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Utilization of Olive Mill Waste in Microbial Electrolysis Cell

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Abstract

Olive oil production is a source of huge amount of residuals knowns as OMW (Olive Mill Waste). The sustainable management and treatment of this waste is challenging due to presence of high amount of specific pollutants. The OMW is characterized by very high COD to BOD ratio with considerable content of polyphenols reaching up to 15g/l. Due to this, the biological utilization of OMW could be hindered or very slow when the conventional aerobic and anaerobic methods are used. In this study, the Microbial Electrolysis Cell (MEC) technology was applied as an alternative treatment approach. The method offers COD reduction and energy recovering in the form of hydrogen. The results demonstrated up to 65% efficiency in terms of COD and polyphenols removal which suggest that MEC, could be considered as an initial treatment stage in OMW utilization.

Keywords: *MEC, OMW, polyphenols*

1. Introduction

The food industry is rarely a source of hazardous or difficult to treat wastewater. Nevertheless, the processing of some specific raw materials can generate waste streams with high amounts of some more complex to treat pollutants. An example in this regard is the processing of olives to olive oil (fig. 1). The effluents from this production, known as Olive Mill Waste or OMW, are suspensions with a high content of insoluble substances, high dissolved organic matter content and extremely high concentrations of polyphenols (reaching up to 15g/l) [1]. Polyphenols expose a highly inhibitory effect on microorganisms and this makes it extremely difficult to treat OMW by standard aerobic and anaerobic bio-processes. The average amount of the wastewater generated during the processing of 1000kg of olives is presented in Fig. 1 although it may vary considerably depending on the particular technology being applied.

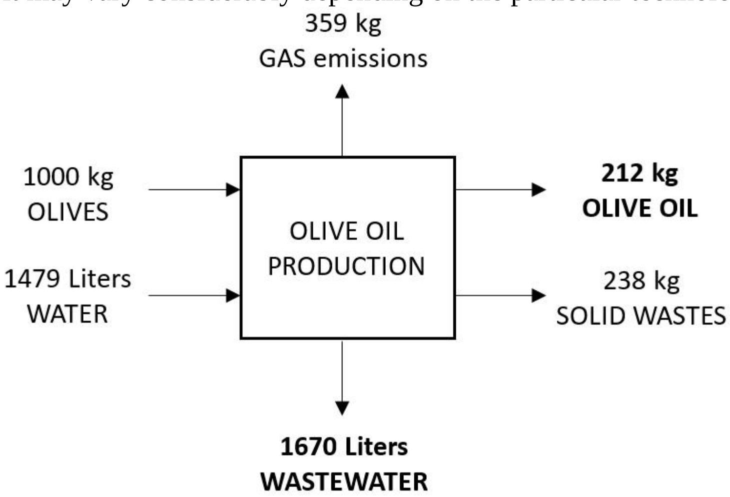

Figure 1. Material flows and balance in the production of olive oil [2].

Several technologies have been developed and applied for the treatment of this wastewater. The different methods offer a different degree of water purification, which depends on the local legislation, the site in which it is discharged, the technological possibilities in the area of water formation, etc. According to the principles on which OMW utilization is based, the treatment methods are classified as: **Physical methods -** evaporating lakes; **Biological methods -** aerobic and anaerobic degradation and composting; **Physico-chemical methods -** membrane technologies (including combined evaporation and wet oxidation), specific removal of phenolic compounds by ion-exchange.

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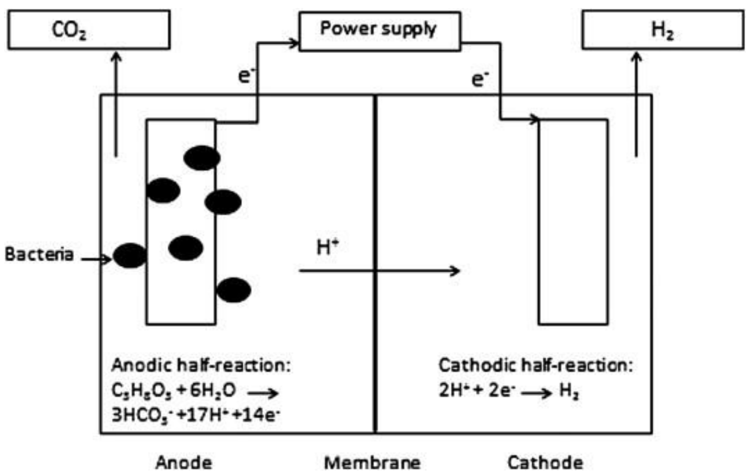

Figure 2. Construction of microbiological electrolysis cell and mechanisms of anodic and cathodic semi-reactions.

Some combined approaches like combination of chemical, physical and biological methods also exist. However, an alternative is strongly demanded due to the low efficiency or high cost of all the currently applied practices. One of the new methods which has been intensively studied in the recent years are the bio-electrochemical reactors such as Microbiological fuel cells (MFC) [3]. They are reactors that convert the biodegradable substrate directly into electricity through biological oxidation by the so called electrogenic bacteria [4, 5]. Microbiological electrolysis cells (MECs) are a type of bio-electrochemical reactors which, unlike the conventional MFC, lacks a terminal acceptor of the electrons which could result in production of hydrogen in the cathode compartment (fig. 2). Properly working MEC is directly converting organic matter (pollutants) into hydrogen. This approach is interesting in the context of the increasing popularity of hydrogen as an alternative energy source which could replace partially the fossil fuels. Typically, a disadvantage of this type of bio-electrochemical reactors is the need for an external source of energy required to overcome the thermodynamic limitations of the cathode reactions. At first glance this makes MEC less attractive than traditional MFCs. However, the intensive development of variety renewable energy sources and in particular the use of solar energy is a factor that eliminates this disadvantage. Especially taking into account the fact that the cultivation and processing of olives takes place in areas usually characterized by favorable climate conditions and accessibility of solar energy.

2. Experimental

2.1. Microbial Electrolysis cell

The microbiological electrolysis cell was made of transparent materials in order to observe the eventual accumulation of hydrogen in the cathode space. Carbon cloth electrodes and Nafion proton exchange membrane with a rectangular section were prepared and staked into the assembled cell in corresponding compartments (fig. 3). The anodic compartment was filled with OMW and distilled water was used as a cathode solution. An additional source of electricity was included in the external circuit while maintaining a constant potential difference of 1-1.2 V. During the experiments, the concentrations of phenolic compounds and the COD of the waste water in the anode chamber were determined periodically.

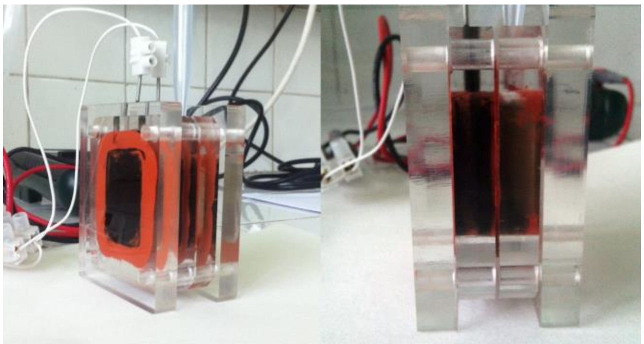

Figure 3. Lab Scale MEC

2.2. Analytical Methods

2.2.1. COD

The COD determination was performed with Hach Lange LCK314 test and Hach Lange DR3900 automated spectrophotometer following the procedure described by the manufacturer. The samples were diluted to fit the test range of 15-150 mgO2 /l.

2.2.2. BOD

BOD of the OMW samples was determined using the LoviBond OxiDirect analyzer according to the protocol described by the manufacturer.

2.2.3. Total Phenolic Compounds

To determine the total phenols in the samples studied, the colorimetric method of Folin–Ciocalteu was used in the following analytical procedure: a sample of 1 ml was diluted in 1:100 ratio with distilled water and 5ml 0.5M Na2CO3 and 1ml Folin–Ciocalteu reagent were added. Then the samples were incubated at 28° C for 30 minutes. The intensity of blue staining of the test samples are measured on a spectrophotometer at 660nm. The final results were obtained by calibration equation obtained previously with standard solutions:

$$x = \frac{(y*R)+0{,}0603}{0{,}0104} \quad [mg/l],$$

where y is the light absorption of the sample taken at 660nm. R- dilution factor

2.2.4. TSS

Determination of the total suspended solids (TSS) in the OMW samples was carried out by *Metler* Moisture Analyzer. Sample processing includes pre-filtration and drying to constant weight at 105°C.

2.2.5. Other methods

The electric parameters during the experiments were monitored using a MY-66 digital multimeter. The microbiological analysis of the OMW involves classic cultivation techniques and incubation of the samples in rich medium at 28°C for 72 hours.

All measurements are made in three iterations and are presented as averages in "Results and Discussion".

3. Results and discussion

3.1. Initial Characteristics of the OMW Samples

The subject of this study were real OMW samples from Lesvos island, Greece obtained from for press method olive oil production. The main parameters and target pollutants in the wastewater were analyzed and the data obtained are presented in Table 1.

Table 1: Initial parameters of the OMW samples

Pollutant	Value
COD	122 gO_2/l
BOD	48 gO_2/l
TSS	23 g/l
Total phenols	8,9 g/l

Typically for this type of waste flows, the COD / BOD ratio is extremely high. This is an indication for the presence of a pollution fraction with low biodegradability. Probably part of this negative effect is due to the high concentration of polyphenols (nearly 9 g/l).

In addition to the chemical characterization, the microflora presented in the sample was also analyzed. It was found out that the microbial population is dominated by a yeast species identified as a representative of the Pichia genera known for their role in the fermentation of the organic substrates, especially in the conversion of polyphenolic

compounds in volatile derivatives with specific smell. This activity, for example, is associated with the deterioration of some wines and their organoleptic qualities [6, 7, 8, 9].

3.2. Utilization of OMW in MEC-type reactor

The main focus of the study was on the treatment of wastewater from olive oil production in MEC. For this purpose, a laboratory reactor was constructed (described in "Materials and Methods"). Control of the process was carried out in terms of concentration of phenols and COD. The results of this experiments are presented in Fig. 4 and Fig. 5.

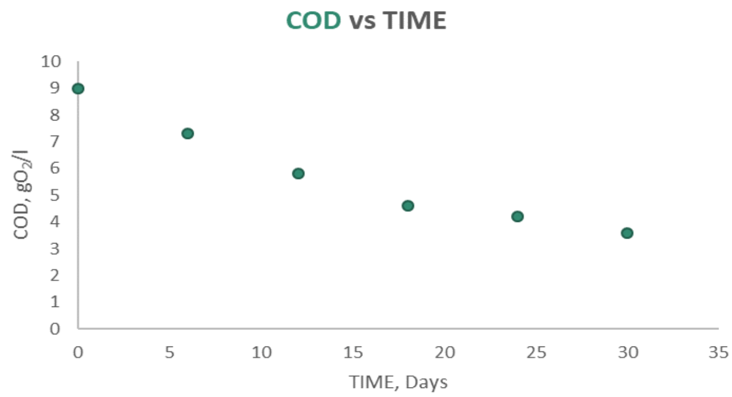

Figure 4: COD removal during utilization of OMW in MEC.

The maximum and average rates of COD reduction observed were of 7.8 and 3.6 $gO_2/l/d$ respectively with total COD reduction of around 65%. The rates and effects observed are comparable to those in conventional biological processes such as anaerobic digestion [10, 11, 12]. However, the MEC technology could hide some extra potential that can be mobilized after optimization of the operating conditions. During the process, partial removal of the polyphenols contained in the OMW was also observed (fig. 5). It should be noted that degradation of the aromatic hydrocarbons (even partial) could have positive effect on the overall biodegradability of this waste flow and makes them available for utilization in conventional bio-processes due to the decreasing inhibitory effect of the phenols.

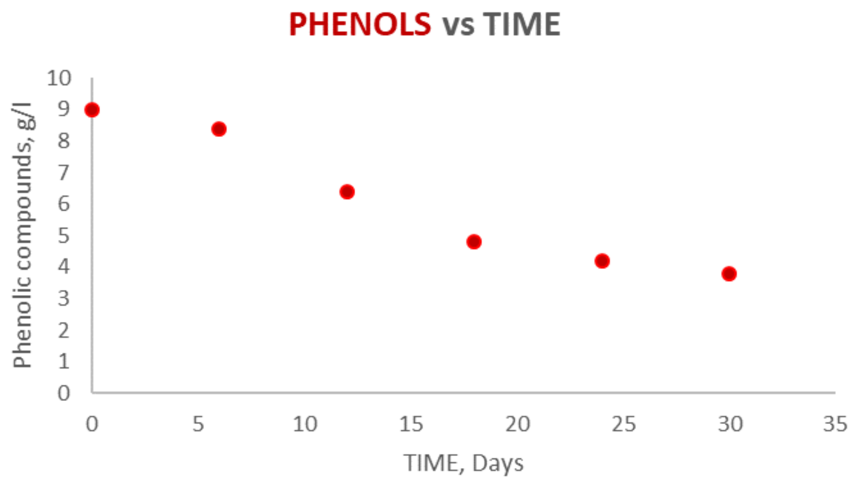

Figure 5. Total phenol concentration during utilization of OMW in MEC.

The main advantage and benefit of the MEC-based technology over the conventional biological processes is the ability to obtain hydrogen form waste. In our experiment, a gas bubbles were observed in the reactor’s cathode chamber

during its operation. Although we did not have a technological possibility to objectively evaluate the composition of this gas, taking the chemistry and mechanism of the cathode reactions into account, it could be assumed that it is probably hydrogen (fig. 6).

Figure 6. Gas bubbles (possibly hydrogen) during the MEC operation.

4. Conclusion

In this study the feasibility of MEC technology in order to simultaneously treat OMW streams and recover energy in the form of hydrogen was proved in laboratory conditions. The possibility of direct conversion of organic waste into hydrogen could be alternative to anaerobic digestion and methane production when it comes to energy recovery. The evaluation of these two processes should be a result of an in-depth thermodynamic and economic analysis, taking into account the cost of equipment, operating costs and overall yields of energy (both in the form of hydrogen and methane).

Acknowledgements

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