

Electrohydrolysis of Olive Mill Wastewater: Effect of Applied DC Voltage

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Abstract— The aim of this study is the investigation of electrohydrolysis treatment process for olive mill wastewater in terms of pollutants removal and hydrogen production. For this purpose, Different voltages including 4, 6 and 8 V DC were tested for 3 hours. 8 V DC for 3 hours was found to be as the most effective condition. At this optimum voltage, different time periods were also investigated. At 8 V, significant pollutant removal efficiencies were obtained. 68% turbidity, 70% TSS, 52% COD and 19% sCOD removal efficiencies were achieved. Volume of produced gas was 1500±10 ml and hydrogen percent was determined as 85%. Hydrogen production along with pollutant removal is one of the advantages of electrohydrolysis. Therefore, electrohydrolysis can be proposed as a feasible alternative treatment step for wastewaters which is characterized by high organic matter and also suspended matter.

Keywords— Electrohydrolysis, Hydrogen production, Olive mill wastewater, Pollutant removal.

I. INTRODUCTION

MARMARA region including Canakkale is one of the main parts for olive oil production in Turkey. Olive mill wastewater (OMW), has high amount of organic matter and also toxic/ inhibitory compounds such as lipids and phenolic compounds. Therefore it is not easy to treat such strong wastewater with conventional treatment processes.

In literature, several treatment options and strategies including; centrifuge [1], evaporation [2], filtration [3], ecoagulation [4]-[5] and applying to land [6] have been proposed for management of olive mill wastewater. Besides these methods; advanced treatment processes such as ozonation [7]-[8]-[9], photocatalysis [10], electrocoagulation [5]-[11], fenton oxidation [12], ozone and fenton oxidation [13] and wet air oxidation [14] have been tested for olive mill wastewater treatment. However, these processes have a disadvantage of either high operating costs or high sludge quantities which requires additional treatment thereby additional investment and operating cost. Therefore, it has been proposed combined methods comprising of pretreatment unit and advanced treatment steps for olive mill wastewater in order to facilitate the degradation of complex organic matters

and reduction of toxic and inhibitory substances. Chemical, physicochemical, enzymatic and thermal oxidation processes are commonly used as pre-treatment step for OMW.

In recent years, electrohydrolysis (EH) studies has gained momentum as an effective method to produce hydrogen energy from different waste/wastewaters with simultaneous pollutant removal[15]. The main advantages of process are energy efficiency [15], simple equipment, easy operation, environmental compatibility, low capital and low operating cost [16]-[17].

Therefore, the aim of this study is the investigation of electrohydrolysis treatment of OMW in terms of removal of pollutants and simultaneously hydrogen production.

II. MATERIALS AND METHODS

Olive mill wastewater samples which were used in this study, were obtained from TARIŞ Geyikli Olive Processing Factory in December, 2014 as a composite sample. The characterization of Olive mill wastewater sample is given in Table 1.

TABLE I
WASTEWATER COMPOSITION

Parameters	Unit	Wastewater Sample*
Ph		4,991
Conductivity	µs/cm ²	13950
Turbidity	NTU	16100±35
Color	ptCO	38200±42
TS	mg/L	48544±200
TVS	mg/L	41272±160
TSS	mg/L	20900±60
VSS	mg/L	19600±50
COD	mg/L	87716±135
TOC	mg/L	23883±20
SCOD	mg/L	40306±45
Total Phenol	mg/L	6560±50

Electrohydrolysis was performed in glass reactors (1L capacity) with consists a cover supporting two parallel aluminium electrodes. Experimental set up is given in Fig. 1.

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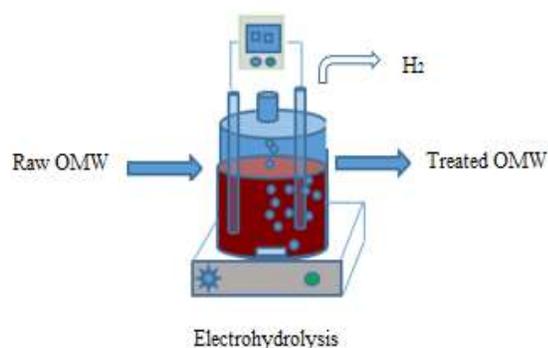


Fig. 1. Experimental set-up

Selection of electrode type is the main part of an electrochemical process and it is directly related to removal efficiencies. The most common electrode materials for electrohydrolysis are aluminium and iron because they are cheap, readily available and effective. In this study, aluminium electrodes are selected according to previous studies. Sample volume was 500 ml for experiment. There were 2 cm distance between electrodes and 2 cm distance between the electrodes which allowed easy stirring of the effluent. A direct current with different voltages including 2, 4, 6 and 8 voltages were tested by using a power supply (TT-T-ECHNI-C MCH-305D-II) for different reaction periods. During the experiments, the change in voltage and the current were monitored by multimeter (UNI-T UT61D Digital Modern Multimeters UT-61D AC/DC Tester). After electrohydrolysis process, the samples were allowed to settle down during 12 hours. The supernatant were used for determination of pollutants' concentrations. During the process, produced gas was controlled with gas counters and hydrogen yield of produced gas was determined by GC.

III. RESULTS AND DISCUSSION

In electrohydrolysis; 4, 6 and 8 V DC were examined for different duration until three hours in order to determine optimum conditions for both hydrogen gas production and pollutant removal efficiencies. Further electrohydrolysis durations could not be applied to the wastewater due to the excessive foaming and floatation of suspended solids found in OMW at high concentration. The supernatant were used to determine of pollutant concentrations according to standard methods. The changes in olive mill wastewater samples after electrohydrolysis process are summarized in Table 2. As seen in Table II., COD removal efficiencies were enhanced while applied DC voltage was increased 4 to 8 V. However after 8 V; further increases in applied DC voltages, were not significantly improved the effluent COD concentrations. Therefore at 8 V direct current which is selected as optimal DC voltage; 68% turbidity, 70% TSS, 52% COD and 19% sCOD removal efficiencies were obtained.

TABLE II

WASTEWATER COMPOSITION AFTER EC PRETREATMENT

Parameters	Direct Voltage, V		
	4	6	8
Ph	6,188	6,344	6,592
Conductivity	12360	12490	13170
Turbidity	1900	1600	1500
Color	13300	11500	11400
TS	47400	31524	18160
TVS	37168	20700	11632
TSS	3700	3450	3250
COD	50290	45676	42498
SCOD	40016	35870	32563
Total Phenol	1852	1755	1641

When pollutant removal efficiencies were evaluated, it is obvious that most of the organic matter were removed with different mechanisms during the electrohydrolysis process for OMW. There is only two studies which electrohydrolysis experiments were carried out in a Plexiglas bottle with aluminium electrodes for OMW. [18] were investigate the treatment of olive mill wastewater with electrohydrolysis with 0–10 V, using three aluminium electrodes as anodes and four as cathodes. The optimum condition, 76% of COD, 91% of polyphenol and 95% of dark colour removal efficiencies were reported. [19] investigated different DC voltages with aluminium electrodes (0.5–4.0 V) for OMW treatment. When DC voltage was increased to 2 V as optimum condition, 44% COD removal efficiency was achieved.

During electrohydrolysis; reaction duration is one of the main parameters in terms of both removal efficiencies and operational cost [20]. Electrohydrolysis experiments were carried out at different durations (30, 60, 90, 120, 150 and 180 min) in order to determine the reaction time effect. Fig. 2 shows change in concentration of main pollutants (COD, SCOD and TSS) for different duration at optimum DC which is 8 V..

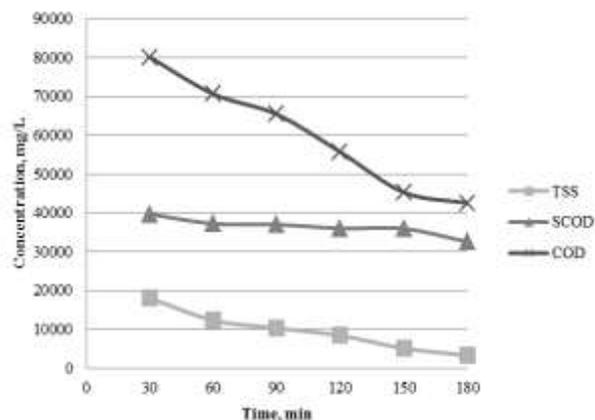


Fig. 2. Pollutant concentrations for different reaction time

As seen from Fig 2.; best removal efficiencies were obtained using 3 hours electrohydrolysis process. Therefore, 3 hours was selected as optimum duration for EH of OMW.

Fig. 3. shows cumulative gas production during electrohydrolysis process. The production of hydrogen gas is an important indicator of electrohydrolysis process in terms of organic matter removal. It has been stated that current determines bubble production rate, bubble size and the flocs growth which affect the efficiency of the electrohydrolysis process. [21]. Hydrogen gas production increased with increasing in DC voltage and reached the highest level (1500 ml H₂) at 8 V DC voltage for three hours.

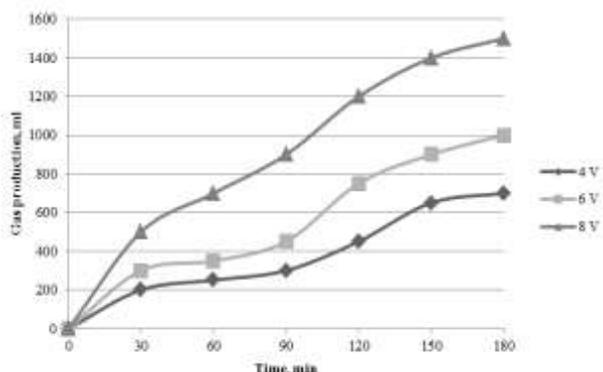


Fig 3. Gas production during EC

There is a little increase in hydrogen content of gas in different conditions. During the experiments, hydrogen yield of the gas were determined as 85%, 87%, and 88% for 4 V, 6 V and 8 V current voltage, respectively. There is only 4% increase in hydrogen content of gas at 8 V when compared to 4 V.

In Table III. reported studies about electrohydrolysis of different industrial wastewaters were summarized

TABLE III
STUDIES ON ELECTROHYDROLYSIS OF DIFFERENT WWS

Wastewater	DC Voltage, V	Time, Hour	COD removal, %	Hydrogen yield, L H ₂ /g COD _{rem}	Ref
OMW	4	96	44	55	[19]
Leachate	5	96	77	40	[22]
Vinegar wastewater	4	96	12	27	[23]
OMW	8	3	52	33	Our study

As seen from Table, in this study, unlike reported studies, better COD removal efficiency was achieved with higher DC voltage in shorter reaction duration. The studies in the literature were carried out at lower DC voltages (4-5 V) for longer period of time (96 hours). COD removal efficiencies were reported as between 12% for vinegar wastewater and 77% for leachate. For OMW, COD removal efficiency has been reported as 44% at 4 V DC for 96 hours [19]. In our

study, COD removal efficiency has been determined as 52% with OMW. The difference between the results could be attributed to the different initial characteristics of wastewaters

IV. CONCLUSION

In this study, electrohydrolysis is proved to be an efficient process for OMW with 70% TSS, 52% COD and 19% sCOD removal efficiencies in optimum condition (8 V DC for three hours). Based on the results; a considerable amount of organic matter and suspended solids were removed with the application of electrohydrolysis to OMW. Therefore, the efficiency of electrohydrolysis were found to be satisfactory for such a high strength wastewater in a low treatment time period. In spite of this statement, the method can not be proposed as a whole treatment scheme in order to maintain discharge standards, however, it can be used as pretreatment step for facilitating successive alternative treatment processes. According to obtained data, electrohydrolysis process was found to be relatively more environmental friendly process compared to other treatment alternatives for OMW since pH adjustment is not required and high amount of chemical sludge is not produced. Moreover, hydrogen gas production, which is a clean energy source, from wastewaters is another advantage for management of OMW

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