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Combined Treatment by Coagulation-Flocculation and Oxidation of Olive Mill Wastewater

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Abstract

Olive mill wastewaters (OMW) with its physicochemical and microbiological properties is one of the most important problems facing the Mediterranean countries, due to its adverse effects on different ecosystems and because they reject without any treatment. The objective of this work is the treatment of OMW by combining two chemical processes: coagulation-flocculation and oxidation. We are interested in the first step to the physicochemical characterization of olive oil mill wastewater, in second step to the chemical treatment of OMW by coagulation-flocculation, followed by oxidation with hydrogen peroxide (H_2O_2). A jar-test apparatus equipped with 4 glass beakers of 1L was employed for coagulation–flocculation experiments. This lasts was coupled with H_2O_2 oxidation which was carried out in a 250 ml Pyrex reactor equipped with a magnetic stirrer. The effluents had a highly acidic pH (4.93) and are loaded on organic matter (COD=112 g/l). Tests showed that the coagulation-flocculation's optimal conditions are 1.5 g/l of $Al_2(SO_4)_3$ and 3 g/l of quicklime and a equal to pH=8.5. In these conditions the values of removal of OD and COD are respectively 8.5 and 45.2 %. The value of COD removal can reach 91 % if the coagulation flocculation is followed by oxidation step using the hydrogen peroxide at a rate of 30 g/l. The application of two methods coagulation-flocculation and oxidation can significantly reduce the COD value of olive mill wastewaters. Indeed, a reduction greater than 91% was obtained in our experiments.

Abbreviations

OMW	Olive Mill Wastewater
COD	Chemical Oxygen Demand
OD	Optic Density

1. Introduction

The three phase olive oil extraction process generates a dark colored effluent usually called olive mill wastewater (OMW). This effluents result from the mixture of "vegetation water" coming from the olives, and water added during the process. Approximately 30 million m^3 of OMW are produced annually in the Mediterranean area, which are characterized by a high pollutant load [1]. This pollutant is due to its high organic load and the phytotoxic and antibacterial phenolic compounds, which resist biological degradation.

Mediterranean countries are mostly affected by this serious environmental problem, since they are responsible for 95 % of the world wide olive-oil production. In these countries, about 11 million tons of olives are produced per year from which about 1.7 million tons of olive oil is extracted [8].

Several Mediterranean countries enforce upper limits for OMW discharge into the soil [13] in order to avoid negative environmental impact associated with OMW disposal, but many do not control it. The West Bank of the Palestinian Territory is one case of the latter [14].

The OMW is a foul smelling acidic wastewater composed of water (83-92 wt %), organic matter (4-16 wt %) and minerals (1-2 wt %). The organic load is so high with biological oxygen demand (BOD) up to 100 g l^{-1} and chemical oxygen demand (COD) up to 200 g l^{-1}[14]. These values are about 300 times higher than those of a typical municipal sewage. Because of their antibacterial effects, phenolic compounds of the organic are the most problematic compounds encountered in the OMW [14].

From the seventies mills effluent olive have been the subject of much attention from the scientific institutions, businesses and government agencies to study and propose best technologies for minimizing environmental impacts, recovery or disposal [2]. Given their composition and percentage of organic matter (10-25 %) [3], effluent olive oil mills alone cannot be an interesting product value. Indeed, effluents enriched mixed with other waste, concentrated, dried and/or purified, they can be recycled and used for the production of certain components useful [3]. In science, there are more than 20 processes or for the treatment of effluents from olive oil mills technologies. It is in most cases of elementary or combined tested in the laboratory or pilot plant without any real industrial projection [3].

To reduce pollution caused by OMW, several techniques have been developed such us chemical treatment. Chemical treatment by coagulation-flocculation is neither simple nor efficient for the reduction of organic materials in the OMW. It is also becoming less acceptable nowadays due to the higher costs associated with the large volumes of sludge generated, and the hazardous waste categorization of metal hydroxides [10]. However, this process may be applied to the OMW as a pre-treatment to remove the suspended solids.

For oxidation treatment, several oxidizing agents have been tested for OMW treatment like hydrogen peroxide, ozone, chlorine, chlorinated derivatives (i.e., chlorine dioxide, sodium hypochloride, etc.), or a combination of them [11]. Ozone and hydrogen peroxide systems are preferred because of their high oxidizing potential and the possibility of operating under atmospheric pressure and ambient temperatures without problematic decomposition products of the oxidizing agent [11].

This work focuses on the characterization and treatment of olive mill wastewater taken from a mill situated in Sfax (Tunisia). The treatment of this polluted effluent is carried out by coagulation-flocculation followed by oxidation with hydrogen peroxide (H_2O_2).

2. Material and Methods

2.1. Olive Mill Wastewaters

The OMW were collected from an olive oil mill in the area of Sfax (Tunisia) which used a discontinued process. Before use, the effluent was strongly stirred and decanted; the oily fraction was foamed and the deposit eliminated by decantation.

2.2. Experimental Procedures

A jar-test apparatus equipped with 4 glass beakers of 1l was employed for coagulation–flocculation experiments. Specifically, OMW samples were thoroughly shaken for re-suspension of possible settled solids and then, 1000 ml of the sample were transferred to the beaker. For experiments where both coagulant and flocculant were used, firstly an appropriate dosage of coagulant (Al_2SO_4) was added directly, while stirring for 3 min at 120 rpm; fast stirring was required to increase the effectiveness of destabilization of particles and initiate coagulation. This was followed by a slow stirring for 20 min to increase the contact between coagulating particles and to facilitate the development of large flocs. To improve flocculation step, we introduce a flocculant (CaO) whose role is making the flocs more consistent, heavier and easily decantable. After the addition of reagents, the OMW mixture was left to rest and, as soon as separation was achieved, the supernatant is trapped in order to be analyzed.

For the experiments where coagulation-flocculation was coupled with H_2O_2 oxidation. Oxidation was carried out in a 250 ml Pyrex reactor equipped with a magnetic stirrer. The desired quantity of H_2O_2 was introduced into 250 ml of the supernatant of the pretreated effluent by coagulation flocculation under the optimal conditions with a pH=8.5. The concentrations applied of H_2O_2 vary from 3 to 30 g/l.

2.3. Physical–Chemical Analysis of OMW

PH was measured in a suspension of 50 ml of olive oil mill wastewaters at ambient temperature by a pH-meter instruments (BICASA) immediately after sampling; pH measurement is done directly in the raw effluent olive oil mills at ambient temperature [16].

Electrical conductivity (EC) was measured with a conductivimeter HACH (DR/2000). Turbidity was measured by a turbidimeter HACH (DR/2000). Hydrotimetric titrate was measured by complexometric method by the EDTA (Na_2H_2Y) and it is expressed in °f. Optical density (OD) is the absorptance at 283 nm and was measured by a spectrophotometer HACH.

The TSS is determined by centrifugation a aliquot (50 ml) of crude samples of the olive oil mill wastewaters during 20 min at 4000 rpm, content (MES) is determined by weight difference before and the pellet after centrifugation and drying in an oven at 105 °C for 2 h (AFNOR T 90-105) [16].

Total and dissolved chemical oxygen demand (COD) was determined by a colorimetric method. An appropriate amount of sample was introduced into a commercially available digestion solution and the mixture was then incubated for 120 min at 150 °C in a DCO-meter (thermo BATH ALB 64). COD concentration was measured colorimetrically using UV/VIS spectrophotometer HACH (500 serie DU). The absorbance was determined at 620 nm.

3. Results and discussion

3.1. Characterization of Olive Mill Wastewater

The characteristics of olive mill wastewaters are grouped in the following table.

Table 1: Characteristics of raw olive mill wastewater.

	Unit	**Value**
Conductivity	ms/cm	21
Salinity	mg/l	105.5
pH		4.93
λ max	nm	283
OD		1 .532
Turbidity	FTU	4500
COD	mg/l	112000
TH	°f	3.36
T($Ca^{2+)}$	°f	2.4
TH ($Mg^{2+)}$	°f	0.96
TSS	mg/l	2550

Based on the results of the **Table 1**, it shows the following observations:

The acidic pH is a fundamental characteristic effluent mill with values between (4.5 and 5.32) for different processes trituration of olive oil; these results are confirmed with the values obtained by several researches [15]. These vegetable waters with high acidity (pH = 4.93) may have negative effects on the flora and fauna of environment. This acidity can be explained by the presence of organic acids such as phenolic acids and fatty acids. The acidity of the olive mill wastewaters increases with the duration of storage; this phenomenon can be explained by self-oxidation and polymerization reactions which convert the phenolic alcohols to phenolic acids [6].

These discharges are also characterized by high turbidity equal to 4500 FTU which is explained by the dominance of colloidal fractions in suspended solids with a value of 2550 mg/l.

The OMW studied have a high electrical conductivity value equal to 21 ms. cm^{-1}. This value gives a general idea about the high salt present in these effluents; this content is due to salting practices for the conservation of olives before crushing in addition to the natural wealth of vegetable dissolved mineral salts [4].

Organic matter of olive oil mills effluents consists of polysaccharides (13-53 %), protein (8-16 %), phenolic compounds (2-15 %), lipids (1-14 %), polyalcohols (3-10 %) and organic acids (3-10 %) [6]. This composition results from the destruction of tissue during the olive crushing and oil extraction [7].

The average organic matter content expressed as COD is approximately 112 g/l. This shows the high oxygen demand for the complete oxidation of the organic matter contained in this effluent. This content is very high compared to that stored in other types of waste [5].

3.2. Treatment of olive mill wastewaters

Several physico-chemical technologies have known already proven in the field of treatment of liquid effluent mills. Among these include techniques coagulation-flocculation and oxidation, in effect:

- The coagulation-flocculation is used to reduce turbidity caused by colloidal particles.
- The oxidation by hydrogen peroxide reduces the COD value by transforming part of the organic matter into CO_2.

3.2.1. Treatment by coagulation-flocculation

Coagulation is one of the most effective methods of removing organic matter. It consists in treating the olive mill wastewater with surfactants or certain coagulants. This type of treatment remains the most comprehensive and certainly the least expensive compared to the material eliminated [17].

This section aims the reduction study of turbidity, colloidal matter and organic fillers, using the method of Jar-Test. The clotting assays were performed in the laboratory at ambient temperature and atmospheric pressure.

For a volume of vegetable water three parameters are studied: the effect of pH, coagulant dose and flocculant dose.

a. Effect of pH

To optimize the pH value, the following steps are followed:

- Introduce in each beaker 1 liter of crude olive mill wastewater.
- Putting these solutions in fast stirring (120 rpm).
- Introduce 15 ml of coagulant from a solution with a 0.4*103 g/l concentration in each beaker (always with rapid stirring), and measure the initial pH value of these solutions.
- Adjust the pH values to 5.5, 6, 6.6 and 7 by addition of acid (H_2SO_4) (4N) or basic NaOH (5N).
- After 3 min, add 3 g of quicklime in each beaker.
- Reduce the stirring speed to 30 rpm and after 20 min, stop stirring and read the value of decanted volume.

The results obtained are summarized in the following table:

Table 2: Variation of decanted volume with the pH value.

pH final	4.94	7.18	7.67	7.86	8.5
Decanted Volume (ml)	1000	800	710	700	680

As shown in **Table 2**, the settled volume observed after 24 decreases with the increasing of pH value, which implies that the optimum value of pH is 8.5, which corresponds to a decanted volume (settled solids) equal to 680 ml.

The discharge standard pH is equal to 8.5 and if the pH exceeds this value an acidification step is unavailable to meet this standard.

b. The dose of coagulant

The quicklime CaO was chosen because of its higher density and abundance in active substance compared to the slaked material and hence easier to handle [12]. To optimize the dose of coagulant, the optimal pH is equal to 8.5 and we vary the coagulant concentrations: 1; 1.2; 1.5; 1.7 g/l and 3 g/l of quicklime. After 1.5 hours of settling volumes of solids observed is shown in the figure below:

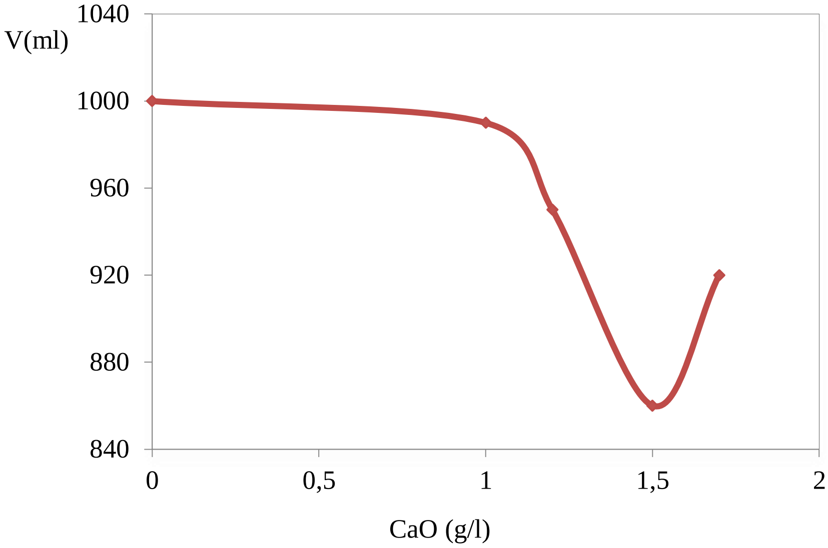

Figure 1: Change in volume of settled solids depending on the dose of coagulant.

Figure 1 shows that the decanted volume change with the variation of the coagulant's dose: this value decreases until reaching an optimum dose of coagulant equal to 1.5 g/l which corresponds to the minimum decanted volume equal to 860 ml.

c. The dose of flocculant

To optimize the dose of flocculant, we fixed the pH to 8.5, the concentration of the coagulant in 1.5 g/l and we make vary the concentration of CaO: 2; 2.5; 3; 3.5 and 4 g/l. The optimal concentration of CaO is deducted on one hand by the evolution of the volume settled after a time of 11 hours and on the other hand by the calculation of the COD of floating obtained. The found experimental values are presented on the following figures 2 and 3:

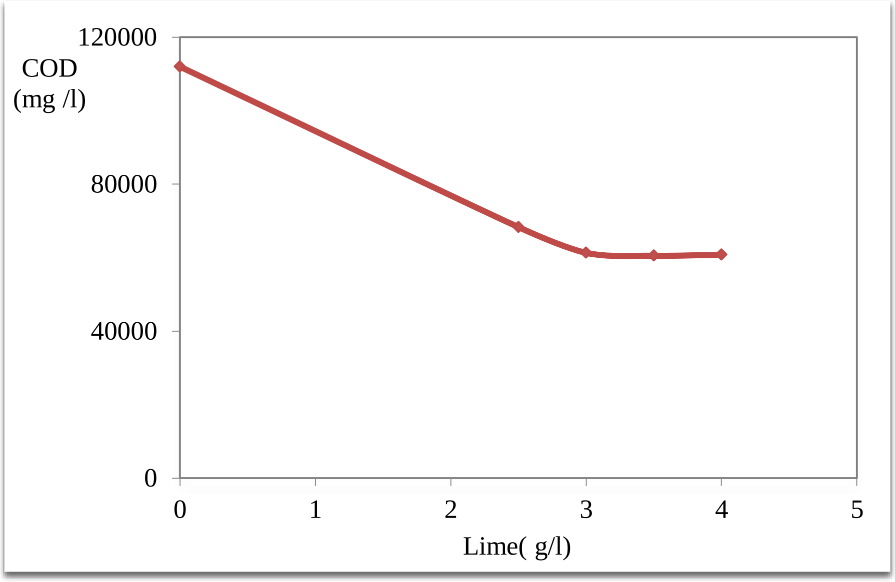

Figure 2: Change in supernatant COD depending on the concentration of quicklime.

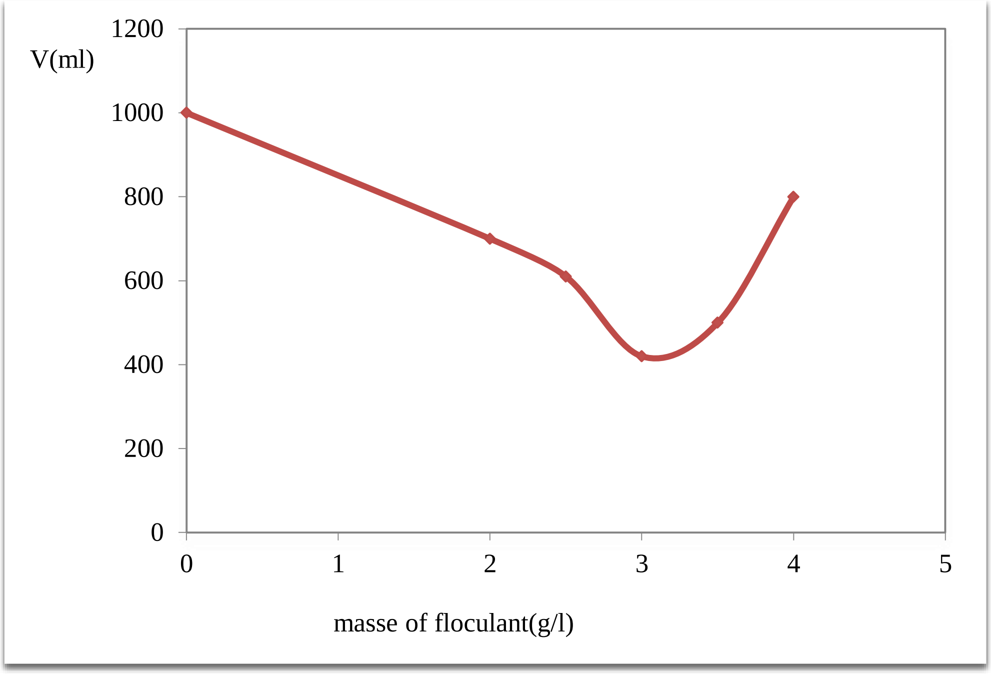

Figure 3: Evolution of settled volume of OMW depending on the mass of flocculant.

According to the **Figure 2**, we notice that the COD decreases gradually with the increase of quicklime concentration to reach a limit value, which from it begins to stabilize. It is deduced that the optimum concentration of CaO is equal to 3 g/l, which corresponds to a minimum of COD= 61350 mg/l (that is a reduction of 45.2 % of COD), and a minimal volume of muds equal to 420 ml (**Figure 3**). To improve the rate of COD dejection and the concentration of polyphenols, we call on to the oxidation by the hydrogen peroxide H_2O_2.

3.2.2. Oxidation by H_2O_2 Treatment

The object of this stage is essentially dedicated to the oxidation of the organic matter contained in the vegetable water using as oxidant: the hydrogen peroxide (H2O2).

The oxidation experiments were carried out on 250 ml of the floating of OMW treated by coagulation flocculation in the optimal conditions with pH=8.5. The applied dose of H_2O_2 varies from 3 to 30 g/l.

The studied parameters are the reaction time and the dose of H_2O_2. The study of the effect of the reaction time of the degradation of organic material in the presence of H_2O_2 is based on the calculation of the COD and the absorbance (OD) at 283 nm over time.

a. Effect of reaction time and dose of H_2O_2 on OD

The results of analysis of samples taken over time are presented on the figure 4. We notice from **Figure 4** that the optic density decreases significantly from 1.4 to 0.5 (64 % of reduction) for a concentration of $[H_2O_2]$ = 30 g/l after 60 min of reaction. However, it decreases from 1.4 to 1.3 (15% of reduction) for $[H_2O_2]$ = 3 g/l after 20 min. For the high dose of H_2O_2, we note that the OD shows an increase after 60 min of reaction that can be explained by the training of reactive intermediates that absorb light at 283 nm.

a. Effect of reaction time and dose of H_2O_2 on COD

The corresponding COD measurements are shown in **Figure 5**. **Figure 5** shows the degradation profile of COD removal at various hydrogen peroxide concentrations as a function of the time. The results indicate that COD removal increased by increasing the concentration of peroxide from 3 to 30 g l^{-1} (COD removal reached 80 % for $[H_2O_2] = 30\ g\ l^{-1}$ and 20 % for $[H_2O_2] = 3\ g\ l^{-1}$) due to the additionally produced HO·. However, the use of excessive concentration of peroxide (for $[H_2O_2] = 30\ g\ l^{-1}$ and after 45 min of reaction), hindered the % COD removal, possibly due to the enhancement of the competition reactions, mainly the recombination of HO· and the reaction of HO· with H_2O_2, contributing to the HO· scavenging capacity [9].Or the formation of reaction intermediates hardly oxidizable by potassium dichromate (oxidant used for the measurement of COD).

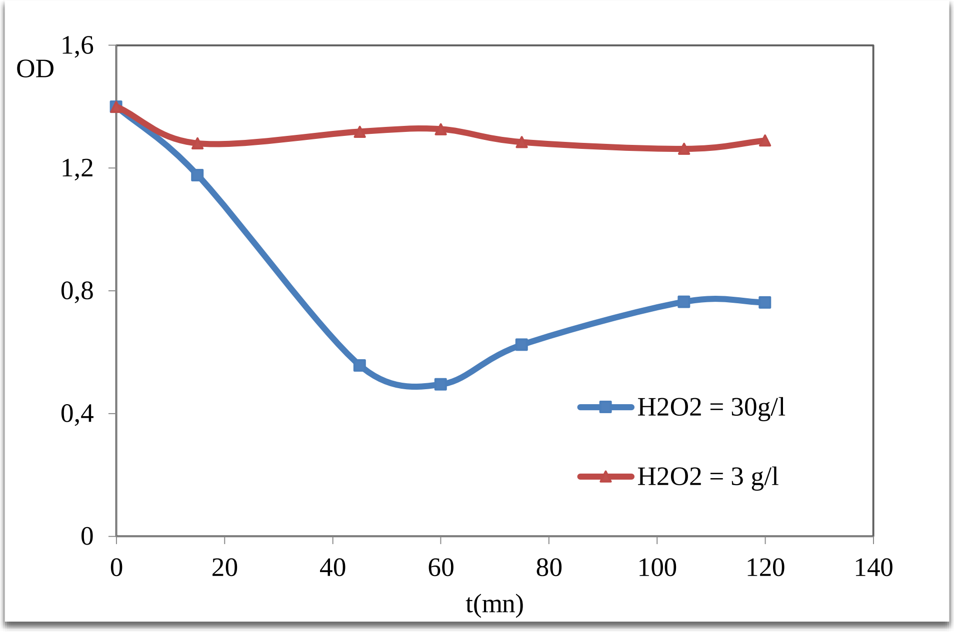

Figure 4: Evolution of OD over time for $[H_2O_2]$ =30 g/l and 3 g/l.

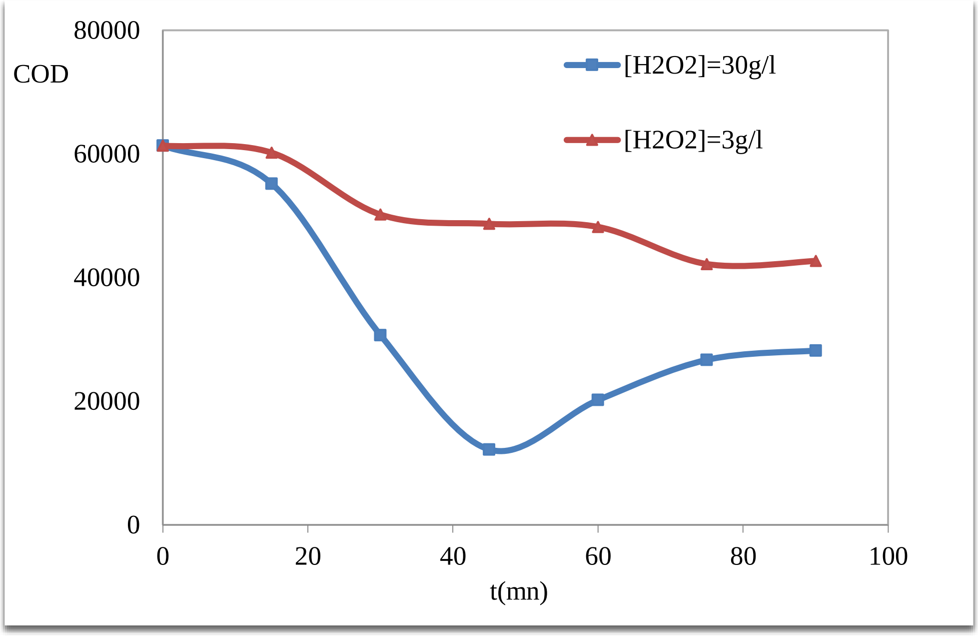

Figure 5: Evolution of COD over time for $[H_2O_2]$ = 30 g/l and 3 g/l.

As can be seen from the **Table 3**, the treatment of vegetable by coagulation-flocculation followed by oxidation by H_2O_2 can eliminate up to 91 % of COD but only 67 % of the OD. However, the applied dose of H_2O_2 is high, and the cost of treatment may be very high.

Table 3: Recapultatif Table.

	OD	**%**	**COD (g/l)**	**%**
Raw OMW	1.53	0	112	0
OMW treated by coagulation-floculation	1.4	8.8	61.35	45.2
OMW treated by coagulation-floculation and oxydation	0.5	67	10	91

With %: reduction percentage

Conclusion

This study aims at the reduction of the COD and OD which characterizes the organic matter and phenolic compounds contained in the olive mill wastewater.

The results obtained in the scale laboratory allow formulating the flowing conclusions: The physico-chemical characterization of the studied OMW shows that it is an acid effluent (pH = 4.93), strongly polluted (COD=112 g/l) and rich in phenolic compounds.

The essays of treatment by coagulation-floculation in Jar - Test showed that the optimal conditions are 1.5 g/l of $Al_2(SO_4)_3$ and 3 g/l of quicklime and a pH = 8.5. In these conditions the values of dejection of OD and COD are respectively 8.5 and 45.2 %. The value of COD removal can reach 91% if the coagulation flocculation is followed by oxidation step using the hydrogen peroxide at a rate of 30 g/l.

In conclusion, the application of two methods coagulation-flocculation and oxidation can significantly reduce the COD value of olive mill wastewaters. Indeed, a reduction greater than 91 % was obtained in our experiments.

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