PILOT-PLANT RESULTS OF OLIVE MILL WASTEWATERS TREATMENT BY ANAEROBIC DIGESTION: EFFECT OF POLYPHENOLS REMOVAL BY ELECTRO-POLYMERIZATION

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SUMMARY: To enhance the anaerobic digestion of OMW, electro-polymerization pre-treatment stage was necessary to reduce the amount of total phenolic compounds and associated toxicity. An anaerobic filter was fed with the undiluted pre-treated OMW at a first loading rate of 1g COD l^{-1} day^{-1} followed by higher loading rates. Results showed that the COD reduction was 75 %. The biogas productivity rise gradually when increasing the loading rate. At a loading rate of 10 g COD l^{-1} day^{-1}, the percentage of methane in the biogas produced by the anaerobic digester was found to be in a range between 75 and 85%, with a corresponding methane yield of about 0.34 CH_4 g^{-1} COD. The biomethanisation process was found to be stable during 4 months of operation without any apparent toxicity.

1. INTRODUCTION

Olive mill wastewater is considered to be one of the most polluting effluents of the food industry and constitutes a source of important environmental problems for olive oil producing countries of the Mediterranean area. Generally, this wastewater is characterized by very high chemical oxygen demand (COD) values (in the range of 50-200 g l^{-1}), BOD values (12-60 g l^{-1}), total solids content (40-150 g l^{-1}) and acidic pH (about 5). Another negative property of OMW is the high concentration of polyphenols, up to several grams per litre, which are toxic to bacteria commonly used in biological oxidation plants.

The clear advantages of anaerobic digestion of the organic matter make it the process of choice (Borja *et al.,* 1992). However, many problems concerning the high toxicity and inhibition of biodegradation of OMW have been encountered during anaerobic treatments because of the presence of phenolic compounds (Sayadi *et al.,* 2000). Therefore, the elimination or the reduction of these compounds from OMW is an important objective in order to reduce its toxicity and to permit the occurrence of microbial fermentation. Physico-chemical pre-treatments including flocculation-coagulation, ultrafiltration and reverse osmosis, have been also considered for reducing the solid and toxic compound content, but they are generally very expensive and/or unable to solve the problem completely of the need to dispose the sludge derived from the process.

Fenton reagent as an advanced oxidation process based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, has been used with an increasing interest due to their high oxidant power (Kestioglu *et al.,* 2005).

The electro-Fenton systems are of three main types: in the first, the H_2O_2 is generated from two-electron reduction of sparged oxygen on the cathode while Fe^{2+} is added. The second uses added H_2O_2 and electrogenerated Fe^{2+} which are produced via the oxidation of iron, the sacrificial anode (Brillas *et al.,* 1997). In the third type, H_2O_2 is added while Fe^{2+} is electrogenerated via the reduction of ferric sulphate or ferric hydroxide sludge. In the electrolysis treatment of the OMW using iron electrodes, the second type of the EF system is established, as was also demonstrated by the thickness of the anode.

The objective of this research was to study the treatment of OMW by combined process electro-Fenton reaction using iron anodes, followed by anaerobic digestion.

2. MATERIALS AND METHODS

2.1. Wastewater

Fresh OMW was obtained from a discontinuous olive oil processing plant located in Sfax (southern Tunisia). Table 1 shows the typical characteristic parameters of OMW from the region.

Table 1: Characteristics of raw OMW, electro-Fenton treated OMW after sedimentation (EF+Sed) and anaerobic treated effluent (Eff).

Parameter	OMW	EF+Sed	Eff
pH	6.5	8.17	8.3
Coloration at 395 nm	72±5	25±2	20.5±3
COD g l^{-1}	95±4.5	45±2.3	11±1.5
BOD_5 g l^{-1}	19±2	22.3±1.6	3.8±0.4
TSS g l^{-1}	15±4	2.5±0.7	1.5±0.5
Lipids g l^{-1}	9.75±1.2	0.67±02	not detected
Polyphenols g l^{-1}	11.5±1.6	2.5±0.8	1.2±0.4
Monomers mg l^{-1}	2740±50	876.25±27	495.7±12

2.2. Description of the whole process

Raw OMW was pre-stored in a 300 l static separator in order to remove suspended solids. pH and H_2O_2 concentration of decanted OMW were adjusted in the first tank. This OMW effluent was fed into the electro-Fenton reactor at a 9 l h^{-1} rate of alimentation using a pump. After 4 hours of residence time, the EF treated OMW was recovered in a second static decanter and successively in a second basin. Pretreated OMW was fed into the anaerobic filter at 6 times per day using a pump connected to a programmer.

2.2.1. Electro-Fenton pre-treatment

A pilot scale reactor (36 l), divided in four compartments, was used for the electro-Fenton (EF) reaction. A direct current was imposed by a stabilized power supply during the treatment. All the quantity of H_2O_2 was added at once in the first OMW tank where pH was regulated and the mixture was stirred. Current intensity of 20 A was applied to electrolysis system which was supplied with effluent at a flow rate of 9 l h^{-1}. Each four days (96 h) the electrolysis system was stopped and the reactor was emptied to clean the electrodes plates.

2.2.2. Anaerobic biotreatment

The anaerobic treatment of electro-Fenton pre-treated OMW was performed in an up-flow anaerobic filter (AF). This AF reactor already acclimated for degrading OMW, consisted of a 300 l double jacket stainless steel column packed with PVC rings. The working volume of the reactor was 275 l. The temperature of the reactor was adjusted to 37°C. The OMW pre-treated with EF was fed into the reactor, without dilution and pH regulation, 6 times per day using a pump connected to a programmer. The mean loading rates varied from 1 to 10 g COD l^{-1} d^{-1}. For monitoring the volatile fatty acids (VFA) inside the reactor, three sampling ports were made in the AF. Level (A) was at the bottom of the reactor. Level (B) corresponded to the middle and level (C) was at the top of the reactor.

Gas production was measured by a biogas counter. Gas samples were taken with a syringe from the biogas tank. CH_4, CO_2 and N_2 were measured using a gas chromatograph.

2.3 Physicochemical analysis

The value of COD was estimated using the method described by Knechtel (1978). BOD_5 was determined by the manometric method with a respirometer (BSB-Controller Model 620 T (WTW)). The coloration was monitored by measuring the absorbance at 395 nm, the wavelength at which OMW presented the maximum absorbance, using a spectrophotometer. Total polyphenols were quantified by ethyl acetate method as described by Sayadi *et al.,* (2000). The standard method of Soxhlet solid/liquid (organic solids of OMW/hexane) was utilised for the dosage of lipids. The ortho-diphenol concentrations were determined by the method described by Folin and Ciocalteau (1927).

2.4. Analysis of simple aromatic compounds and molecular mass distribution of polyphenols

Concentration of simple aromatic compounds and analysis of molecular-mass distribution of OMW polyphenols were determined by HPLC (Khoufi *et al.,* 2006).

3. RESULTS AND DISCUSSION

3.1. Electro-Fenton pre-treatment

In order to produce sufficient pretreated effluent for the post-biotreatment, EF of OMW was realised in a 36 l reactor functioning in semi-continuous mode. The HRT of OMW in the EF reactor was 4 h that yielding a daily production of about 216 litres of treated effluent.

Fig. 1 a shows the evolution of the COD concentration of influent and effluent during the semi-continuous EF treatment. The COD feeding was variable and ranged between 65 and 100 g l^{-1} while the effluent COD ranged between 35 and 50 g l^{-1}. The EF treatment resulted in an average COD removal of 48%.

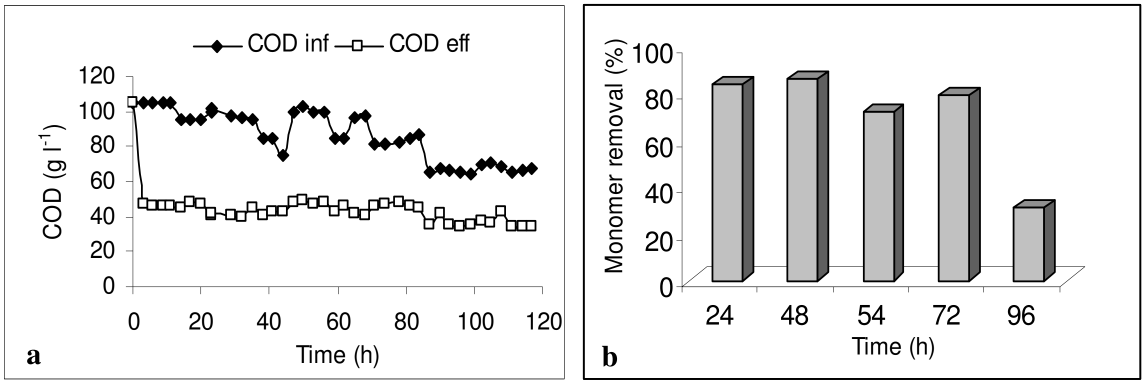

Figure 1: Evolution of the COD concentration of influent and effluent (a) and monomers removal (b) during EF treatment of OMW in semi-continuous mode.

After the electrochemical treatment, the high concentration of suspended solids was separated by decantation. Table 1 shows the characteristics of OMW after EF-sedimentation treatment (EF). During the sedimentation step, pH of EF treated OMW shows a decrease from 8-9 to 6.8-7.5 (Table 1). These values are favourable for biological post-treatment. The soluble COD removal was approximately 53% after EF and sedimentation treatment. After 2 days of sedimentation, the obtained effluent presents a lesser quantity of TSS (2.5 g l^{-1}) in comparison with the raw OMW (15 g l^{-1}). These results seem to be clear evidence that EF pretreatment provides a good clarification, and a rapid settling sludge (polymeric product). The analysis of total aromatic compounds (polyphenols) shows a decrease from 11.5 g l^{-1} to 2.5 g l^{-1} (Table 1). Moreover, the concentration of lipids was decreased to about 93% (Table 1).

The formation of TSS was due to the polymerization of polyphenols during the electrolysis treatment (Khoufi *et al.,* 2004). The molecular-mass distribution of crude OMW and effluent after 2 and 4 h of EF treatment using Size Exclusion-High Pressure Liquid Chromatography provided the hypothesis of polymerisation of low molecular-mass phenolic compounds (LMM) to compounds of high molecular-mass (HMM) (Fig. 2). However, the peak corresponding to aromatics of HMM showed a decrease after 4 h of EF treatment.

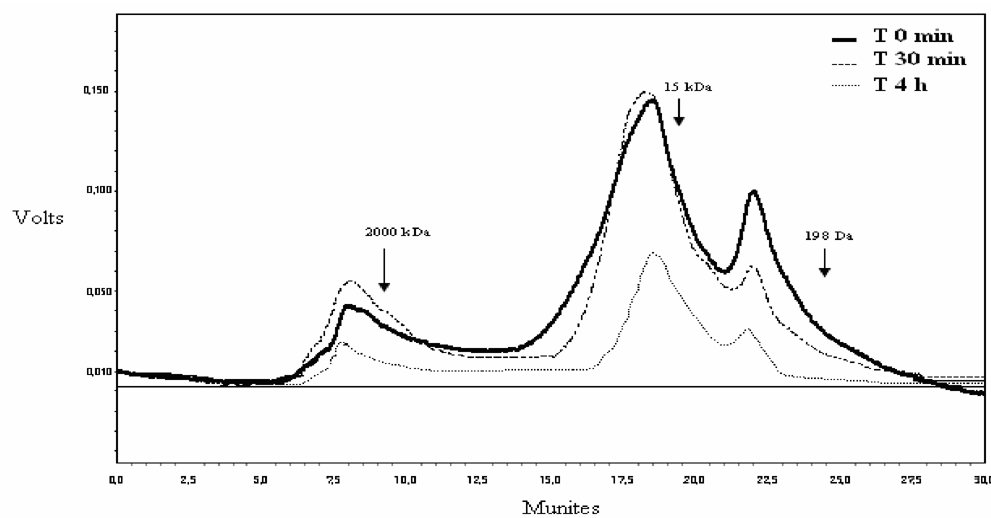

Figure 2: Molecular mass distribution of phenolics from crude OMW and treated OMW at 30 min and 4 hours of EF treatment in batch mode.

Chromatographic studies indicated that highly toxic simple phenolic compounds such as hydroxytyrosol and 3, 4 dihydroxyphenyl acetic acid, could be totally removed by electrolytic process. Quantitative evolution of total monomers measured by HPLC during 3 days of continuous EF treatment was also determined. The total concentration of these compounds was reduced from 2740 to 436 mg l^{-1} after 4 h of EF treatment (Fig. 1b). This value remained stable up to 72 h of continuous treatment. However, after 96 h of continuous EF treatment, the concentration of simple phenolic compounds increased to 1875 mg l^{-1}. This can be explained by the inefficiency of the treatment system due to the adhesion of polymeric product on the anode surfaces. For this reason the EF reactor was stopped at 96 h to clean the electrodes plates.

These results confirm the hypothesis that the electrolysis reaction would have an important role in elimination of polyphenolic compounds and lipids from OMW. In fact, under acidic conditions, a Fe^{2+}/H_2O_2 mixture produces $OH^{\cdot}$ radicals. These radicals have an oxidizing potential of 2.8 V and are capable of oxidizing a wide range of organics in wastewater. Fenton oxidation has been used in the treatment of organics like phenol (Kavitha and Palanivelu, 2004), chlorophenol (Kang *et al.,* 2002) and 2, 4 dinitrophenol (Kang *et al.,* 1999). Results of this study proved the effect of hydroxyl radicals on the oxidation of simple monomers and the effect of complexes on the polymerization and precipitation of the polyphenols of LMM and HMM as well as the long chain fatty acids. COD, polyphenols and lipid removals are consistently important. In fact, the effluent quality of the pre-treated OMW by EF-sedimentation process was excellent. It could be directly used as influent to anaerobic reactor without dilution and pH regulation. Fenton's reagent showed three very important advantages: removal of COD and phenolic compounds, pH neutralization and lower production of residual sludge that can be used for composting.

3.2. Anaerobic biotreatment

The anaerobic digester was fed with the undiluted pre-treated OMW at a first loading rate of 1 g COD l^{-1} d^{-1} followed by higher loading rates. The evolutions of the COD of influent and effluent, organic loading rate, biogas production and methane yield during the anaerobic treatment are presented in Fig. 3. Results showed that the mean COD reduction was 75% during the period of digester function (Fig. 3a). However, at a loading rate of 8-10 g l^{-1} d^{-1}, the removal efficiency of COD showed a progressive decrease. This can be explained by the low retention time of influent into the reactor. Fig. 3 b-c shows that the biogas productivity increased with increasing the loading rate. The percentage of methane in the biogas produced by the AF was found to be in the range of 70% (data not shown), with an average methane yield of about 0.33 l CH_4 g^{-1} COD introduced. The system could generate more than 1200 l of biogas per day at an organic loading rate of 10 g COD l^{-1} d^{-1}. Fig. 3 (b-d) shows that at the highest loading rates (9-10 g COD l^{-1} d^{-1}) the yields obtained were approximately 0.3 l of CH_4 g^{-1} of COD introduced. The higher values of yields (0.32 to 0.34 l CH_4 g^{-1} COD introduced) were obtained with loading rates less than 10 g COD l^{-1} d^{-1}. The biomethanization process was found to be stable during 4 months of operation without any toxicity phenomenon.

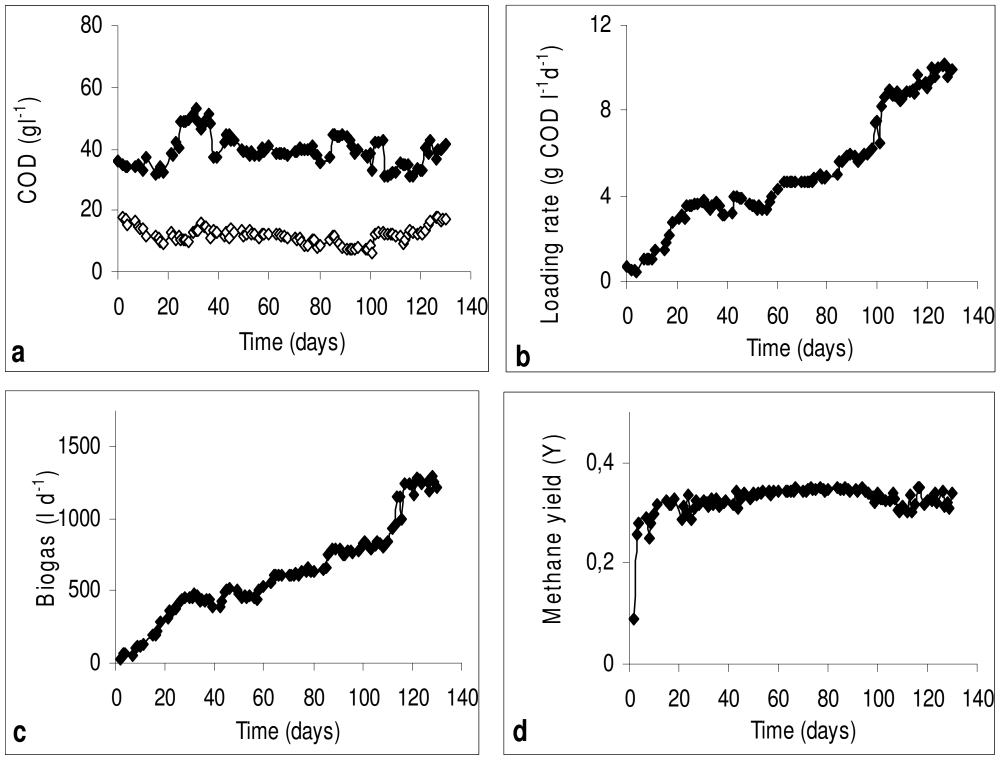

Figure 3: Evolution of the COD of influent and effluent (a), organic loading rate (g COD l^{-1} d^{-1}) (b), biogas production (l d^{-1}) (c) and methane yield (l CH_4 g^{-1} COD introduced) (d) during anaerobic digestion of electro-Fenton pre-treated OMW at pilot scale.

The methane production was proportional to the loading rate. Anaerobic digestion is a complex process consisting of a series of microbial transformation of organic materials to methane and volatile fatty acids (VFA) such as acetate, propionate, butyrate, iso-butyrate, valerate and iso-valerate. These VFA have long been recognized as the most important intermediates in the anaerobic process and have been proposed as a control parameter (Mechichi and Sayadi, 2005). Therefore, changes in VFA concentration can be in response to variation in temperature, organic loading rates or the presence of toxicants. The dynamics of VFA production and pH measurements at the bottom (A), the medium (B) and the top (C) of the reactor are shown in Fig. 4. The pH at the bottom of the reactor, where OMW is introduced, showed a low pH value (acid), whereas no such change was observed at the top and the medium of the reactor (Fig. 4a). The values of pH at levels B and C were optimal (higher than 7.2) and stable. The VFA concentrations were low even at the higher loading rates at the different levels of the reactor (Fig. 4b).

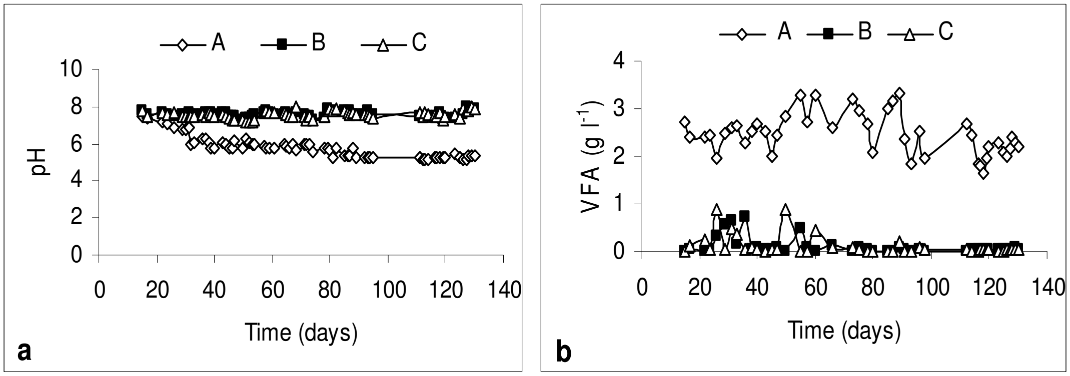

Figure 4: Evolution of the pH (a) and the VFA concentration (b) in the anaerobic filter during the methanization of electro-Fenton pre-treated OMW (A: bottom of the reactor, B: middle of the reactor, C: top of the reactor).

Knowing that in the same conditions, untreated OMW causes inhibition of methanisation and acidification of the reactor at a loading rate of 3.5 g COD l^{-1} d^{-1} (Khoufi *et al.,* 2006), we can conclude that pre-treatment of OMW by EF process resulted in decreasing the toxic effect of this wastewater on anaerobic digestion and promote the methane productivity. Thus, the utilization of the above-described semi-continuous EF technique with anaerobic digestion at pilot scale seems to be a very attractive method for OMW processing. These results confirm the possible scale-up of the OMW treatment process suggested by Khoufi *et al.* (2006) at laboratory scale.

5. CONCLUSION

Treatment of OMW by combined process EF system and anaerobic digestion was investigated at pilot scale. Results of EF-sedimentation treatment yielded 52.6% removal of total COD, 83.77% removal of TSS, 78% removal of polyphenols and more than 93.13% removal of lipids. The resulting effluent was more readily degradable anaerobically than the original untreated effluent. The anaerobic processing of EF treated OMW involved no inhibition phenomena at a loading rate increasing from 1 to 10 g COD l^{-1} d^{-1} and yielded a high production of methane. This result opens promising perspectives since its conception as a fast and cheap pre-treatment prior to conventional anaerobic post-treatment.

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