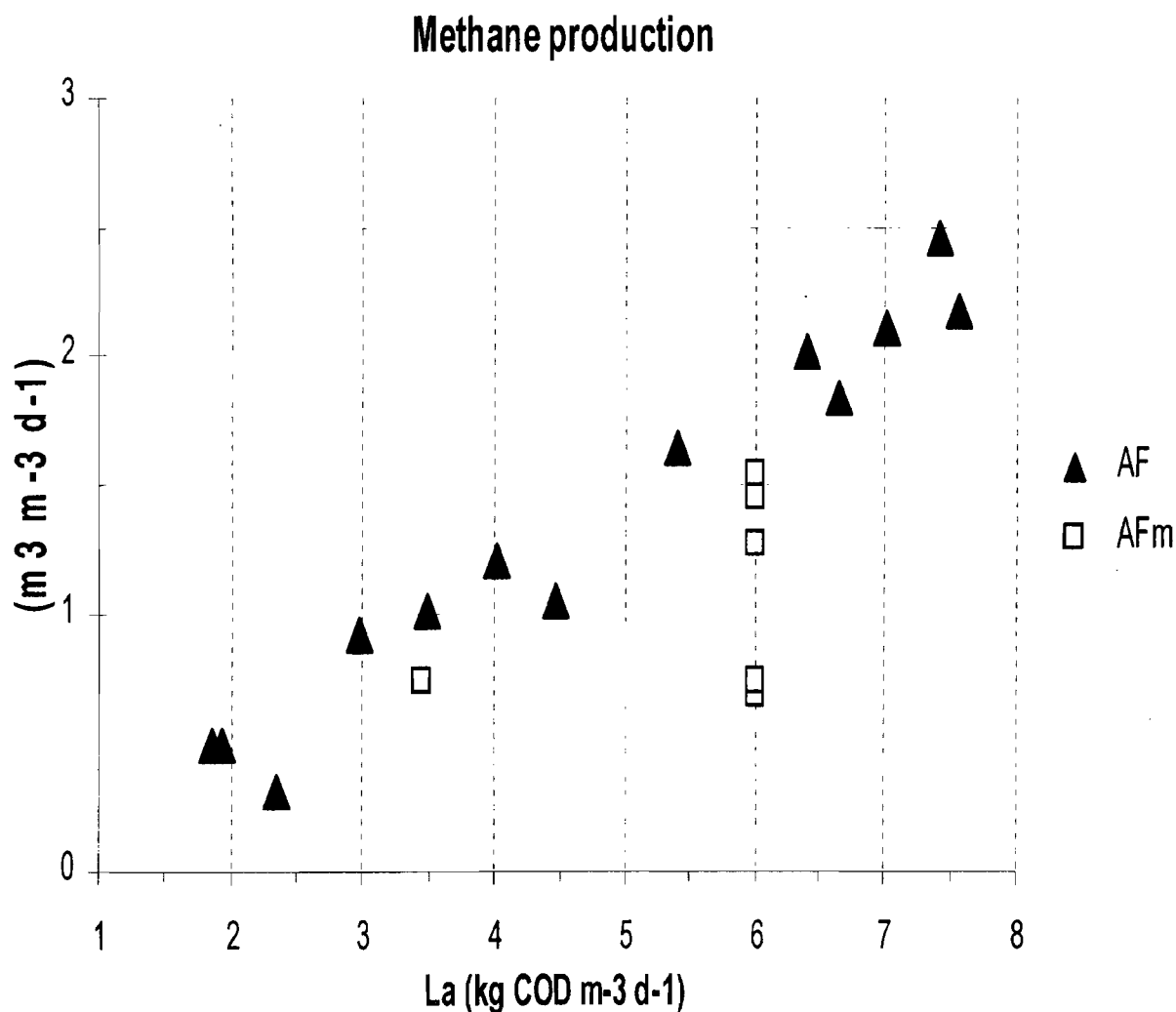


Figure 2. Methane production obtained from AF and AFm digesters.

effluents. It presents an alternative promising procedure insofar as it will allow the lipidic matter recovery to biogas production in the subsequent anaerobic step without detrimental effects on the process and will also allow operating the digester in a continuous mode.

CONCLUSIONS

Electrochemical oxidation of lipidic effluents can be advantageously used as the anaerobic digestion pre-treatment. The introduction of the smaller tested portions (25 and 50% COD influent) of pre-treated oleate and oleate in AF and AFm, respectively, did not affect substantially the behaviour of each unit. Comparatively, the AF digester has offered a higher gas production but a lower COD removal level than AFm (2.0 vs 1.5 m³ CH₄ m⁻³ d⁻¹; 76-85 vs 91-93% COD removal). The higher COD removal capacity and the larger proportion of VSS concentration of effluent observed in AFm than AF (5.69 vs 0.26 kg m⁻³) suggests that the phenomenon related to the retention of influent compounds inside the digester causing the biomass washout was more important in the former unit than in AF.

The concentration increase of oleate in AFm feed (75 and 100% COD influent) had a detrimental effect on the digester performance along the trial period operating at La of 6 kg COD m⁻³ d⁻¹ (75% COD influent of oleate) and 6 and 12 kg COD m⁻³ d⁻¹ (100% COD influent of oleate). Biogas production decreased significantly and the COD removal decreased from values higher than 90% to 83-75%. A considerable decline of methane yield from 276-323 to 88-149 dm³ kg⁻¹ COD removal was observed. At the same time, effluent VSS concentrations reached values as high as 10-12 kg m⁻³.

The pre-treated oleate as the only AF feed at La of 1.9-

4.5 kg COD m⁻³ d⁻¹ led to gas productions comparable to the values already obtained in the same digester working without pre-treated oleate. The obtained methane yield of 288-359 dm³ kg⁻¹ COD removal reveals that the bacterial population kept its capacity of converting the COD influent. The unit was not affected in its COD removal capacity or in its effluent quality, the COD reduction being maintained at values higher than 80% and the effluent VSS in a low concentration range of 0.15 kg m⁻³.

The results obtained stand out that the pre-treated oleate was better accepted by the AF system than the oleate was by the AFm. The presence of oleate in the AFm feed caused a relevant alteration on its behaviour whereas the AF showed capacity to convert the pre-treated oleate as sole carbon source. The electrochemically driven anodic conversion of oleate stands for a promising procedure insofar as it will allow the lipidic matter recovery to biogas production in the subsequent anaerobic step and will also allow to continuously operating the digester.

Physicochemical pre-treatment processes are widely applied in anaerobic wastewater treatment. Lipids are usually removed physically before biological treatment. The application of electrochemical anodic conversion of lipids based effluents could be a promising way to transfer the energetic potential of lipids into biogas, removing the potential toxic effect of LCFA.

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