Chemical Engineering and Processing 50 (2011) 37–41

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Treatment of olive mill wastewater by the combination of ultrafiltration and bipolar electrochemical reactor processes

O. Yahiaoui[a], H. Lounici[a], N. Abdi[a], N. Drouiche[a,b,*], N. Ghaffour[c], A. Pauss[d], N. Mameri[d]

[a] Ecole Nationale Polytechnique Alger, Biotechnology Laboratory BIOGEP, 10 Avenue Pasteur, El Harrach, Algiers, Algeria
[b] Silicon Technology Development Unit (UDTS), 2, Bd Frantz Fanon, BP140 Algiers-7-merveilles, Algiers 16200, Algeria
[c] Water Desalination & Reuse Centre, King Abdullah University of Science and Technology, (KAUST), Saudi Arabia
[d] University of Technology of Compiègne, Chemical Engineering Departement, B.P. 20.509, 60205 Compiègne cedex, France

ARTICLE INFO

Article history:
Received 15 August 2010
Received in revised form 24 October 2010
Accepted 5 November 2010
Available online 13 November 2010

Keywords:
Electrocoagulation
Iron bipolar electrodes
Olive mill wastewater
Mineral membrane
Ultrafiltration

ABSTRACT

The main purpose of this study was to investigate the removal of the chemical oxygen demand (COD) from olive mill wastewater (OMW) by the combination of ultrafiltration with electrocoagulation process. Ultrafiltration process equipped with CERAVER membrane was used as pre-treatment for electrochemical process. The obtained permeate from the ultrafiltration process allowed COD removal efficiency of about 96% from OMW. Obtained permeate with an average COD of about 1.1 g dm^{-3} was treated by electrochemical reactor equipped with a reactor with bipolar iron plate electrodes. The effect of the experimental parameters such as current density, pH, surface electrode/reactor volume ratio and NaCl concentration on COD removal was assessed. The results showed that the optimum COD removal rate was obtained at a current density of 93.3 A m^{-2} and pH ranging from 4.5 to 6.5. At the optimum operational parameters for the experiments, electrocoagulation process could reduce COD from 1.1 g dm^{-3} to 78 mg dm^{-3}, allowing direct discharge of the treated OMW as that meets the Algerian wastewater discharge standards (<125 mg dm^{-3}).

1. Introduction

The manufacturing process of olive oil is one of the most complex wastewater generated in the Mediterranean region. The extraction and manufacturing of olive oil in these countries are carried out in several small plants that operate seasonally and generate each year more than 30 billions of wastewater effluents [1,2]. This wastewater is characterized by large suspended solids content and high chemical oxygen demand (COD) values (in the range of 50–250 g $O_2 dm^{-3}$) [3,4]. Generally removal efficiency of biorecalcitrant and toxic pollutants obtained by conventional processes such as using chemicals or biological treatment, are environmentally acceptable. In industrial countries, these concentrations are higher than the international standards. Such standards could be met by combination of membrane processes such as ultrafiltration and electrochemical process [5]. The electrocoagulation technique and ultrafiltration are potentially considered to be an effective tool for the treatment of OMW with high removal of organic pollutants. Unfortunately, there has been little research into the treatment of OMW wastewater by the combination of electrocoagulation and ultrafiltration [6–13].

There are also literature reports on the combined use of physical–chemical treatment and biological treatment. None of the simple physical treatment processes alone such as dilution, evaporation, sedimentation, filtration and centrifugation were able to reduce the COD to an acceptable level. A combination of these processes appears to be the most efficient in terms of acceptable limits of COD discharge [4–18].

The present work investigates the efficiency of the combination of ultrafiltration and electrocoagulation processes to remove COD from OMW. The ultrafiltration process, equipped with CERAVER mineral membranes, was firstly used under optimum hydrodynamic conditions previously determined in the literature [7]. Then the obtained permeate was treated with electrochemical reactor equipped with iron plate electrodes functioning in bipolar mode. The effect of current density, pH, surface electrode/reactor volume ratio (S/V) and NaCl concentration (NaCl used as supporting electrolyte) has been performed.

2. Materials and methods

Olive mill solid wastewater was obtained from an olive oil processing plant located in Tadmait (east of Algiers) and transported

* Corresponding author at: Silicon Technology Development Unit, Department of Environmental Engineering, 2, Bd Frantz Fanon, BP140 Alger-7-mervielles, Algiers 16000, Algeria. Tel.: +213 21 279880x192; fax: +213 21 433511.
E-mail addresses: lounicih@yahoo.fr (O. Yahiaoui), nadjibdrouiche@yahoo.fr (N. Drouiche).

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doi:10.1016/j.cep.2010.11.003

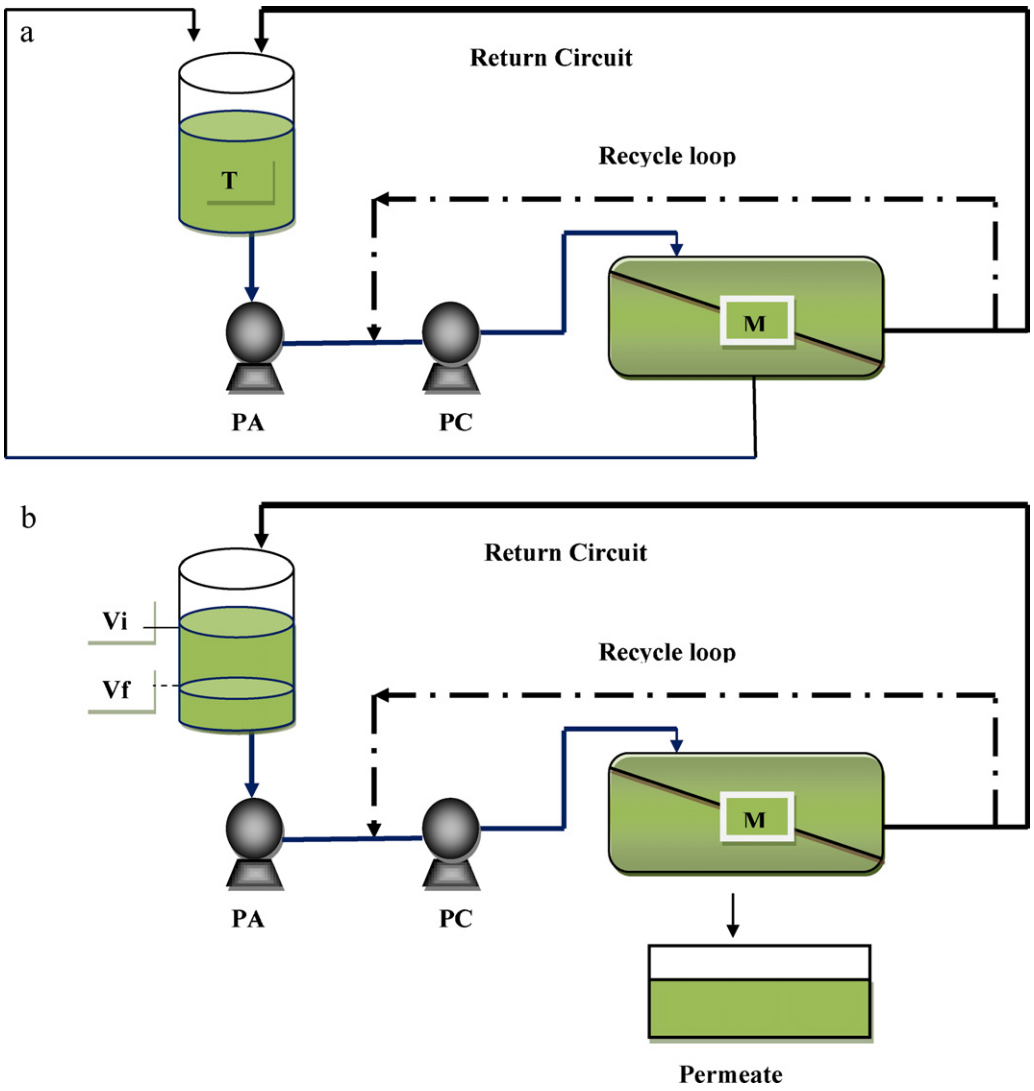

Fig. 1. Ultrafiltration process. T: feed tank, PC: recycling pump, PA: feed pump, M: ultrafiltration module.

to the laboratory at low temperature, $T = 4\,^{\circ}C$. The main physicochemical characteristics of OMW are given in Table 1.

2.1. Ultrafiltration unit

Ultrafiltration unit Microlab 130 S (purchased by Gammafiltration Company, France) was equipped with Membralox-Ceraver module. This module (P19-40) was multi-channel ceramic membrane composed by ultrafine porous ZrO_2 (0.05 μm) supported by coarse porous alumina (15 μm). The total filtration area of this module is 0.2 m^2. The ultrafiltration unit is presented in Fig. 1. The operating mode used in this study consists of operation concentration of the OMW solution without permeate recirculation (Fig. 1b). Two operating modes of the UF process were used, as shown in Fig. 1(a) and (b), with and without permeate recirculation, respectively. The first mode was used to study the influence of the hydrodynamic parameters [the average trans-membrane pressure (Pa) and the cross-flow velocity (U)] on the permeate flux whereas the concentration mode was used to study the effect of OMW concentration on the UF process efficiency.

Optimum hydrodynamic parameters, mainly the trans-membrane pressure ($\Delta P = 3 \times 10^5$ Pa) and tangential velocity ($U = 4\,ms^{-1}$), previously determined with a similar membrane during the optimization of the treatment of the OMW by ultrafiltration, were utilized in this study [7]. Permeate solution obtained is collected and then treated with the electrochemical reactor.

Table 1
The main physicochemical characteristics of OMW.

Parameters	OMW
TSS ($g\,dm^{-3}$)	49.5
pH	4.8
Electrical conductivity (mS/cm)	32
Total polyphenols (as C_6H_5OH in $g\,dm^{-3}$)	2.9
COD ($g\,dm^{-3}$)	28
BOD_5 ($g\,dm^{-3}$)	17.6

2.2. Electrochemical reactor

The electrochemical reactor was equipped with iron plate electrodes. Iron was selected on the basis of a previous study indicating that this metal is more effective than aluminium as electrodes during electrocoagulation of OMW [8]. The extern electrodes were used as cathode and anode. Other conductive iron plates were placed between two electrodes having opposite charges without any electric connection. The two neutral sides of the plate iron will be transformed to charged sides which have an opposite charge compared to the parallel beside the electrode. This electrode is com-

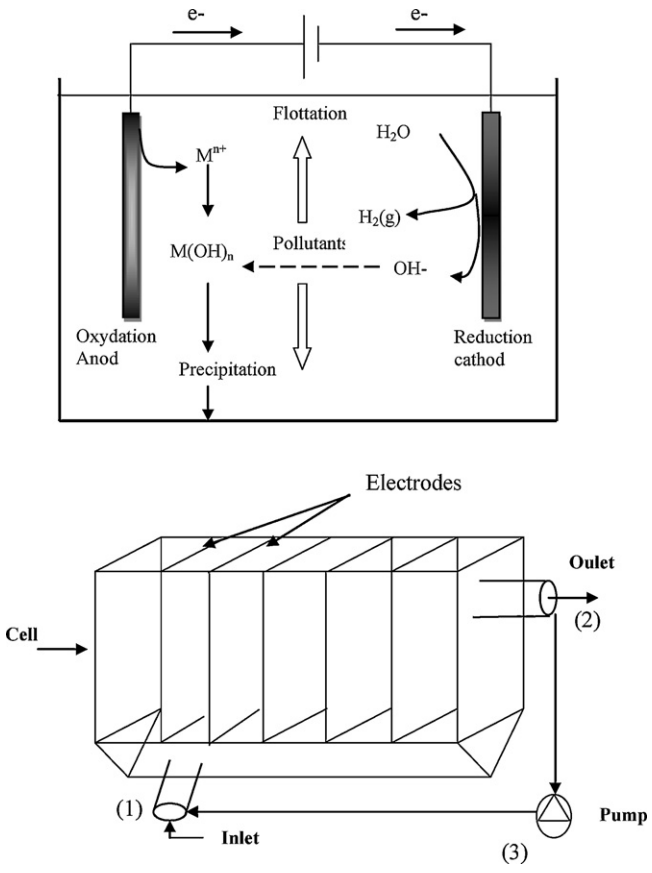

Fig. 2. Electrocoagulation reactor.

monly called the bipolar electrode. The dimensions of the outer electrodes in the two electrochemical reactors were reduced to prevent electric field dispersion. The purity of the aluminium electrodes was about 99.5%.

The electrochemical reactor used in this study represents a laboratory cell (Fig. 2). The permeate solution enters by the leading tube (1) and leaves the delivery tube (2). The volume capacity of the reactor cell is about 0.8 dm^{-3}. The dimensions of the bipolar electrodes were 125 mm × 60 mm. Permeate is injected into the electrochemical reactor cell. Electromagnetic feed pump (3), which allows flow rates of up to 0.46 $m^3\ h^{-1}$ was used to maintain the homogenization of the solution during electrochemical run.

The experiments were conducted in a batch mode with an electrochemical reactor.

The current density was maintained constant by means of generator Fontaine MC 3030C-France (1). The effect of pH on the process performance was studied at various pH values ranging from 4.5 to 9.5 obtained by the addition of 1 M NaOH solution or 1 M HCl acid solution. The effect of salinity was studied by dissolving various amounts of NaCl in feed tank with salt concentrations ranging from 0.1 to 1.5 g dm^{-3}.

2.3. Analysis techniques

The influence of the different experimental parameters was studied by following the change of COD during the experiments. The kinetic curves describing the abatement of the COD of the water were drawn by following the evolution of the COD of the treated water at short and regular intervals. COD values were determined by the spectrophotometer SHIMADZU, 1240CE at wave length of λ = 600 nm as recommended by standard methods [19].

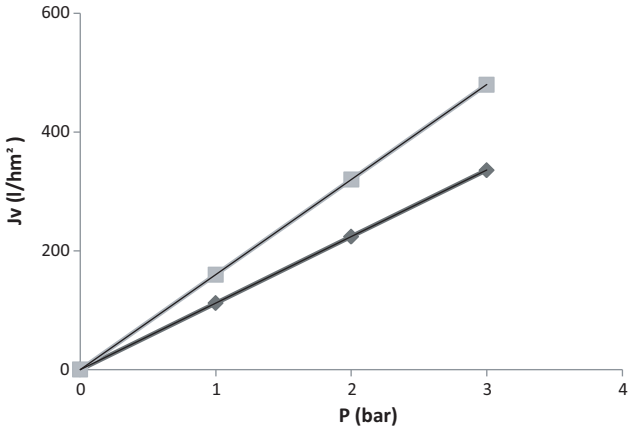

Fig. 3. Determination of the membrane permeability CERAVER. (□) Virgin membrane and (◊) membrane after UF.

All experimental results presented below were triplicate and average values are presented with standard error less than ±8%.

3. Results and discussion

3.1. Ultrafiltration of OMW

Ultrafilration experiments were carried out in concentration mode without recirculating the permeate in the feed tank (Fig. 1b) and at the optimum hydrodynamic conditions ($\Delta P = 3 \times 10^5$ Pa and $U = 4\ ms^{-1}$). Indeed, COD percentage abatement of about 96% was obtained. Furthermore, the determination of hydraulic membrane permeability measured before and after ultrafiltration of OMW indicates that an acceptable decrease of about 30% was observed after the concentration operation of OMW. The permeability of the membrane was calculated by deducing the slope of the linear curves obtained by plotting the change of the permeate flux against the average trans-membrane pressure during the filtration of pre-filtered water (Fig. 3). The initial membrane permeability was always recovered rapidly after the cleaning operation.

Although the high removal of COD was obtained with ultrafiltration, one can note that the remaining concentration (in the range of 1 g dm^{-3}) obtained after treatment by this process is not in agreement with the water standards [20]. To improve the water quality, electrocoagulation technique was used as the final step.

3.2. The effects of parameters on electrochemical treatment

To determine the optimum experimental conditions of the electrocoagulation process, the influence of different parameters such as *S*/*V* ratio which is the ratio between the specific anode area and the volume of the treated solution, current density, initial pH and concentration of supportive electrolyte (NaCl) were studied.

The effect of *S*/*V* ratio on the performance of the electrochemical reactor was studied by following the change of COD during the experiments. The results presented in Fig. 4 show that the COD decrease was observed at various *S*/*V*. At higher *S*/*V* ratios, improvement in COD removal efficiency was observed. These results may be explained by an increase of anodic area which made an augmentation of Fe^{2+} and Fe^{3+} production possible resulting in the formation of both hydroxyls $Fe(OH)_2$ and $Fe(OH)_3$. These metallic hydroxyls are the active entities which bind organic matters and therefore reduce the COD. It was also observed that at *S*/*V* ratio superior to 22.5 m^2/m^3, the efficiency of the electrochemical process to remove COD was practically constant and independent from *S*/*V* ratio values. Then, *S*/*V* of 22.5 m^2/m^3 was retained as an optimum value.

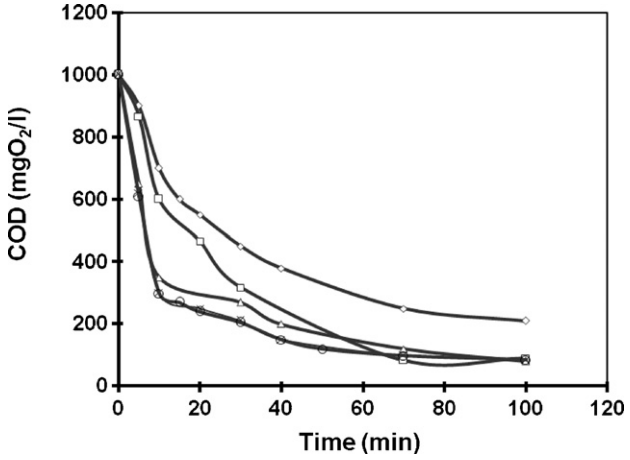

Fig. 4. Influence of the ratio S/V on COD abatement. $i = 93.3 A/m^2$, pH 6.8 and $S = 0.5$ g/l. (◊) $S/V = 9\ m^2/m^3$, (□) $S/V = 13.5\ m^2/m^3$, (△) $S/V = 18\ m^2/m^3$. (×) $S/V = 22.5\ m^2/m^3$ and (○) $S/V = 27\ m^2/m^3$.

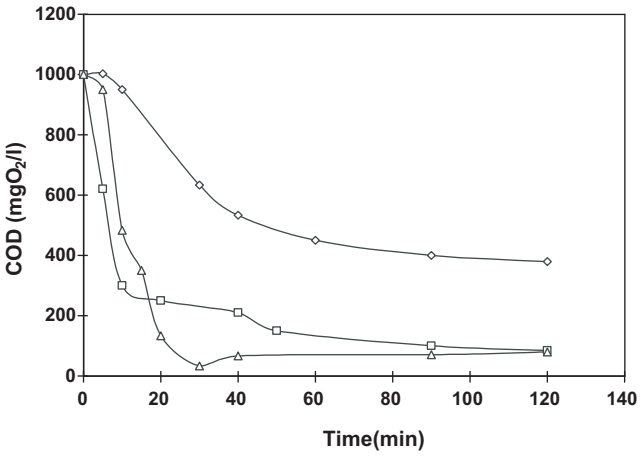

Fig. 6. Influence of the pH on cod abatement. $S/V = 22.5\ m^2/m^3$, $i = 93.3\ A\ m^{-2}$ and $S = 0.5$ g/l. (◊) pH 9.8, (□) pH 6.8, (△) pH 4.7.

The removal of COD was also faster and more efficient with the highest current density reaching $93\ A\ m^{-2}$ (Fig. 5). At this optimum value, the electrocoagulation process reached the steady state regime in 40 min with a COD abatement ratio of about 96%. Similar results were previously obtained with different wastewater of high COD [21,22]. One can note that an increase in current density does not only induce an augmentation of the amounts of dissolved metallic cations but also increase the H_2 gas which characterizes the electroflotation phenomenon. Indeed, during the experiments at higher current density, it was observed more quantities of the complex iron oxides–organic matters, on the top of the solution, namely called flocs [22–24].

The influence of the pH on the performance of the electrochemical reactor was determined by a current density of about $93\ A\ m^{-2}$. The results, presented in Fig. 6, indicate that COD abatement kenitic was more faster at pH ranging from 4.5 to 6.5. Indeed at lower pH (pH 4.5), the electrochemical reactor reached the steady state regime in 30 min. Similar results were presented during the electrocoagulation of OMW with aluminium electrodes and with coupled iron–aluminium electrodes [10,11].

This result may be explained by the POURBAIX diagram which indicates that at positive potentials and pH value of about 6, the formation of $Fe(OH)_2$ and $Fe(OH)_3$ is encountered.

It is important to note that the initial pH of OMW is in the optimum range was previously adjusted by adding 0.1 M NaOH or 1 M HCl. Then, the utilization of the electrocoagulation process to remove high COD of OMW is allowed.

The influence of NaCl concentrations used as supporting electrolyte on the performance of the electrochemical process was studied at various NaCl concentrations. The results, presented in Fig. 7, indicate that the efficiency of the electrocoagulation process was influenced by the salt concentration. Higher concentration reduced the efficiency of the process in terms of COD removal capacity. The abatement ratio of the COD at optimum experimental conditions was about 92%.

Similar results are reported by previous research. Calvo et al. [21], during the purification of soluble oil wastes of high COD by electrocoagulation indicate that at NaCl concentration higher than $0.9\ g\ dm^{-3}$, the efficiency process was considerably reduced. Mollah et al. [23] determined that the treatment of orange II azo dye by electrocoagulation using iron electrodes at NaCl concentrations higher than $0.102\ mole\ dm^{-3}$ does not improve the process efficiency. The NaCl concentration retained in this study was about $0.034\ mole\ dm^{-3}$ and allowed to reduce undesirable production of chloride toxic by-products.

In this work, the initial NaCl concentration of the North African's water (in the range of $1\ g\ dm^{-3}$) could be allowed to be used directly without adding supporting electrolyte to the permeate.

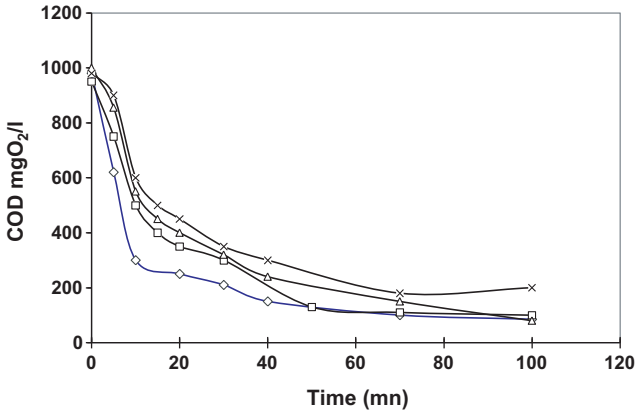

Fig. 5. Influence of the current density on COD abatement. $S/V = 22.5\ m^2/m^3$, pH 6.8 and $S = 0.5$ g/l. (◊) $i = 93.3\ A\ m^{-2}$, (□) $i = 66.7\ A\ m^{-2}$, (△) $i = 44.4\ A\ m^{-2}$, (×) $i = 31.1\ A\ m^{-2}$.

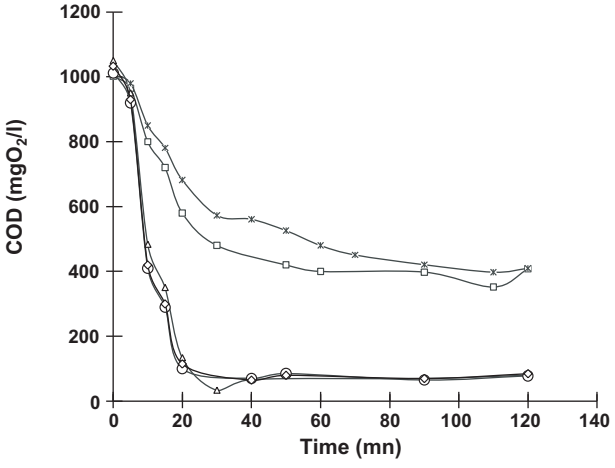

Fig. 7. Influence of the NaCl concentration on COD abatement. $i = 93.3\ A\ m^{-2}$, pH 6.8 and $S/V = 22.5\ m^2/m^3$. (◊) $S = 0.1$ g/l, (□) $S = 0.3$ g/l, (△) $S = 0.5$ g/l, (×) $S = 1$ g/l and (○) $S = 1.5$ g/l.

Table 2
Experimental results during OMW treatment and standards.

Parameter	Before treatment	After ultrafiltration	After ultrfiltration and electrocoagulation	Standards [15]
COD (mg dm^{-3})	28,000	1100	78	<125
Abatement ratio		96	99.8	

Thus, the optimum experimental conditions of the electrochemical reactor were as follows: $i = 93\ A\ m^{-2}$, $S/V = 22.5\ m^2/m^{-3}$, $C_{NaCl} = 0\ mg\ dm^{-3}$, pH 4.5–6.5.

3.2.1. Treated water quality

The combination of ultrafiltration and electrochemical reactor processes allowed to reduce considerably the COD from OMW at acceptable values. Indeed, the main results summarized in Table 2 indicate that the combination of both processes allowed reaching a very high COD removal. The combination of membrane technique and electrochemical process could reduce COD from 28 g dm^{-3} to 78 mg dm^{-3} allowing direct rejection of the treated OMW as this meet with the wastewater discharge standards (<125 mg dm^{-3} [17]).

4. Conclusions

COD removal from olive mill wastewater by means of ultrafiltration membranes was satisfactory as the process reduces COD from 28 g dm^{-3} to 1.1 g dm^{-3}, a COD abatement ration of about 96%. The obtained values are still higher than the wastewater discharge standards (<125 mg dm^{-3}). The proposed combination of the use of ultrafiltration process as pre-treatment and an electrochemical reactor equipped with iron bipolar electrodes as second treatment was very satisfactory as the COD was further reduced to 78 mg dm^{-3}.

This process is very efficient and may be considered ecologically friendly wastewater treatment technology. Further work needs to be carried out at pilot scale to assess the technical and economic feasibility of the process.

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