Assessment of electrocoagulation as a pretreatment method of olive mill wastewater for biofuels production in a biorefinery concept

G. Antonopoulou¹, I. Ntaikou¹, M. Alexandropoulou¹, D. Vayenas^{1,2}, G. Lyberatos^{1,3}

¹Institute of Chemical Engineering Sciences, Stadiou, Platani, Patras, GR 26504, Greece ²Department of Chemical Engineering, University of Patras, Karatheodori 1 st, GR 26500, Patras, Greece ³School of Chemical Engineering, National Technical University of Athens, GR 15780 Athens, Greece

Presenting author email: geogant @chemeng.upatras.gr

Extended abstract

During the last decades, increasing attention has been paid to discovering alternative ways of handling olive oil mill wastewater (OMW), and a wide range of processes have been proposed, aiming to the reduction of the organic load and the pollutant effects, especially those of phenolic compounds. Electrocoagulation is a promising method for wastewater treatment which has been used for OMW (Sounni et al., 2017). With this technology, in situ generation of coagulant species by electrolytic oxidation of sacrificial anode materials, triggered by electric current applied through the electrodes, is carried out. The metal ions generated by electrochemical dissolution of a consumable anode spontaneously undergo hydrolysis in water, depending on the pH, forming various coagulant species including hydroxide precipitates (able to remove pollutants by adsorption/settling) and other metallic ion species. In addition, several side reactions, such as hydrogen bubble formation and the reduction of metals on cathodes, also take place in the cell. On the other hand, microbiological methods, such as composting or biofuels production processes, have been proposed so far for the simultaneous valorization of OMW. In terms of biofuels production, biogas via anaerobic digestion (AD) is the most studied one (Abdallah et al., 2017), whereas bioethanol generation and biohydrogen production via dark fermentation (Ntaikou et al. 2008; Nikolaou and Kourkoutas, 2017) have also been investigated lately. However, the presence of toxic compounds such as phenolic compounds, to archea, bacteria and yeasts which are used in microbial processes, appears to be a significant problem for process stability and efficiency.

In the present study, EC and its combination with precipitation or centrifugation was assessed as a pretreatment method for enhanced biofuels production from three phase decanter OMW including also the wash waters of the olive oil production process. Experiments were performed using Al or Fe electrodes, in an electrocoagulation reactor consisted of one anodic and two cathodic electrodes, with an effective surface area of 12 cm² each, and a current density supply of 0.17 A/cm². Undiluted and diluted with tap water OMW (1:2 and 1:3) were treated for 120 min, under 2 A and the main results obtained are presented in table 1.

Electrode	Dilution	COD (%)	d-COD (%)	Sugars (%)	Phenols (%)
Al	no	54.71 ± 3.56	17.47 ± 1.19	5.17 ± 0.02	36.96 ± 2.36
	1:2	39.10 ± 2.15	30.57 ± 2.47	12.61 ±0.36	74.77 ± 5.16
	1:3	45.69 ± 2.45	36.76 ± 2.08	$18.04\pm.098$	68.14 ± 4.23
Fe	no	48.48 ± 3.45	$12.88\pm.098$	14.30 ± 1.25	20.36 ± 0.97
	1:2	46.71 ± 3.45	26.78 ± 2.20	20.85 ± 1.29	72.61 ± 2.15
	1:3	27.14 ± 2.25	35.96 ± 2.15	36.67 ± 2.36	70.65 ± 5.15

Table 1. Reduction in the main characteristics of OMW during EC at different dilutions with Al and Fe electrodes

In the second set of experiments, diluted OMW (1:2) was subjected to EC with 2 A current for 90 min, with either Al or Fe electrodes and further combination with precipitation of centrifugation was investigated. Precipitation as combined with EC treatment results to lower phenolic removal for both electrodes tested compared to centrifugation and, as such, centrifugation can be considered preferable for combined pretreatment. In the third set of experiments, the effect of current density (0.05, 0.5 or 1 A) for 180 min during the combined EC – centrifugation process was assessed and a trend for higher COD, d-COD and phenolics reduction for the higher current applied, i.e. for 1A was observed.

The different fractions of the combined pretreatment methodologies were assessed as substrates for methane and hydrogen production via mixed acidogenic consortia as well as for bioethanol production using *Saccharomyces cerevisiae*. It was shown that even with lower phenolic concentration, EC at the conditions of 2 A, 90 min, did not enhance biofuels production and combination of EC (at these conditions) with physical methods also led to lower biofuels yields. However, reduction of the current during EC to 0.05 A or 0.5 A, led to higher methane and ethanol yields, for both electrodes (figure 1, results from Fe electrode).



Figure 1: Methane, hydrogen and ethanol production yields for raw and pretreated samples different current densities

From fig. 1 it can be seen that the reduction of the current during EC to 0.05 A or 0.5 A, led to higher methane yields. Regarding the hydrogen yield, decrease of current to 0.05 led to 115 % increase of hydrogen potential compared to 2 A. Regarding ethanol production, decrease of current to 0.05 led to 3 fold increase of ethanol potential compared to raw OMW, while decrease of current to 1 A led to 2 fold increase of ethanol yield.

In figure 2 the energy recovery in the form of methane, hydrogen and ethanol in a biorefinery concept, is presented. It is obvious that the concept of using the solid and liquid fraction after EC with Al, and then centrifugation, towards methane lead to the production of 1630,8 kJ/ L OMW, while the respective value for Fe is 1902, kJ/L OMW.



Figure 2: Energy recovery in the form of biofuels at the optimum scenario.

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