DEPOLLUTION OF OLIVE MILL WASTEWATER THROUGH ELECTROCOAGULATION AND ADVANCED OXIDATION

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Abstract: The goal of the Research described in this paper is to treat Olive Mill Wastewater (OMWW) to cause its decolorization, thus enabling its safe and legal release in main water streams. To this end, two different methods were tested on samples of OMWW collected from Ain Taoujdate, a small town that is located 25 km to the south of Fez, Morocco. These samples were freshly diluted by a factor of 20 prior to a treatment by either electrocoagulation or the photo-Fenton process, a type of advanced oxidation. It was found that an electrocoagulation treatment of two hours, at 22V DC with aluminum plates, was satisfactory to get nearly clear and colorless water (93% decolorization). A phenolic content reduction by 92.4% was obtained using this same technique. Photo-Fenton was tested with the use of H_2O_2/Fe(II), O_2/Fe(II), and H_2O_2/O_2/Fe(II) at a wavelength of 254 nm. With this technique, the best operating conditions afforded 78% decolorization. A discussion on the viability of each technique concludes this study.

Keywords: Wastewater, Pollution, Electrocoagulation, Oxidation, Fenton

Introduction

With an annual production of 140 000 tons of olive oil in 2014-2015, Morocco is ranked the 5th biggest producer of olive oil in the world. Unfortunately, like in nearly all industries, the production of this good is accompanied by the production of wastes that represent a major environmental issue and that must be dealt with. During the olive oil production process, two kinds of residues are generated: a wet solid waste called “crude olive cake” and an aqueous waste called “olive mill wastewater, OMWW”. OMWW is a dark liquid effluent characterized by high concentrations of organic compounds, including organic acids, sugars, tannins, pectins and phenolic substances that makes it phytotoxic and inhibit bacterial activity. In 2014, the amount of OMWW generated in Morocco alone was estimated to be 250-400 000 m^3 per year and given that 1 m^3 of OMWW is equivalent to 100-200 m^3 of domestic sewage(Morocco Department of Environment, 2014; Alami, 2014). OMWW treatment and disposal is a problem with great complexity due to the strong nature of the waste and also to several economical, technical, and organizational constraints involved in the olive oil sector (Tsagaraki et al., 2007). Over the last 60 years, practically all treatment processes developed for domestic and industrial wastewaters have been tested on OMWW but none of them appeared suitable to be generally adopted (Tsagaraki et al., 2007). These processes include aerobic processes (Cereti et al., 2004; Lanciotti et al. 2004) , anaerobic processes (Borja & Gonzalez, 1994; Dalis et al. , 1996; Zouari, 1998; Zouari & Ellouz, 1996; Azbar et al., 2004; Rozzi & Malpei, 1996), anaerobic digestion (Niaounakis & Halvadakis, 2004), pH neutralization (Mitrakas et al., 1996), coagulation (Niaounakis & Halvadakis, 2004), electro-coagulation (Khoufi et al., 2007) , advanced oxidation processes (Gernjak et al., 2004 ; Rivas et al, 2001; Ouardaoui, 1996; Ouardaoui et al., 1995; Ouardaoui et al., 1997), distillation/ evaporation (Rozzi & Malpei, 1996; Niaounakis, 2004) , and membrane processes (ultrafiltration, microfiltration, reverse osmosis (Yahiaoui et al., 2011; Petrotos et al., 2014 ; Coskun et al., 2013) . When not dumped illegally directly into nearby aquatic bodies, i.e. rivers, lakes, or even the sea (Galiatsatou et al., 2002) nearly all olive mills in Morocco, and around the globe at large, dispose of OMWW in evaporation ponds or storage lakes (lagoons), such as the one shown in Figure 1. This technique consists in storing the waste outdoor and let its water evaporate naturally in ambient air by exposure to sunlight.

Figure 1. OMWW evaporation pond beside an olive mill in Ain Taoujdate, Morocco (Feb. 2016).

In spite of having low energy costs and being simple to operate, this method has important drawbacks; it requires a long waste residence time (7-8 months) and a large land surface area (~1 m^2 for each $2.5m^3$ of OMWW). Furthermore, it raises several ecological concerns including the possibility of groundwater contamination if the bottom of the pond is not properly lined against infiltration and leakage – as it is often the case – and the emissions of methane in the atmosphere due to the anaerobic fermentation of the waste that occurs in the pond (Tsagaraki et al., 2007; Azbar et al., 2004; Rozzi & Malpei , 1996). Finally, these ponds and lagoons cause serious nuisance to their neighborhood because they attract insects and cause foul smells.

Materials and Methods

Chemicals and Equipment

Sodium hydroxide was supplied by Fluka, Switzerland. Aluminum sulfate was supplied by AppliChem Panreac, Spain. Ferrous sulfate heptahydrate was supplied by Fluka, Switzerland. Oxalic acid monohydrate, 99% pure, was supplied by PanReac Applichem, Germany. Hydrogen peroxide, 110 vol., was supplied by Société Nouvelle Pharmac, Morocco. Ethanol, 96% pure, was supplied by Carlo Erbo, Spain. Anhydrous sodium carbonate was supplied by Sigma-Aldrich. The Folin-Ciocalteu reagent was supplied by Educomptoir, Morocco. Medical grade oxygen gas was supplied by Maghreb Oxygen, Morocco.

For centrifugation, a 5500 rpm centrifuge, *Hettich Zentrifugen* model EBA 30, was used. Vacuum filtrations were performed by means of piston-powered vacuum pump with a pressure of 0.85 atm and an air flow of 38 L/min. Weights were measured by an *AND* balance with a readability of 0.01g model EK610i, an *OHAUS* balance with a readability of 0.0001g model AS120, or a *KERN* balance with a readability of 0.05g model KB10K0.05N. pH and temperature were measured by using a *Hanna* instruments pH meter model HI 9318.

Preparation of solutions for phenolic content determination was done by means of 25 µL and 100µL syringes, supplied by *HAMILTON*, Switzerland. For heating and stirring, digital stirring hotplates were used. Either *DLab* MS-H280-pro or *VWR* VMS-C7 advanced series. For electrocoagulation, a *Tektronix* voltage meter model PS280 was used. For measuring the absorbance, a *Jenway* spectrophotometer model 6320D was used. Wavelength scan was done with a *JASCO* spectrophotometer model V-530. Conductivity was measured with a *YSI* conductivity meter model 33. Ultraviolet light was generated by a *CAMAG* UV transilluminator model CM3 with wavelengths of 254 nm and 366 nm, and a *FOTODYNE* UV transilluminator model C3-3501. A Q.10 *CHANDOS* quartz cuvette was used to perform photo-Fenton reactions.

Phenolic content determination

The determination of total phenolics in treated OMWW samples was based on a micro method reported in the literature (Waterhouse, 2012). It was performed by spectrophotometry with gallic acid as standard. A calibration curve was plotted by preparing six standards. The latter were made in 4-mL glass vials by mixing 20 µL of gallic acid solution being in the concentration range 0-50-100-150-250-500 mg/L, 1.58 mL of distilled water and 100 µL of Folin-Ciocalteu reagent. After vigorous shaking for 1 min at room temperature, 300 µL of aqueous saturated sodium carbonate solution was added. Next, the solution was shaken again and heated at 40°C for 30 min by means of a bain-marie. The resulting blue solution was transferred entirely into the cuvette of a spectrophotometer and absorbance was measured at a wavelength of 765 nm. A 5000 mg/L aqueous gallic acid stock solution was used to prepare these solutions accurately.

Electrocoagulation experiments

All OMWW samples that were treated by electrocoagulation were first diluted with distilled water by a factor of 20. Next, they were filtered, centrifuged for five minutes at 5500 rpm, and re-filtered in order to measure their absorbance at a wavelength of 395 nm. The applied voltage for all electrocoagulation experiments was 22 V DC unless stated otherwise. Filtrations were done under vacuum over cotton wool.

Four different aluminum cells with various sizes and geometries were constructed and tested in the laboratory (Figure 1).

Cell #1 **Cell #2** **Cell #3** **Cell #4**

Figure 1. Aluminum cells tested in the electrocoagulation experiments.

Characteristics of these cells are given in Table 1.

Table 1. Aluminum cells tested in the electrocoagulation experiments.

Cell name	***Shape***	***Number of plates***	***Effective surface area (cm^2)***
Cell #1	rectangular	2	139
Cell #2	rectangular	4	256
Cell #3	square	2	783
Cell #4	round	2	2791

Photo-Fenton experiments

Since photo-Fenton experiments require an exposure to UV light (λ= 254 nm), they were conducted directly in the quartz cuvette of a spectrophotometer having a thickness of 1.0 cm. When performed on a larger scale, experiments were conducted in a 50mL glass beaker placed below a UV lamp. The source of Fe (II) chosen for our experiments is iron (II) oxalate, FeC_2O_4. This compound was made by mixing equal volumes of aqueous solutions of 30 mM iron (II) sulfate, $FeSO_4$ and 5 mM oxalic acid, $C_2H_2O_4$. The photo-Fenton experiment consisted in reacting within a cuvette, 0.5 mL of iron (II) oxalate solution, FeC_2O_4, 1 mL of 8mM hydrogen peroxide solution, H_2O_2, and 1.5mL of OMWW sample. When need be, a gas tubing was inserted in the reacting mixture to allowing bubbling of oxygen gas with a controlled flow rate.

Results and Discussion

Conventional coagulation

Our first attempts to treat OMWW were done by performing conventional coagulation experiments by using two coagulants known to be effective in the field of wastewater treatment: iron (II) sulfate, $FeSO_4$, and aluminum sulfate, $Al_2(SO_4)_3$. In spite of a treatment time as long as 24 h and the testing of different pH conditions, none of our attempts with conventional coagulation was successful. Therefore, in our hands this technique, and these two simple coagulants, did not seem suitable for an effluent as complex as OMWW.

Electrocoagulation

Electrocoagulation differs from conventional coagulation mainly with the fact the coagulant – in our case aluminum hydroxide – is generated in situ. This technique turned out to be very successful when applied on OMWW. Figure 2 shows the evolution of a sample of OMWW being treated for 19 h with cell#2.

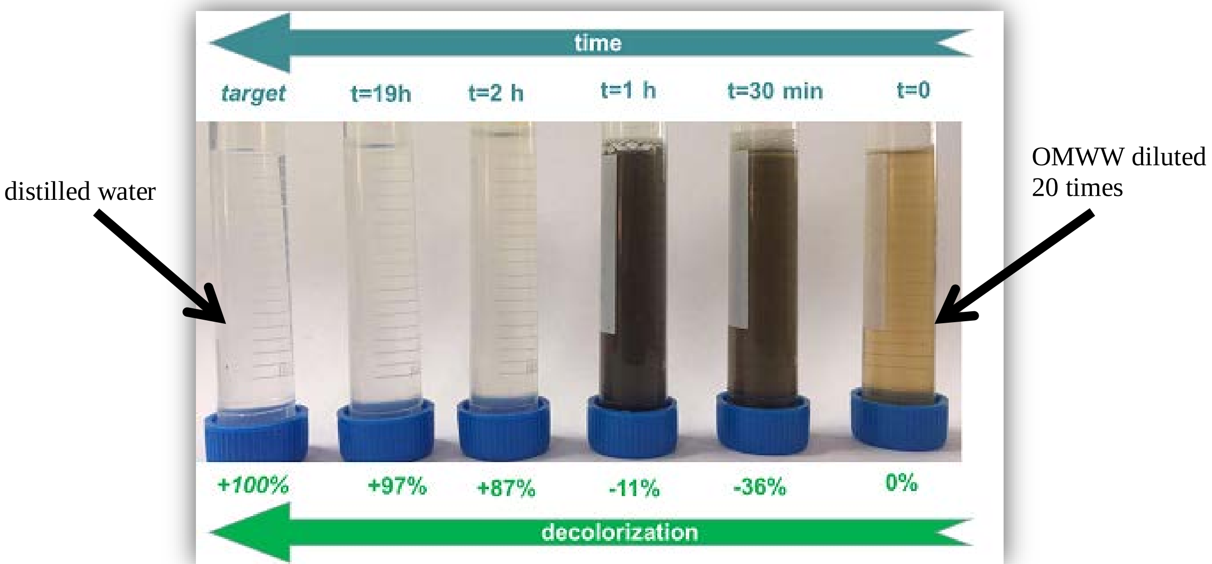

Figure 2. OMWW sample being treated by electrocoagulation with cell #2.

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As shown in Figure 2, the OMWW gets initially darker and darker in the initial stage of the treatment. This phenomenon is presumably caused by the absence of a critical mass of coagulant at the outset. However, once the treatment has been carried out long enough, a high decolorization of the sample is attained (+87% in 2 h). Decolorization starts taking place when flocs are formed and precipitated; however, their particle surface charge are affected by various parameters, one of which is the pH of the solution. Evidence for this explanation was obtained by monitoring the pH and the absorbance simultaneously (Figure 3). Indeed, Figure 3 shows that after 60 min of treatment, the increase of pH causes an immediate drop of the absorbance and therefore a decolorization. This increase in pH, which is typical in electrocoagulation, is caused by the formation of hydroxide ions at the cathode.

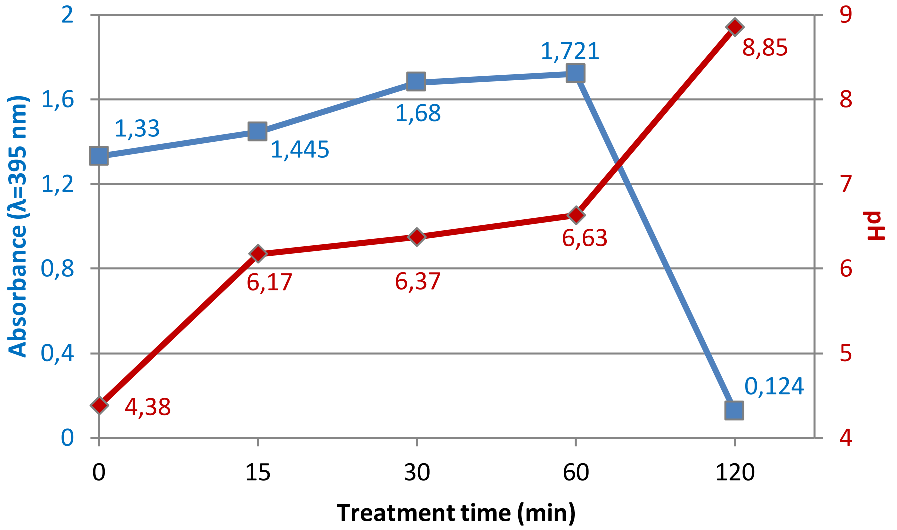

Figure 3. Monitoring of absorbance and pH in the electrocoagulation of OMWW with cell #2.

The effect of pH on decolorization is due to the solubility of the different aluminum hydroxide species in different pH ranges (Holt et al., 2005) Indeed, depending on the pH, aluminum hydroxide will exist either as a monomeric species (e.g $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_4^{-}$), a polymeric species (e.g. $Al_2(OH)_2^{4+}$, $Al_2(OH)_2^{5+}$) or an amorphous and less stable species (e.g. $Al(OH)_3$)(Bensadok,et al., 2008)

Table 2 compares the results obtained with each of the cells employed in our electrocoagulation experiments.

Table 2. Results obtained with cells 1-4 in the electrocoagulation experiments

Entry	Cell name	Conditions				Results		
		Volume of OMWW treated (L)	**Voltage applied (V)**	**EC[(a)] treatment time (h)**	**Settling time (days)**	**Decolorization[(b)]**	**pH**	**Conductivity (µS/cm)**
1	Cell #1	0.475	22	2.5	0	+84.0%	6.22	690
2	Cell #2	0.790	22	2	2	+ 92.3%	6.13	510
3				19	2	+ 97.4%	-[(c)]	300
4	Cell #3	9	14	15.5	10	+ 93.5%	7.41	550
5	Cell #4	5	11-13	8	10	+ 93.2%	7.65	550

(a) EC: electrocoagulation.
(b) Based on the change of absorbance at λ=395 nm. Sample centrifuged for 5 min beforehand.
(c) Not determined.

Determination of the phenolic content reduction was done for OMWW treated with cell #3. The concentration of polyphenols, expressed as mg of gallic acid equivalent, was found to drop by 92.4%; an excellent result given the detrimental effect of these polyphenols to the environment.

Photo-Fenton

Results obtained in the treatment of OMWW with the Fenton and photo-Fenton process are shown in Table 3.

Table 3: Results obtained in the Fenton and photo-Fenton experiments. $[Fe^{2+}]$initial = 3 mM].

Entry	**UV light[(a)]**	**O_2 (g)[(b)]**	**$[H_2O_2]$**	**Treatment time**	**Type of OMWW treated[(c)]**	**Decolorization[(d)]**
1	no	no	5 mM	20h	Untreated	+8.0%
2					Pre-treated by EC	+2.1%
3	no	no	8 mM	20h	Untreated	-3.9%
4					Pre-treated by EC	**+15.6%**
5	yes	no	8 mM	2h	Untreated	-21.3%
6					Pre-treated by EC	-29.1%
7	yes	no	5 mM	5h	Untreated	+4.1%
8					Pre-treated by EC	-13.5%
9	yes	no	5 mM	5h + 15h settling	Untreated	+9.6%
10					Pre-treated by EC	-6.8%
11	yes	yes	0 mM	2h + 15h settling	Pre-treated by EC	-10.9%
12	yes	yes	8 mM	2h	Pre-treated by EC	-17.5%
13				2h + 3 days settling	Pre-treated by EC	**+78.2%**

(a) λ=254 nm.
(b) Flow rate: 40 mL/min.
(c) Untreated = only diluted with distilled water by a factor of 20. EC = electrocoagulation.
(d) Based on the change of absorbance at λ=395 nm. Sample centrifuged for 5 min beforehand.

First, **entries 1-4** show the level of decolorization attained in the Fenton process (i.e. absence of UV light). Under the conditions tested, the best result was obtained in the treatment of OMWW pre-treated by electrocoagulation for 20h with 8mM H_2O_2 and 3mM Fe (II), to afford a color reduction by 15.6%. In the case of untreated OMWW, it was found that a lower concentration of H_2O_2 is favorable to a rapid degradation of organic pollutants (**entry 1** vs **entry 3**); however, the opposite trend is observed when dealing with OMWW pre-treated by electrocoagulation (**entry 2** vs **entry 4**). Therefore, our data seems to indicate that the efficiency of the Fenton process can be fairly variable since it can be affected by both the oxidant concentration and the quality of the effluent to be treated. **Entries 5-13** deal with the photo-Fenton process (i.e. UV-induced degradation). Comparison of **entries 5,7,9** vs **entries 6,8,10** shows that better results are obtained by processing untreated OMWW rather than the pre-treated one. It was found that an increase of the treatment time from 2h to 5h, in spite of a reduction of the oxidant concentration from 8mM to 5mM, leads to a higher level of decolorization (**entry 5** vs **entry 7**). Also, our data shows that settling of the solution over a prolonged period of time is also beneficial to the purification process when used post-treatment (**entry 7** vs **entry 9**). When oxygen gas, O_2, was used either as a replacement of H_2O_2 or as a co-oxidant (**entries 11-12**), poor results were obtained. However, with proper reaction conditions of time and oxidant concentration, the combination of O_2 and H_2O_2 as oxidants afforded an exceptionally high level of decolorization (+78.2%, **entry 13**).

Conclusion

A total of four techniques were tested in our investigation, namely coagulation, electrocoagulation, Fenton, and photo-Fenton. One the one hand, coagulation and Fenton performed poorly in terms of decolorization of OMWW. On the other hand, electrocoagulation and photo-Fenton in presence of oxygen gas both proved to be potent and efficient solutions when performed under the right experimental conditions of time and oxidant concentration. Though electrocoagulation affords the best results in terms of decolorization (>93%) and phenolic content reduction (>92%) at the scale of the laboratory, its utilization at the olive mill scale may be challenging because of the inherent high energy cost of the technique. Consequently, the future of this technique will be largely dependent on its optimization by for example powering it with inexpensive energy sources. Regarding the photo-Fenton process, the identification of unique experimental conditions enabled to reach a decolorization of pre-treated OMWW by more than 78%. This technique is attractive because of its practicality; however, its use at a large scale may be hampered by the cost of usage and maintenance of UV light. This study has clearly shown that the issue of OMWW treatment can be hardly solved by a single method, but that it rather relies on the clever combination of a sequence of finely tuned processes to be operated individually. Electrocoagulation and photo-Fenton have been proved to be very good examples of such processes.

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