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Hydrogen gas production and pollutant removal from olive mill wastewater by electrohydrolysis

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Abstract

Olive Mill Wastewater (OMW) is characterized by strong organic content and also by a high number of inhibitory/complex compounds such as phenolic ones. An effective treatment method has not been sufficiently defined for the wastewater, so far. Therefore, the treatment of OMW is a major concern for manufacturers in Mediterranean countries. There is a growing interest for the application of alternative treatment methods. In this study, OMW was subjected to 10 V DC voltage for hydrogen gas production and COD, sCOD, total solids and total suspended solids, turbidity and color removal. Application of electrohydrolysis at 10 V DC for six hours; 1500±50 ml gas was produced and hydrogen content of gas (88%) was obtained. After 24 hours of settling, COD, sCOD, turbidity, TS, TSS and color removal efficiencies were determined as 75%, 56%, 93%, 61%, 94% and 92% in supernatant, respectively.
Keywords: electrohydrolysis, olive mill wastewater, phyco-chemical treatment, hydrogen production, pollutant removal, COD removal.

1 Introduction

There is a considerable increase in global energy demand as a result of rising populations and expanding economies. Another challenge for many countries is wastewater management which is essential for human/environment health and sustainable economic development. Main targets in industrial wastewater treatment facilities are to maintain a desirable effluent quality together with long-term process stability. Besides, in recent years, another concern is to obtain energy from waste/wastewater by using it as an energy source (at least for the self-support of the industry and/or treatment plants). Especially high strength industrial wastewaters such as olive mill wastewater (OMW) can be used as a potential source of energy. OMW is characterized by strong organic content and also a high number of inhibitory/complex compounds such as phenolic ones whose characterization and treatment have not been sufficiently addressed. Therefore, the treatment of OMW is a major concern for manufacturers due to its high organic load and oil content that make wastewater treatment relatively expensive in order to meet effluent discharge standards. It also requires high chemical consumption and additional cost due to high sludge production. Therefore, there is a growing interest in the development of new treatment methods or alternative management methods to control this type of wastewaters due to increasing restrictive environmental legislation and enforcement. Rather than using energy to treat waste/wastewater, it is a viable option to get clean energy (such as hydrogen and methane) directly from it. Hydrogen is considered as an excellent energy carrier with high calorific value, low emission at the point of use. There are several routes for hydrogen production including photobiological processes (Bridgewater [1]; Yetis *et al.* [2]; Eroğlu *et al.* [3]), dark fermentation (Liu *et al.* [4]; Kim *et al.* [5]) and bioelectrochemical systems from waste and wastewater. But these processes are limited by many factors such as maintaining process stability, practical application of methods and low yields of hydrogen, etc. In recent years, researchers have shown that electrohydrolysis can be used to produce energy from different industrial wastewaters. Despite promising results obtained from the studies, both hydrogen amount and organic matter reduction of the wastewaters has been reported to be limited. Hydrogen gas production by electrohydrolysis is possible through the reaction of protons released from volatile fatty acids (VFA) and electrons provided by DC current.

In literature, there are limited studies about electrohydrolysis of OMW (Adhoum and Monser [6]; Kargı *et al.* [7]; Inan *et al.* [8]). In these studies, different DC voltages and electrode types were tested and desirable COD removal efficiencies (up to 50%) were reported.

Therefore, in this study, hydrogen production efficiencies from OMW via electrohydrolysis have been determined and pollutant removal efficiencies have been investigated.

2 Material and method

Electrohydrolysis process was performed in a lab-scale 1 L glass reactor with a 600 ml sample volume. Two parallel aluminum electrodes were used and a power supply (TT-T-ECHNI-C MCH-305D-II) were used for 10 V DC for six hours. According to recent electrohydrolysis studies for different wastewater in literature, 0–100 V direct current was commonly used. There is a wide range in electrohydrolysis operation time for different wastewater in literature. In this study, the longest and most efficient electrohydrolysis duration time was aimed. However, at longer than 6 hours' operation time and higher than 10 V DC, there were bulking problems in the OMW samples and samples were not sufficiently settled after process. Therefore, in this study it is decided to test 10 V DC for 6 hours in OMW samples. After a day settlement, COD, sCOD, turbidity, TS, TSS and color were monitored in the supernatant according to standard methods (APHA [9]). In addition, gas production was monitored via milli gas counters and hydrogen content of gas was determined by GC.

The raw OMW samples were taken from an olive oil production plant from Canakkale Turkey (TARIS) on 15.12.2014 and OMW composition is summarized in Table 1.

Figure 1 shows the electrohydrolysis experimental set up.

Table 1: OMW composition.

Parameter	Unit	Value
pH	–	4,735
Turbidity	NTU	19,300
Total Solid	mg/l	41,280
Total Suspended Solid	mg/l	26,375
Total Chemical Oxygen Demand (tCOD)	mg/l	90,683
Soluable Chemical Oxygen Demand (sCOD)	mg/l	51,958
Color	PtCO	45,400

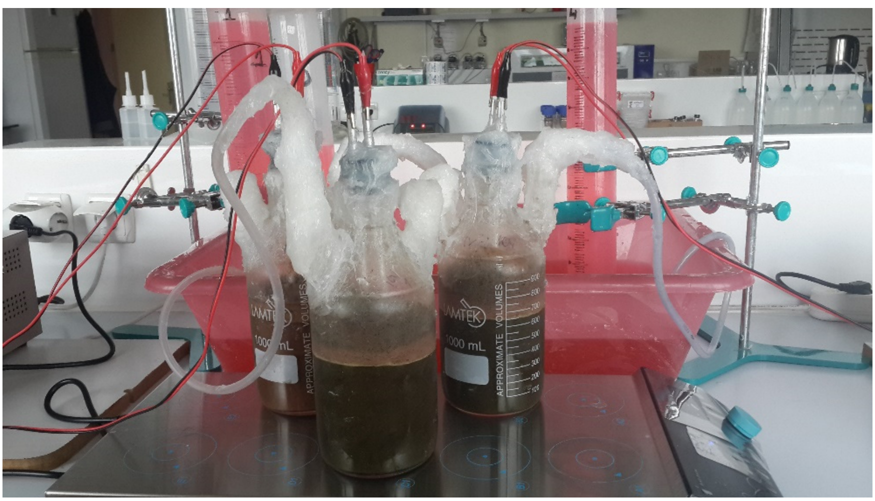

Figure 1: Electrohydrolysis experimental set up.

3 Results and discussion

In this study, electrohydrolysis of OMW were investigated according to pollutant removal efficiencies and hydrogen production rate. In electrohydrolysis; 10 V DC were tested for six hours. The supernatant was used in COD, sCOD, turbidity, TS, TSS and color experiments and gas production was monitored with milli gas counters and the hydrogen portion of produced gas was determined by GC. Table 2 shows the comparison between raw and treated OMW with electrohydrolysis.

Table 2: Changes in OMW after electrohydrolysis.

Parameters	Raw	10 V Electrohydrolysis
pH	4,735	4.9
Turbidity	19,300	1317
Total Solid	41,280	16,247
Total Suspended Solid	26,375	1646
Total Chemical Oxygen Demand (tCOD)	90,683	26,989
Soluble Chemical Oxygen Demand (sCOD)	51,958	23,026
Color	45,400	3801

After six hours' electrohydrolysis and a day settlement, significant pollutant removal efficiencies were obtained in supernatant. Figure 2 shows the pollutant removal efficiencies after the electrohydrolysis process.

The results showed that electrohydrolysis process has a sufficient effect on pollutant removal for OMW. In literature; there are only two studies about electrohydrolysis of OMW (Adhoum and Monser [6] and Kargı *et al*. [7, 10] so far. In these studies; 46% to 76% of COD and 95% of dark color removal efficiencies were reported.

In these study; After for 24 hours settling, COD, sCOD, turbidity, TS, TSS and color removal efficiencies was determined as 75%, 56%, 93%, 61%, 94% and 92% in supernatant, respectively.

Hydrogen gas production is the main aim of electrohydrolysis process with simultaneously pollutant removal. Total gas production and hydrogen gas yield during electrohydrolysis process for six hours is shown in Figure 3.

As seen in Figure 3, application of electrohydrolysis at 10 V DC for six hours; 1500±50 ml gas was produced and hydrogen content of gas was obtained as 88%.

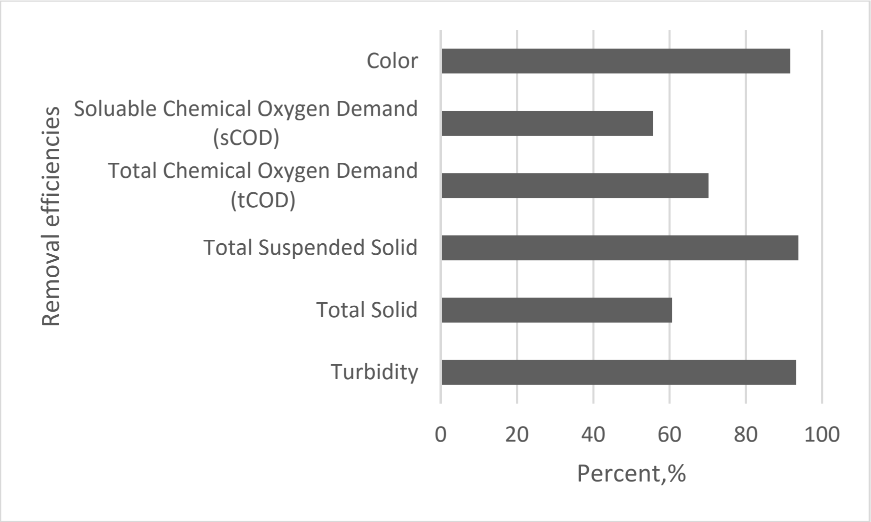

Figure 2: Pollutant removal efficiencies after electrohydrolysis.

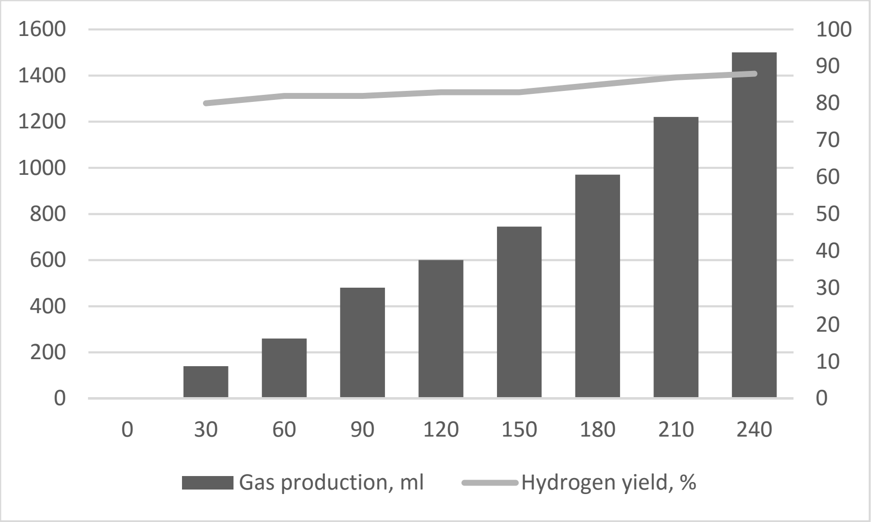

Figure 3: Total gas production and hydrogen gas yield during electrohydrolysis process for six hours.

4 Conclusion

In recent study, electrohydrolysis process has investigated in terms of hydrogen gas production and pollutant removal for olive mill wastewater which has a high amount of organic load. 10 V DC was applied for raw OMW for six hours. After electrohydrolysis process; desirable hydrogen production and pollutant removal efficiencies have detected. The results indicated that hydrogen gas production with simultaneously pollutant removal by electrohydrolysis of olive mill wastewater can be considered as an applicable and feasible process for both pollutant reduction and clean energy production. Electrohydrolysis of OMW has a great potential for commercial applications due to its simplicity, low DC voltage requirements and high pollutant removal efficiencies.

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