Treatment of Olive Mill Wastewater by Electrocoagulation Processes and Water Resources Management

Walid K. M. Bani Salameh, Hesham Ahmad, Mohammad Al-Shannag

Abstract**—**In Jordan having deficit atmospheric precipitation, an increase in water demand occurs during summer months. Jordan can be regarded with a relatively high potential for wastewater recycling and reuse. The main purpose of this paper was to investigate the removal of total suspended solids (TSS) and chemical oxygen demand (COD) for olive mill wastewater (OMW) by electrocoagulation (EC) process. In the combination of electrocoagulation by using coupled iron–aluminum electrodes, the optimum working pH was found to be around 6. Results indicated that the electrocoagulation process allowed removal of TSS and COD of about 82.5% and 47.5%, respectively at 45 mA/cm^2 after 70 minutes by using coupled iron–aluminum electrodes. It was demonstrated that the maximum TSS and COD removals were obtained at some optimum experimental parameters for current density, pH, and reaction time.

Keywords**—**Olive Mill Wastewater, Electrode, Electrocoagulation (EC), TSS, COD.

I. Introduction

THE increasing scarcity of clean water sets the need for appropriate management of available water resources. Particularly, regions suffering from a lack of water urgently need integrated environmental protection and resource conservation technologies in order to enable effective management of the available water resources. In addition, a bridge is made between environmental protection and water resources management. Electrocoagulation treatment is considered as the core technology for removes of suspended solids and organic compounds from many industrial wastewaters. Jordan has been characterized by a significant increase in urban and touristic activities, particularly over the past twenty years. As a result of this development, the majority of the population has become concentrated in a northern region. In many cases the infrastructure required to support this type of economic development is inadequate. Although underground water resources are estimated to be sufficient to cover all water needs, the lack of proper organization and infrastructure has led to serious problems, due to increased water demand particularly during the dry periods.

Black liquor is one of the main by-products of olive mill wastewater, which is considered as pollutant because it contains high concentration of organic substances [1], [2]. Olive mill Wastewater is one of the major water-intensive chemical processes [3]. The total area of cultivated olives in the Kingdom of about 127600 hectares, equivalent to 72 percent of the area planted with fruit trees and 34 percent of the entire cultivated area in Jordan, and the estimated number of olive trees planted about 17 million trees.

Due to the expansion of olive trees plantation and hence the expansion in olive milling industries in Jordan, the amounts of generated wastewater increased to over 200,000 m^3 in 2007 and around 95,000 ton of solid waste produced from one hundred and thirty mills in Jordan. In the absence of wastewater treatment it is disposed of through put in landfills dedicated to it are isolated and lined with a layer of plastic to prevent leakage into the groundwater. Such landfills accommodate about fifty thousand cubic meters of olive mill wastewaters (OMW).

Olive oil production is a major agricultural contributor to the national economy of Jordan. Olive production capacity in Jordan has increased from 73,000 ton in 1990 to 191,000 ton in 2004 to 175,000 to in 2011. On the other hand, olive oil production increased from 11,000 ton in 1990 to 29,000 ton in 2004 to 27,000 ton in 2011 [4].

II. Description of EC Processes

A. Description of Electrocoagulation (EC)

Electrocoagulation is the process of destabilizing suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electric current into the medium. In its simplest form, an electrocoagulation reactor may be made up of an electrolytic cell with one anode and one cathode [5], [6]. The conductive metal plates are commonly known as 'sacrificial electrodes' and may be made of the same or different materials. This process has proven very effective in removing contaminants from water and is characterized by reduced sludge production, no requirement for chemical use, and ease of operation: (1) Electrolytic reactions at electrode surfaces, (2) formation of coagulants in the aqueous phase; (3) adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or flotation [7], [8].

The main reactions at the electrodes are:

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Anode: $Al \rightarrow Al^{3+}_{aq} + 3e^-$ (1)

Cathode: $3\,H_2O + 3\,e^- \rightarrow 3/2\,H_{2g} + 3OH^-_{aq}$ (2)

Overall: $Al^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+$ (3)

Similarly, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric ions, and polymeric hydroxyl complexes, namely: $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ depending on the pH of the aqueous medium [9]-[13].

III. Experimental Details

A. Reagents and Analytical

Olive mill wastewater was obtained from local olive extraction plant which uses a classical process in Irbid northwest of Jordan. The characteristics of the OMW are given in Table I. OMW was collected in a closed plastic container and stored at 0^0C. Determination of COD was determined by the procedure described in the standard method. The total suspended solids TSS content was measured by drying a 50 ml of OMW at 105 ^{o}C until a constant mass was obtained [14]. The pHs of the samples were measured continuously using a pH meter (pH meter 3151 WTW, Germany) and to measure the conductivity were used a conductivity meter (HQ40D).

TABLE I
SOME CHARACTERISTICS OF OMW

Parameter	Value
COD	67.1(g/L)
BOD	48.05(g/L)
EC	8.6 (mscm^{-1})
TSS	31.3(g/L)
pH	4.56 (-)

B. Electrocoagulation Procedure

The electrocoagulation (EC) setup is shown in Fig. 1. The electrocoagulation unit was constructed from Plexiglas having a dimension of 0.10 m×0.15 m×0.25 m with a gentle stirring rate of about 200 rpm was applied to allow the chemical precipitate to grow large enough for removal. The total volume of wastewater in each experiment was approximately 3 dm^3. There are six iron (aluminum) plates were constructed in the electrochemical reactor three electrodes were connected as anodes and three as cathodes, the distance between plates was fixed at approximately 2 cm.

The electrodes having an immersed area of 102 cm^2 each (length 3 cm × height 17 cm ×2 faces) were fixed on the sides and there was a 2cm distance between the bottom of the electrodes and the bottom of cell which allowed easy stirring**.** The electrodes were connected to a DC power supply (GW. GPC-3030D) providing 0-30V (0-6A) with galvanostatic operational selection for controlling the current density. In the experiment, the 3 liters of wastewater was poured into the cell, an initial sample was taken. The samples of 5ml were taken at 10 minutes intervals for up to steady state and filtered to determine the TSS and COD.

In order to evaluate the removal of organic pollutant during the electrocoagulation processes the COD conversion was defined in the form:

$$COD_r = (COD_i - COD_f / COD_i) \times 100\% \quad (4)$$

where COD_i and COD_f are concentration ions of COD before and after treatment process by electrocoagulation.

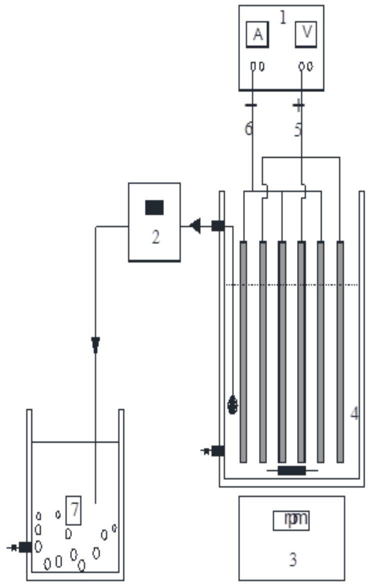

Fig. 1 Experiment set up (1) power supply, (2) pump, (3) magnetic stirrer, (4) wastewater reservoir tank, (5) cathode, (6) anode, (7) wastewater reservoir tank

IV. Results

A. Effect of Initial pH

This study is mainly focused on the electrocoagulation of olive mill wastewaters (OMW) with very high concentration of TSS and COD for determining effects of the basic operating parameters such as pH and current density. The effect of the initial pH on the electrocoagulation using aluminum and iron electrodes was investigated at constant 45 mA/cm^2 current density and 90 min of electrolysis. Firstly, the aluminum electrodes, the aluminum can form different species depending on the pH of the solution. For example, Al^{3+} ions hydrolysis my generate the aqueous complex $Al(H_2O)_6^{3+}$, which is prevalent at pH>4.5. Between 5.5 and 6.5 the prevalent hydrolysis products is $Al(OH)_3$ also found that Solubility of $Al(OH)_3$ was minimum at pH around 6, insoluble form $Al(OH)_3$ predominate at the pH near 6.5.

To investigate the effects of the initial pH on the electrocoagulation of olive mill wastewaters (OMW) the laboratory experiments were done by modifying the initial pH from 4.5 to 8.5. Figs. 2, 3 show the TSS percent removals for different initial pHs as a function of time. The drop of removal efficiency occurred when pH tends towards acidic or basic values and is in accordance with the amphoteric character of aluminum hydroxide $Al(OH)_3$ that precipitates at pH=5.5 to 6.5 and its solubility increases as the solution becomes either more acidic or alkaline. Efficiencies of TSS removal using aluminum plate electrodes by electrocoagulation were 76% for original pH of the OMW, 82.2% for pH of 6, and COD removal were 31.3% for original pH of the OMW, 38.5% for pH 6. The greatest pollutant removal which corresponded to outlet TSS and COD concentration of 31.1 g/L and 67.3 g/L consequently was achieved with the initial pH of 6 at the end of 70 min. Therefore, the pH 6 was taken as optimum initial pH, which is employed for all subsequent electrocoagulation experiments.

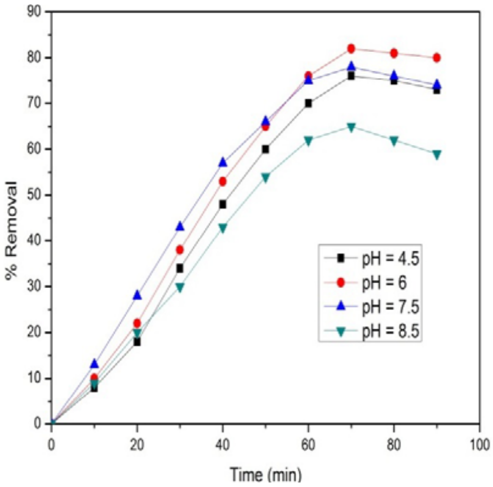

Fig. 2 Variation percentages of TSS removal efficiency with time for different pH using aluminum electrodes (DC = 30 mA/ cm^2)

Secondly the iron electrodes, the iron also can form different species depending on the pH of the solution. For example, Fe^{3+} and Fe^{2+} ions hydrolysis my generate of both hydroxyls $Fe(OH)_2$ and $Fe(OH)_3$. At the pH 6 the main Fe^{n+} species formed in solution is $Fe(OH)_2$, which can neutralize organic substances and suspended materials leading them to aggregation process. At higher or lower pH, instead of $Fe(OH)_2$ other species prevail, such $Fe(OH)_3$ or $Fe(OH)_4^-$ these species is not very effective coagulants [15] .

Efficiencies of TSS and COD removal using iron plate electrodes by electrocoagulation are represented in Figs. 4 and 5 for different initial pHs as a function of time were 68.1% for original pH of the OMW, 74.2% for pH of 6, and COD removal were 42.3% for original pH of the OMW, 47.5% for pH 6. The greatest pollutant removal which corresponded to outlet TSS and COD concentration of 31.1 g/L and 67.3 g/L consequently was achieved with the initial pH 6 at the end of 70 min. After ~ 70 min of electrocoagulation the effectiveness of organic substance and suspended solids removal underwent a small decrease ,which suggests that the coagulated flocks can be partially re-dissolved ,this effect maybe resulted from pH elevation during the electrocoagulation or heating. From these results it appears clearly that both materials are effective in reducing COD and TSS. However ,aluminum electrodes was found to be more effective in removing the TSS than iron, but iron electrodes was found to be more effective in removing the COD than aluminum electrodes, which suggests to use coupled iron –aluminum electrodes [16], [17].

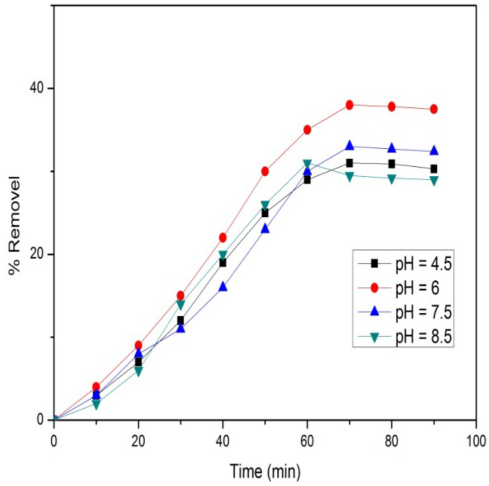

Fig. 3 Variation percentages of COD removal efficiency with time for different pH using aluminum electrodes (DC = 30 mA/ cm^2)

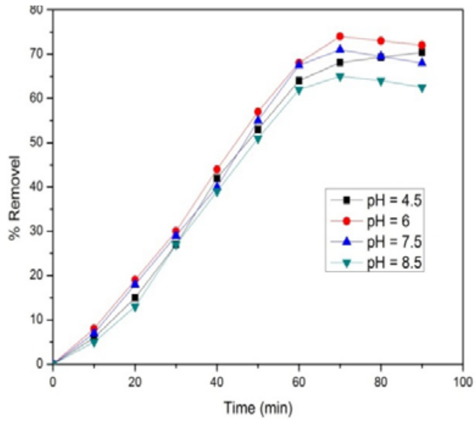

Fig. 4 Variation percentages of TSS removal efficiency with time for different pH using iron electrodes (DC = 30 mA/ cm^2)

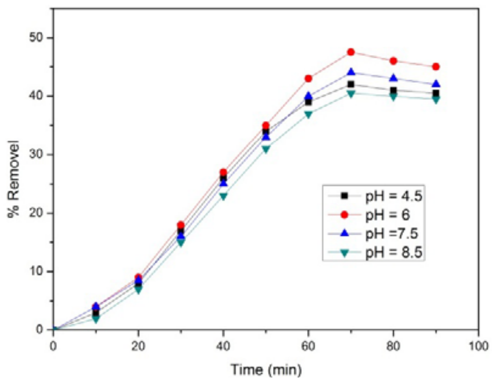

Fig. 5 Variation percentages of COD removal efficiency with time for different pH using iron electrodes (DC = 30 mA/ cm^2)

B. Effect of Current Density

It is known that the current density (CD) is an important operating influencing the performance of electrocoagulation process which determines the ions of irons and aluminum. Therefore, the effect of current density on the pollutant removal was investigated. Figs. 6 and 7 show TSS and COD removal upon electrolysis time when current density was varied from 15 to 60 mA/cm^2. It can be seen from Fig. 4 that the rate of percent removal of TSS and COD is high after a few minutes of process and reduces gradually to steady state at the end of the process. One can note that the rate of removal increases with current density for limited time. The removal efficiency of TSS was 57.1% at15 mA/cm^2. 70.2% at 30mA/cm^2, 82.5% at 45 mA/cm^2 and 81.3% at 60 mA/cm^2 after 70 min. The removal efficiency of COD was 30.2% at 15 mA/cm^2, 41.3% at 30 mA/cm^2, 47.5% at 45mA/cm^2 and 47% at 60 mA/cm^2 after 70 min. In addition, it was demonstrated that the current density increases the rate of percent removal is faster. As the current decreased, the time needed to achieve similar results. This expected behavior is explained by the fact that the treatment efficiency was mainly affected by charge loading (Q=I×t). This means that detention time of the olive mill wastewaters (OMW) in the electrocoagulation unit could be optimized with an optimum current density and acceptable removal efficiency for the lowest total investment and operational cost. The cost of the process is determined by electrical energy and the consumption of the electrodes which economically are the advantages of this method [18], [19]. The amount of metal oxidized is calculated using the Faraday's law [6]:

$$M= (Q/z)\ (M/F) \tag{5}$$

where I is the current density, t is the time, M is the molecular weight of electrodes g/mol, z is the number of electrons transferred in the reaction (=3), Q is the total electric charge passed through the substance and F is the Faraday's number (96486 c/mol). These results suggest 45 mA/cm^2 as an optimal current density for the treatment of OMW, since it ensures the faster removal rate with lowest cost.

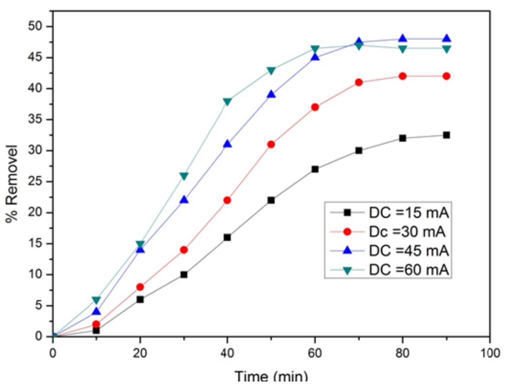

Fig. 6 Variation percentages of TSS removal efficiency with time for different current density and pH=6 using coupled iron–aluminum electrodes

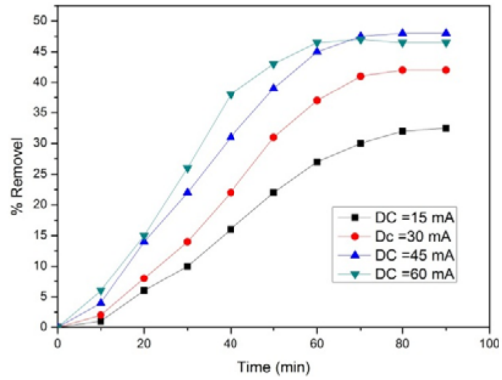

Fig. 7 Variation percentages of COD removal efficiency with time for different current density and pH = 6 using coupled iron aluminum electrodes

V. CONCLUSIONS

In this study the electrocoagulation of olive mill wastewater characterized by high TSS and COD concentrations has been investigated. The results of experiments have shown that coupled iron–aluminum electrodes can be preferred to aluminum or iron owing to better removal efficiency. The current density is the most important operational variable, the optimal current density can be determined as a function of percent removal of TSS, COD, energy consumption and electrode consumption as well as creating an economic situation where the electrocoagulation is applied. The most effective removal capacity was achieved at pH=6.

REFERENCES

[1] Zakaria Al-Qodah, Abeer Al-Bsoul, Eman Assirey, Mohammad Al-Shannag, Combined ultrasonic irradiation and aerobic biodegradation treatment for olive mills wastewaters, Environmental Engineering and Management Journal, 8 (2014) 2109-2118.

[2] Zakaria Al-Qodah, Mohammad Al-Shannag, Khalid Bani-Melhem, Eman Assirey Kholoud Alananbeh, Nahla Bouqellah, Biodegradation of olive mills wastewater using thermophilic bacteria, Desalination and Water Treatment (2014) doi: 10.1080/19443994.2014.954148.

[3] Ministry of water and irrigation (1999) wastewater management and reuse –country profile.

[4] Agricultural Statistics (2002) Agricultural Statistics, department of statistics, Amman, Jordan.

[5] Rozzi A. and Malpei F. (1996) Treatment and disposal of olive mill effluents. Intern. Biodeterior. Biodegrad. 135-144.

[6] Mohammad Al-Shannag, Zakaria Al-Qodah, Khalid Bani-Melhem, Mohammed Rasool Qtaishat, Malek Alkasrawi, Heavy metal ions removal from metal plating wastewater using electrocoagulation: kinetic study and process performance, Chemical Engineering Journal, 260 (2015) 749-756.

[7] A. S. Koparal, U. Tezcan Un, U. Bakir Ogutveren, Electrochemical oxidation of sulfite ions in aqueous solutions, Int. J. Environ. Pollut. 21 (6) (2004) 579–587.

[8] O. Ya P. Longhi, B. Vodopivec, G. Fiori, Electrochemical treatment of olive oil mill wastewater, Annal. Di Chim. 91 (3–4) (2001) 169– 174.

[9] Walid .K. Lafi, Mohammad Al-Anber, Zaid A. Al-Anber, Mohammad Al-Shannag, Adnan Khalil, Coagulation and Advanced Oxidation Processes in the Treatment of Olive Mill Wastewater (OMW), Desalination and Water Treatment, 24 (2010) 251-256.

[10] B. Zhu, D. A. Clifford, S. Chellam, Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes,Water Res. 39 (2005) 3098-3108.

[11] P. K. Holt, G. W. Barton, M. Wark, C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A 211 (2002) 233–248.
[12] Walid K. Lafi, Benbella Shannak, Mohammad Al-Shannag, Zaid Al-Anber, Mohammad Al-Hasan, Treatment of olive mill wastewater by combined advanced oxidation and biodegradation, Separation and Purification Technology, 70 (2) (2009) 141-146.
[13] Mohammad Al-Shannag, Walid Lafi, Khalid Bani-Melhem, Fawzi Gharagheer, Oqlah Dhaimat, Reduction of COD and TSS from paper industries wastewater using electro-coagulation and chemical coagulation, Separation Science and Technology, 47 (5) (2012) 700-70.
[14] Standard methods for the examination of water and wastewater, 16th ed.,Washington,1985
[15] S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, H. Hamitouche, Electrocoagulation process applied to wastewater containing dyes from textile industry, Chem. Eng. Process (2010). doi:10.1016.cep.2010.08.019.
[16] N. Adhoum, L. Monser, Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, Chem. Eng. Process. 43 (2004) 1281–1287.
[17] H. Inan, A. Dimoglo, H. Simsek, M. Karpuzcu, Olive oil mill wastewater treatment by means of electrocoagulation, Sep. Purif. Technol. 36 (2004) 23–31.
[18] Mohammad Al-Shannag, Khalid Bani-Melhem, Zaid Al-Anber, Zakaria Al-Qodah, Enhancement of COD-Nutrients Removals and Filterability of Secondary Clarifier Municipal Wastewater Influent Using Electrocoagulation Technique, Separation Science and Technology, 48 (4), (2013) 673-680.
[19] Mohammad Al-Shannag, Zakaria Al-Qodah, Kholoud Alananbeh, Nahla Bouqellah, Eman Assirey, Khalid Bani-Melhem, COD reduction of baker's yeast wastewater using batch electrocoagulation, Environmental Engineering and Management Journal, 13 (2014) 3153-3160.