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Electrooxidation as the anaerobic pre-treatment of fats: Oleate conversion using RuO_2 and IrO_2 based anodes

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ABSTRACT

Electrochemical treatment of oleate using RuO_2 and IrO_2 type dimensionally stable anodes in alkaline medium was performed to develop a feasible anaerobic pre-treatment of fatty effluents. The results showed that the pre-treated solutions over RuO_2 were faster degraded by anaerobic consortium than the raw oleate solutions or the electrolysed solutions using IrO_2. In batch experiments carried out with pre-treated solutions over RuO_2 (100–500 mg/L), no lag phases were observed before the methane production onset. On the other hand, raw oleate and pre-treated oleate over IrO_2 had originated lag phases of 0–140 and 0–210 h, respectively.

This study demonstrated that it is advantageous to apply the electrochemical treatment carried out on the RuO_2 type DSA in order to achieve a faster biodegradation of lipid-containing effluent and consequently to obtain a faster methane production.

1. Introduction

The treatment of fatty wastewater by anaerobic digestion has been subject of recent research work (Massé et al., 2002; Pereira et al., 2005). For liquid substrates, the hydrolysis of lipids to long chain fatty acids (LCFA) is not the limiting rate step, but these compounds tend to accumulate onto the sludge and give rise to flotation and washout of biomass. Being so, to treat a wastewater rich in lipids in a high rate anaerobic digester it is advisable to apply a pre-treatment process in order to eliminate the potential problems associated to the LCFA digestion. This can be accomplished either by a physical separation of fat (and eliminating, therefore, the fraction of methane production associated to this organic matter) or by applying a physico-chemical process in which the LCFA are transformed in less harmful compounds. In order to preserve the potential methane production of the effluent, a treatment based on the anodic oxidation of the lipidic matter appears as an interesting route to treat the raw waste prior its anaerobic digestion (Gonçalves et al., 2004, 2005). The excellent electrocatalytic activity of dimensionally stable anodes (DSA) makes them the ideal candidates to carry out the electrochemical conversion of such compounds. Metallic conductive oxides like RuO_2 and IrO_2 are known to be very active catalysts in anodic processes for chlorine and oxygen evolution (Trasatti, 2000). Moreover, several authors have reported the electrochemical treatment of wastewaters using RuO_2 and IrO_2 based anodes (Israilides et al., 1997; Mohan et al., 2001; Polcaro et al., 2000; Kim et al., 2002; Ihara et al., 2006).

The objective of the present work is to evaluate the suitability and performance of the electrochemical treatment of oleate using RuO_2 and IrO_2 based DSAs in alkaline conditions. Cyclic voltammetry experiments were carried out to establish the operational conditions of the electrolysis process. Anaerobic assays were performed in order to compare the cumulative methane production patterns with and without electrochemical pre-treatment. Sodium oleate was used as model since it is one of the most important and more toxic LCFA present in wastewater (Komatsu et al., 1991).

2. Methods

2.1. Voltammetric study

The electrochemical measurements were performed in a conventional three electrodes/two compartments cell. IrO_2 or RuO_2 type dimensional stable anodes supplied by ELTECH Systems Corporation (geometric area = 0.7 cm^2) were employed as working electrodes, being its potential controlled against the saturated

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calomel electrode (SCE) by an EG&G Princeton Applied Research potentiostat model 273. A 2 cm^2 area platinum sheet was used as counter electrode. The experiments have been carried out in alkaline solutions (0.1 M NaOH) in the presence and absence of 10 g/L sodium oleate. The electrooxidation studies were performed by cyclic voltammetry in the potential range of $0 < E < 1.5$ V vs. SCE at scan rates (v) of 10 and 100 mV s^{-1}.

2.2. Electrooxidation of oleate: electrolysis batch experiments

Electrolysis experiments were performed using the conditions previously established in the voltammetric study. They were carried out under potentiostatic conditions using a DC power supply (Unilab) being the anode potential controlled against the reference electrode (SCE) by a voltmeter. The cathode consisted in a large area stainless steel sheet and the anode was RuO_2 or IrO_2 type DSAs (geometric area = 1.4 cm^2). A 0.02 L volume solution of 10 g/L sodium oleate (NaOH, 0.2 M) was used for each experiment. The current intensity was continuously monitored along the electrolysis (28 h).

The solution resulting from the electrolysis experiments by using IrO_2 and RuO_2 type DSAs are designed in this work, by Product IrO_2 and Product RuO_2, respectively, being its characterization and identification still under investigation.

In order to evaluate the performance of the two electrodes, aliquots of pristine and treated lipidic solution were spectrophotometrically analysed, being the biodegradability and toxicity evaluated by means of anaerobic tests.

2.3. Analytical method

2.3.2. UV/Vis spectrophotometry

A Hitachi U-2000 double-beam spectrophotometer scanning the wavelength range of 200–700 nm was employed to monitor the sodium oleate degradation. The intensity of the UV absorption at 271 nm was used as a measure of the sodium oleate concentration.

2.4. Methanogenic activity, biodegradability and toxicity batch experiments

Methanogenic activity, toxicity and biodegradability batch experiments were performed using a pressure transducer technique (Colleran et al., 1992). The methanogenic activity test involves the monitoring of the pressure increase developed in sealed vials, maintained under strict anaerobic conditions and fed with non-gaseous substrates (acetate, propionate, butyrate and ethanol).

The hand held pressure transducer was capable to measure a pressure variation of 0.5 bar (0 to ±50 kPa) over a device range of −50 to +50 mV. The sensing element consists of a 2.5 mm square silicon chip with integral sensing diaphragm and was connected to a digital panel meter module. The device was powered by a 7.5 V DC output transformer. The basal medium used in the batch experiments is composed of cysteine–HCL (0.5 g/L) and sodium bicarbonate (3 g/L) and made up with demineralised water. It was prepared under strict anaerobic conditions and the pH was adjusted to 7.0–7.2 with NaOH 8 M. No calcium or trace-nutrients were added. In the methanogenic toxicity tests, the oleate concentration ranged from 100 to 1000 mg/L and acetate was added as co-substrate in order to evaluate the influence of oleate concentration and of the electrochemical treatment products on the acetoclastic activity. Toxicity tests were performed in triplicate assays.

Biodegradability tests were performed by adding increasing oleate concentrations before and after electrochemical treatment (100, 250, 500 and 1000 mg/L) to the sludge in batch vials. The maximum methane production rate (MMPR), the percentage of methanation (PM) and the lag phases were determined. Background methane production due to residual substrate was discounted in MMPR and PM values. Biodegradability tests were performed in duplicate assays. The specific values of degradation rate and PM were obtained by dividing the methane production rates by the volatile solids (VS) content of each vial determined at the end of experiment. Methane production was corrected to standard temperature (STP) conditions.

The suspended sludge used in the experiments was obtained from a laboratory anaerobic filter fed with skim milk as substrate. The specific methanogenic activity with acetate as a single substrate was 16.9 ± 2.9 mL CH_4/g VSS d.

3. Results and discussion

3.1. Electrochemical experiments

The electrochemical behaviour of the DSA electrodes was tested in the lipid free and lipid containing alkaline solutions. For electrode potentials higher than ~0.6 V the oxygen evolution reaction (OER) takes place. The oxidation of the oleate may be accomplished both by direct electron transfer to the electrode or via redox reaction with the evolved oxygen (Simond et al., 1997). The lower current values recorded for both electrodes at $E = 1.4$ V in the oleate containing solution (particularly for the RuO_2 based DSA) is a sound indication of the adsorption of the oleate to the electrode surface and should correspond to the decrease of the active area available for the OER.

The cyclic voltammograms were performed with different anodic scan limits. From them, a constant potential of 1.2 V *vs.* SCE was selected to carry out the long run electrolysis experiments in order to avoid excessive oxygen generation and at the same time keep the current values at significant values but lower than the limiting current density.

3.2. Efficiency of oleate conversion

UV/Vis spectrophotometric analyses of oleate at different concentrations and of both products of electrolysis were performed. In the case of oleate, a peak at the wavelength of 271 nm was observed and identified as a characteristic peak from oleate. In the spectrum of Product IrO_2 the peak at 271 nm was less defined, likely due to the conversion of oleate molecule in some extent during the electrolysis process. For the Product RuO_2, the peak at 271 nm almost disappeared evidencing the better performance of RuO_2 based anode on the conversion of oleate to other compounds, as already suggested by the cyclic voltammetry experiments.

3.3. Batch experiments

Batch experiments were performed in order to compare the cumulative methane production pattern when oleate and both electrooxidation products (Product IrO_2 and RuO_2) were biodegraded. Table 1 summarizes the results obtained for the maximum methane production rate, the percentage of methanization and the lag phases that preceded the initial methane production over the range of concentrations studied.

When comparing the lag phases obtained from the three tested substrates, it is evident that Product RuO_2 provided the lower one. From 100 to 500 mg/L of Product RuO_2, no lag phases were noticed before the onset methane production rate and only at 1000 mg/L a lag phase of 110 h was observed. Concerning the others substrates, lag phases equal and higher than 70 h were obtained for batch vial concentrations from 250 to 1000 mg/L. In the case of Product IrO_2,

Table 1
Biodegradability batch experiments: maximum methane production rate, percentage of methanization and lag phases

Substrate	Concentration in the batch vial (mg/L)			
	100	250	500	1000
Oleate				
MMPR (mL CH_4/g VSS d)[a]	6.9	2.1	7.7	19.6
PM (%)	79	79	84	78
Lag phases (h)	0	70	140	250
Product IrO_2				
MMPR (mL CH_4/g VSS d)[a]	7.56	4.1	7.1	20.8
PM (%)	70	67	76	69
Lag phases (h)	0	80	210	285
Product RuO_2				
MMPR (mL CH_4/g VSS d)[a]	7.7	1.9	7.3	9.5
PM (%)	64	55	50	56
Lag phases (h)	0	0	0	110

MMPR, maximum methane production rate; PM, percentage of methanation.
[a] Methane (CH_4) at standard temperature and pressure.

a slightly longer lag phases were attained comparatively to the oleate values. Therefore, the initial rate of methane production for Product RuO_2 was significantly higher than for other substrates (Fig. 1). The results obtained using RuO_2 based anodes suggest that the pre-treated oleate was faster biodegraded than the other substrates.

Product RuO_2 exhibited, however, lower rates of methane production and percentage of methanization than other substrates. When oleate was the sole carbon source added in batch vials a conversion of 78% into methane, at least, is recorded, in contrast with 69% and 56% achieved with Product IrO_2 and RuO_2, respectively. At concentrations of 1000 mg/mL, MMPR values of 20.8 and 19.6 mL CH_4/g VSS d were recorded from Product IrO_2 and Oleate, respectively, and only an amount of 9.5 mL CH_4/g VSS d was obtained from Product RuO_2. Additionally, final plateau value achieved for the cumulative methane production was significantly different among the three substrates (Fig. 1), being Product RuO_2 the lower one in the sequence: Product RuO_2 < Product IrO_2 < oleate.

The obtained results led to the following interpretation:

- Electrochemical treatment using RuO_2 based anodes promoted the conversion of a partial amount of oleate into less harmful compounds to the anaerobic consortium. Accordingly, no lag phases were detected during batch experiments. Other initial fraction of oleate was completely mineralised trough the electrochemical treatment, promoting the reduction of COD in the solution. Consequently, the percentage of methanization and maximum plateaux achieved with Product RuO_2 were lower than the values obtained with others substrates.
- The electrochemical treatment of oleate solutions using IrO_2 based anodes was less efficient that observed by employing than RuO_2 type DSAs. The similar behaviour of Product IrO_2 and oleate suggests that no significant transformations of oleate were verified during the electrolytic process.

The potential toxicity of the pristine and electrochemically treated solutions towards the acetoclastic methanogens of the anaerobic suspended sludge was provided by toxicity tests (Fig. 2). The capacity to mineralize the LCFA was observed for all substrates but the lag phases have been raised as the lipid concentration in the solutions increased. This fact was due to the inhibition of acetogens and acetoclastic bacteria as reported by Hanaki et al. (1981). For the concentration of 100 mg/L (Fig. 2a), both the acetate and substrates were virtually degraded at once after the lag phase but for the tested higher concentrations, acetate and substrates followed diauxic behaviour. The methane concentration attained in the first stage could be correlated with the fixed concentration of initial added acetate according to Alves et al. (2001). The second stage of methane production was proportional to the concentration

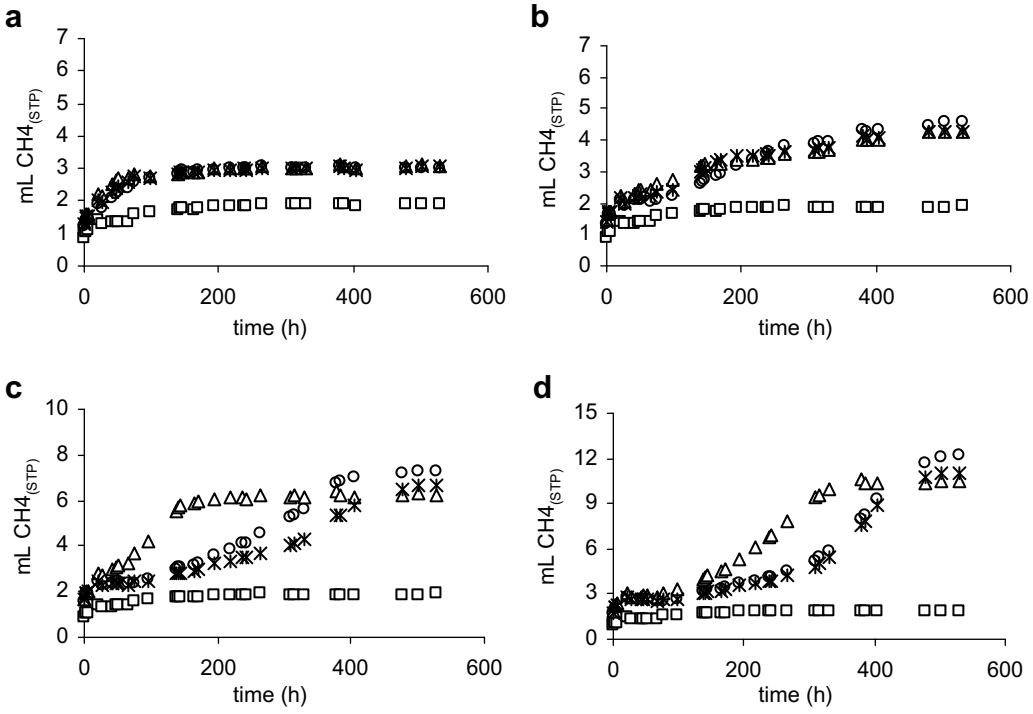

Fig. 1. Cumulative methane production due to the biodegradation of oleate (○), Product IrO_2 (*), Product RuO_2 (△) and in the blank control assay (□). (a) 100 mg/L; (b) 250 mg/L; (c) 500 mg/L; (d) 1000 mg/L.

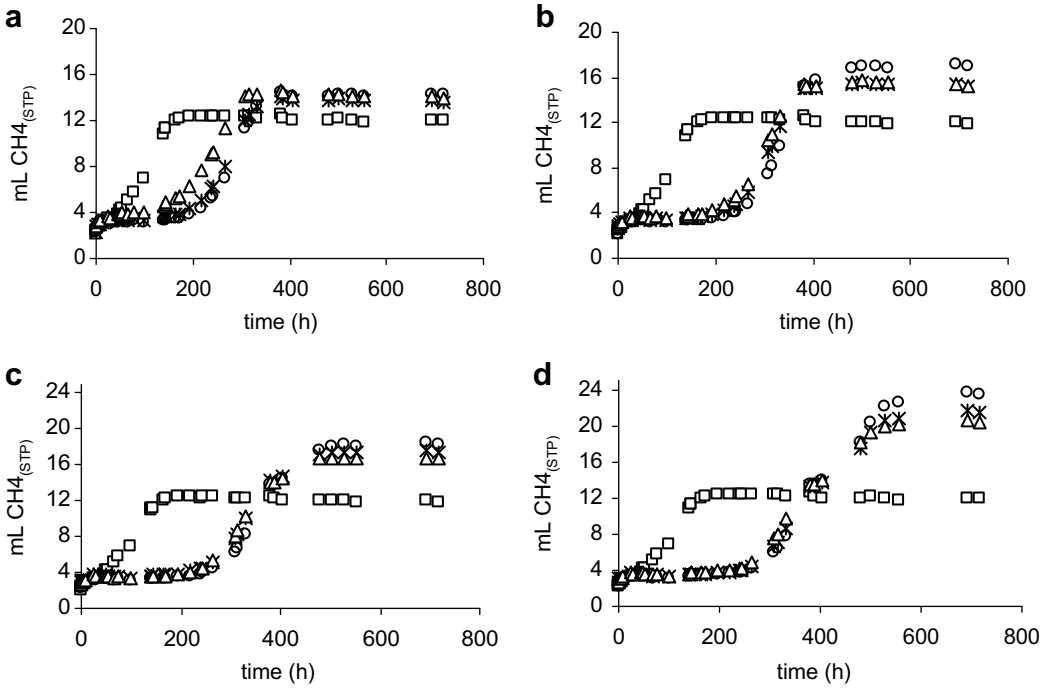

Fig. 2. Results from the toxicity tests. (□) Blank; (○) oleate; (*) Product IrO_2; (△) Product RuO_2. (a) 100 mg/L; (b) 250 mg/L; (c) 500 mg/L; (d) 1000 mg/L.

of oleate or products. Comparing the overall performance achieved by using oleate and the products of the electrochemical treatment, no substantial differences were found. Only for the concentration of 100 mg/L, an initial rate of methane production from Product RuO_2 was seen to be higher than that observed for oleate or Product IrO_2. Furthermore, a slightly lower length of lag phase was recorded for this product, irrespective to the concentration of oleate solutions electrochemically treated. These results indicate that the anodic oxidation of oleate using RuO_2 based DSAs promotes its conversion to compounds slightly less toxic to the bacterial consortium.

4. Conclusions

The anodic oxidation carried out with RuO_2 based electrode was successfully applied to oleate conversion. RuO_2 type DSA provided a higher oleate conversion than the IrO_2 based one and the resulted pre-treated oleate solution was readily degraded by anaerobic population. In batch experiments performed with the pre-treated solutions over RuO_2 (100, 250 and 500 mg/L), no lag phases were observed before the methane production onset and only at the highest tested concentration (1000 mg/L), a lag phase of 110 h was detected. On the other hand, a behavioural similarity was observed between the two other substrates. Concentrations from 250 to 1000 mg/L of raw oleate and pre-treated oleate over IrO_2 had originated the lag phases of 70–250 and 80–285 h, respectively. Furthermore, the initial rate of methane production for Product RuO_2 was significantly higher than for other substrates. In order to achieve a faster biodegradation of lipid-containing effluent and consequently to obtain a faster methane production, it is advantageous to apply the electrochemical treatment carried out on the RuO_2 type DSA. Anodic oxidation of the lipidic wastes prior the anaerobic treatment makes possible to avoid disturbances in the digesters operation related to the wastewater lipidic matter and even to recover the potential methane of this material fraction instead of to reject it.

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