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Removal of organic matter and polyphenols in the olive oil mill wastewater by coagulation-flocculation using aluminum sulfate and lime.

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Abstract

This work aims to treat the liquid discharges from the olive oil crushing units to protect the receiving environments by the coagulation-flocculation process using lime and aluminum sulfate as chemical coagulants. We proceed by studying the effectiveness of the coagulation-flocculation technique in eliminating organic matter and polyphenols that characterize our samples and the possibility of reusing the treated wastewater in irrigation. Analysis shows that adding 1.7 g/l aluminum sulfate can eliminate 58% of COD, 23% of TSS, and 24% of polyphenols, producing 21g/l of sludge, and eliminating 52% of COD, 48% of TSS, and 72% Of polyphenols requires the addition of 20 g/l of lime, but 25 g/l of sludge is produced. Combining two coagulants (1.7 g/l of aluminum sulfate and 20 g/l of lime) reduces 64 % of COD, 72 % of TSS, and 62 % of polyphenols, with the sludge is 29g/l. The germination test by cucumber seeds showed the validity of the use of treated olive oil wastewater in the agricultural irrigation.

Keywords: *Olive Oil Mill Wastewater (OOMW), Coagulation, Lime, aluminum sulfate, irrigation, treatment.*

1. Introduction

In Morocco, olive growing has a great interest and is one of the most developed crops. With the development of this olive growing and the increased demands of the internal and external markets in olive oil, the olive growing industry has also experienced an essential development in the last years, thus generating an important discharge of liquid residues harmful to the environment. The lack of effective treatment and recovery methods and strict control allows mill owners, in most cases, to discharge the olive oil mill wastewater (OOMW) into the natural environment without any treatment. As a result, according to studies [1-3], the OOWM are characterized by high acidity and electrical conductivity as well as a high load in organic matter and polyphenols [4]. This has led to environmental degradation, the destruction of bacterial communities in the soil, the pollution of groundwater and surface water, and the destruction of flora and fauna due to clogged soil eutrophication [5-6], etc. It is in this context that the present study is registered. This work seeks to protect the environment, on the one hand, by solving the problem of pollution caused by the OOMW; on the other hand, by the valorization of OOMW treated in the concept of ensuring the balance of the natural water cycle. Indeed, we studied the effectiveness of the coagulation-flocculation technique in eliminating organic matter and polyphenols remaining in the OOMW and the possibility of reusing the treated OOMW in irrigation.

2. Materials and methods

2.1. sampling

OOMW samples were collected mainly from a semi-modern crushing unit located in the province of Al-Hoceima, Morocco, during the olive-growing season (November 2019 until January 2020. The analytical results and their interpretation depend closely on the manner of collection, packaging, and the duration of storage. The samples were taken from the OOMW storage tank, and transported to the laboratory in a 5-liter container, and stored at 4°C. Then pre-treated and fermented immediately. No chemical additives were used During the production of olive oil.

2.2. OOMW treatment by coagulation and flocculation

2.2.1. Test jar

The coagulation tests were carried out in the laboratory at room temperature with samples of OOMW diluted ten times from the 2019/2020 olive season. These tests were performed using a Jar-test ban (figure 1). The Jar-test was based on the phenomenon of coagulation and flocculation: a series of 6 beakers include the same samples and are stirred in the same way. Increasing doses of the coagulant are added to this series to determine the optimum dose. Several researchers have applied this technique to remove the organic matter [7,8].

Figure 1. The Jar test ban used during experiments.

All tests were performed using the following steps:

- **Rapid agitation (150 rpm)** for 5 minutes to ensure excellent dispersion of reagents and good chemical destabilization of colloids.
- **Slow agitation (30 rpm)** for 30 minutes using a paddle stirrer to promote contact of the contiguous particles and avoid breaking the flocs formed.
- **Decantation for 2h.**

After decanting, the supernatant is filtered under vacuum using filters with a porosity of 0.45 µm to be analyzed.

The doses of aluminum sulfate ($Al2\ (SO4)\ 3,\ 18\ H2\ O$) (2% solution) used vary from 0 to 3.5 g /L with and without pH adjustment. This adjustment was made by adding sulfuric acid (4N) or sodium hydroxide (5N).

By applying the same agitation conditions, the same set of beakers containing a suspension of OOMW (500 ml) was subjected to increasing doses of lime, 0 to 30 g/l. The flakes were left to rest for two hours, and the supernatant is siphoned for analysis.

The effect of the combination of the two coagulants on the same types of OMW was studied by adding increasing amounts of aluminum sulfate and fixed lime and reciprocally.

The performance of the treatment was evaluated, visually and analytically, by monitoring the reduction rate of TSS, COD, and polyphenols. The assessment of the reduction rate by a factor X, indicated as a percentage, is based on the following formula (1):

(X) % Reduction(X) = [Ci (X) - Cf (X)] *100 / Cf (X). (1)

Ci: Initial concentration of X in the Olive Oil Mill Wastewaters.

Cf: Final concentration in treated Olive Oil Mill Wastewaters.

2.2.2 ***The quantity of sludge produced.***

The coagulation-flocculation treatment process generated solid sediment (sludge). The latter was determined by measuring its weight remaining in the beaker after coagulation-flocculation and based on three repetitions. The beaker containing the residue is dried in an oven at 100 ° C for four h and weighed [9]. The quantity of sludge produced is calculated according to the following formula (2):*

Sludge produced (g/l) = (P1 - P0) /V (2)

P1: weight of the beaker with the solid residue (g)

P0: weight of the empty beaker (g)

V: volume of the sample test (l).

2.3. Dosing methods:

The physical and chemical characterization of the margins was based on studying the following parameters: pH, Electrical Conductivity, Temperature, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD5), Total Suspended Solids (TSS), and Polyphenols.

The analyzes were carried out in the laboratory, according to the following protocols:

The pH: The pH was measured using a sension benchtop pH-meter from the Hach company. The test was repeated three times.

Electrical conductivity: The electrical conductivity was measured using a Hach sension+ EC7 lab conductivity meter.

The Chemical Oxygen Demand (COD): the COD was determined on OOMW samples according to AFNOR NF T90-101 standard by ECO thermo-reactor (V 230; Hz 50-60; w700), diluted to 1/1000 given the high load of organic matter. The principle consists of oxidizing the organic matter contained in the OOMW by an excess of potassium bicarbonate in an acidic medium for two hours and in the presence of potassium sulfate as a catalyst. Mohr's salt carried out the determination of this excess in the presence of ferroin. To avoid the interference of chlorides with organic matter, they were complexed with mercuric sulfate.

Biological Oxygen Demand (BOD_5): The BOD COD was determined on OOMW samples according to AFNOR T90-103. The samples were diluted to 1 / 200th to reduce the toxic effect of polyphenols on microorganisms and were incubated in a BOD-meter, which gives the amount of oxygen consumed by bacteria for five days at 20 ° C in the dark.

Total Suspended Solids (TSS): TSS was determined by filtration through membranes with 0.45 µm pore diameter. The TSS content was determined by the difference in weight of the filter before and after filtration and drying in an oven (Daihan LabTech co., LTD/ 220 V. 60 Hz: 1 phase) at 105 °C for 4 h (AFNOR T 90-105). Carrying out a dilution was necessary because of the overload of certain OOMW with suspended solids, which causes clogging of the filters.

Polyphenols: the mixture of phosphotungstic acid (H2 PW12O40) and Folin's reagent (H3 PW12O40) was reduced to tungsten blue oxide (W8 O23), the coloration exhibits maximum absorption at 760 nm.

3. Results and discussions:

3.1. Physical-chemical characteristics of OOMW:

The OOMW utilized in this work was taken from a semi-modern olive oil crushing (centrifugation system) at the production unit located in Beni Bouayache, Al-Hoceima, Morocco, in 2019/2020. **Table 1** presents the average of the Physic-chemical characteristics of the OOMW studied. The tests are repeated three times to ensure that each parameter's analysis values are correct. The OOMW were characterized by acidic pH (4.6) due to organic acids (phenolic acids); Thus, the values recorded matched with results already found (4.2 to 5.9) [10]. The electrical conductivity value was high (9.4 ms/cm) and due to the use of salt during the storage of olives in crushing units.

Table 1: The characteristics of the OOMW.

Parameters	Units	Raw OOMW	Filtered OOMW dilute 10 times
pH	-	4.6	4.86
Electrical conductivity	ms/cm at 20°C	9.4	1.89
COD	g of O_2 /l	84.56	78.7
BOD_5	g of O_2 /l	53.68	43.64
TSS	g/l	59.7	23.27
Polyphenols	g/l	1.86	1.23

The concentration of suspended solids was relatively high at 59.7 g/l. By comparing this value with the maximum value of the centrifuge already found [11], (161,2 g/l), This could be explained by the fact that the centrifuge system must dilute the olive paste with hot water which could cause the OOMW produced to be diluted. Concerning the organic matter that expressed BOD_5 and COD Analysis terms, the OOMW was very rich in organic matter. Thus, according to **table 1**, the values obtained were 53.68g of O_2/l and 84.56 g of O_2/l, respectively. Moreover, the content of phenolic

compounds was 1.86 g/l. This value was found to be in the range (0.4 - 7.1) [11]. Comparing the characteristics of the raw OOMW and the precipitation shows that the total dry matter concentration was reduced; due to the filtration and adsorption of large molecules on the settled particles [12]. In these two cases, the other characteristics were similar, but the reduction of COD and BOD_5 was slight.

3.2. OOMW treatment by coagulation-flocculation (Jar-test)

3.2.1. Aluminum sulfate application

Before applying the process of coagulation-flocculation pretreatment, the first step was to determine the optimum dose of alumina sulfate, which allows for the better elimination of organic matter and suspended matter. The results of coagulation tests using aluminum sulfate will be presented as follow. figure 2 indicates that the gradual addition of aluminum sulfate to filtered OOMW diluted 10 times resulted in a significant decrease in the pH from 4.8 to 3.35.

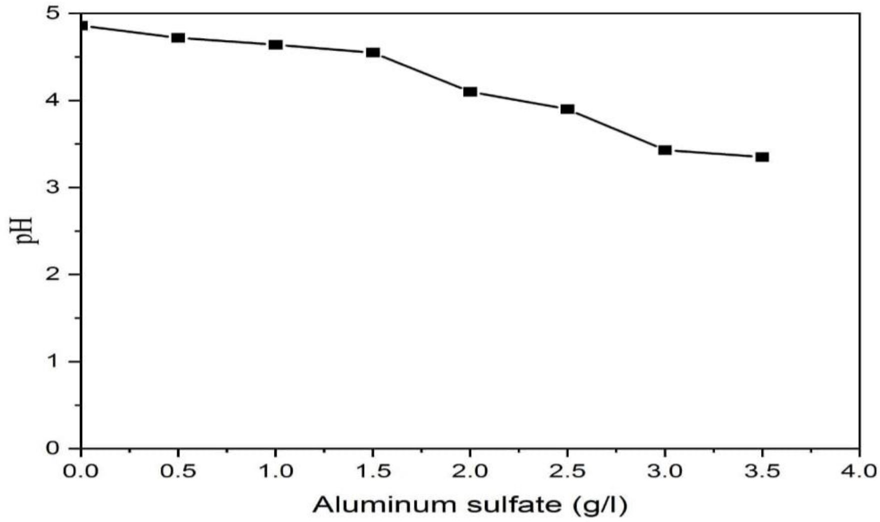

Figure 2: Variation in pH depending on the concentration of aluminum sulfate.

Figure 3 illustrates two stages of the change: increasing the rate of decrease in the pollutant load, then the stage of decreasing the rate. In the pH range (4.67-6.7), because aluminum ions (Al^{3+}, $Al(OH)_2^+$, $Al(OH)_3$) dominate, the rate of pollution load reduction accelerates in this area (figure 4). At the same time, the decrease in the abatement rate was due to overdose by coagulating, which caused the destabilization of colloidal particles. The 1.7 g/l dose of aluminum sulfate allows the elimination of 58% for COD, 23% for TSS, 24% for polyphenols, and the sludge produced was 21g/l. Thus, it is inferred from figure 2 and 3 that the pH domain obtained does not eliminate the pollutant load, especially polyphenols. This low elimination rate (low concentration of Al^{3+} and pH concentration ranged between 4.67 and 4.54) under these conditions can be attributed to the absence of the flocculated form of the $Al(OH)_3$ coagulant that would trap the neutralizing substance. The OH functional group related to polyphenols seems to reduce the complexing capacity to aluminum at pH = 4.6; some researchers have noticed the same phenomenon [13]. This low elimination was due to the conditions of distribution of the Al^{3+} ions and the concentration of phenoxide.

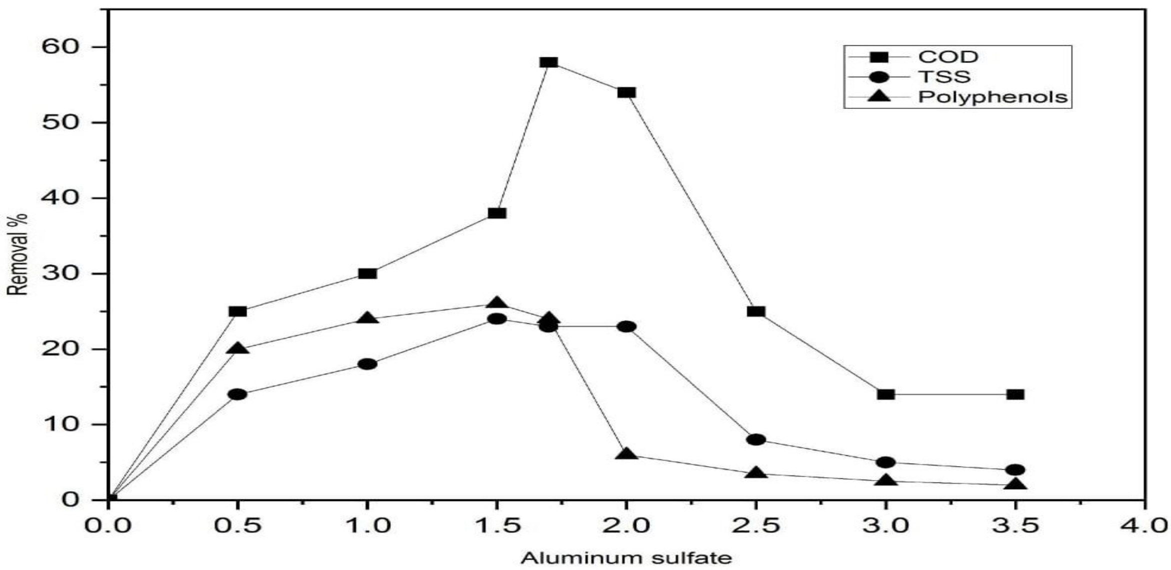

Figure 3: Evolution of the percentage (%) reduction of TSS, COD, and polyphenols as a function of the concentration of aluminum sulfate without the pH adjustment.

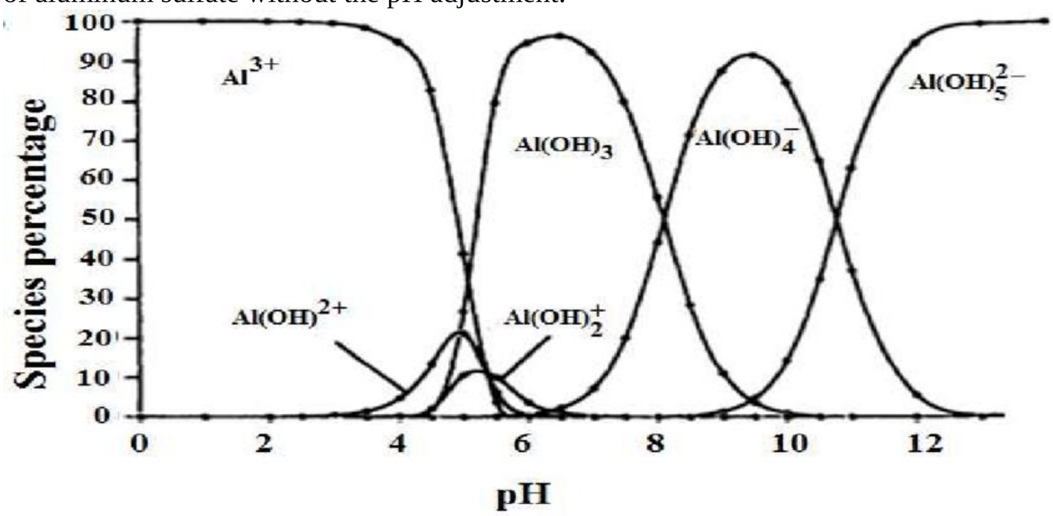

Figure 4: Distribution diagram of hydrolyzed species of aluminum according to pH [14].

PH impact

This research also studied the influence of pH on coagulation-flocculation by aluminum sulfate; to adjust the pH of the solution we use NaOH or HCL. Figure 5 shows the evolution of the removal efficiency of TSS, COD, and polyphenols; the best removal effect is when the pH value is between 5.8 and 7.1; hence the reduction of COD and TSS was around 56% and 24%. Regarding the polyphenols, it was noted that the removal efficiency increased from 28% to 42% in the same pH range. This may be due to changes in the coagulation mechanism. For example, non-dissociated compounds are beneficial to adsorb on the aluminum hydroxide flocs that dominate this range. Therefore, we have changed from the neutralization phenomenon of negative charges to colloidal Al $(OH)_3$ Adsorption of flocs [14]. Finally, note that the pH could be influenced by the temperature of the environment, which impacted the solubility of aluminum forms and the dissociation of organic substances.

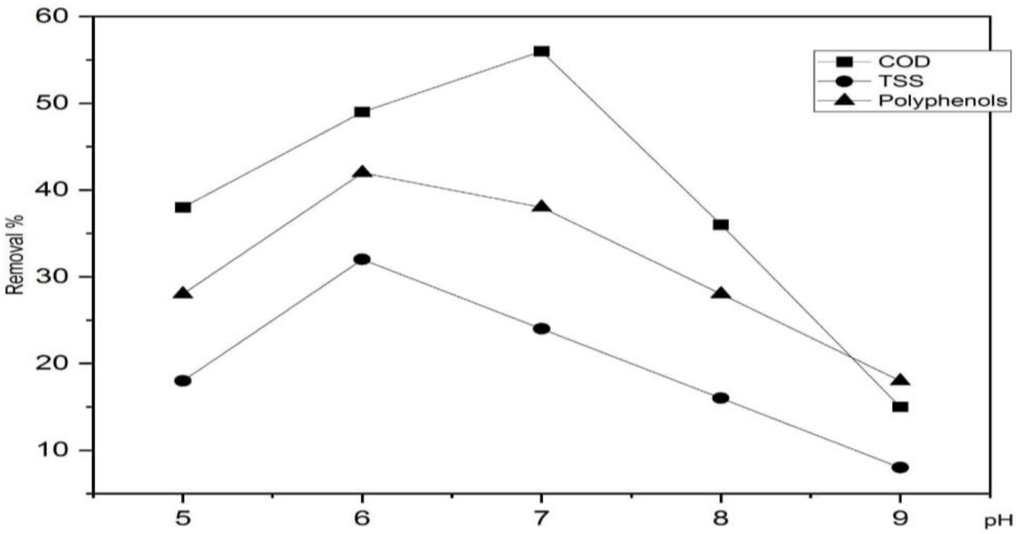

Figure 5: pH influence on coagulation by aluminum sulfate at the optimal dose of 1,7 g/l.

Temperature effect

Experimental studies have shown that at low temperatures below 7°C, the coagulation of particles is low [15]; this current study chose to keep the temperature below this threshold. Figure 6 illustrates the influence of temperature on eliminating organic matter in the OOMW by a dose of 1.7 g/l aluminum sulfate. The yield was passed through two phases: the first one went from 10°C to 25°C, which experienced an improvement in the reduction of organic matter production, and then the production decline stage. The increase in pH could explain this decrease as the temperature increases, and the optimal pH previously obtained for the removal of the pollutant material was from 5.8 to 7.1.

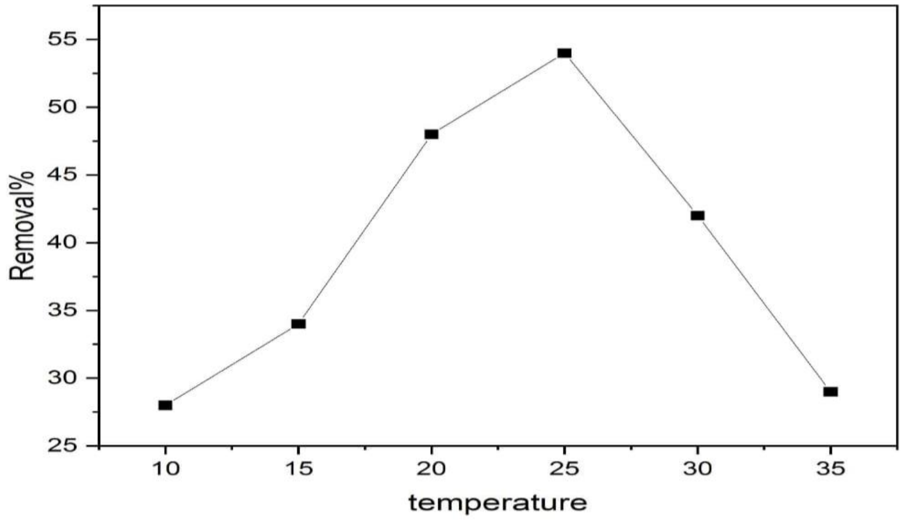

Figure 6: The influence of temperature on the efficiency of removing organic matter by coagulation (1.7g/l of aluminum sulfate).

3.2.2. lime application

In this part, doses of 0 to 30 g/l of lime were added in series of beakers contain the same types of samples. Figure 7 shows that as the lime concentration increases, the pH increases too; after the dose 15 g/l of lime, it stabilizes at 12.

According to figure 8, the optimal dose for removing organic matter and polyphenols is 20 g/L lime, removing 52% of COD, 48% of TSS, and 72% of polyphenols, and the sludge produced was 25g/l. This elimination occurs through the adsorption of precipitated and dissolved substances on the floc in the presence of Ca $(OH)_2$.

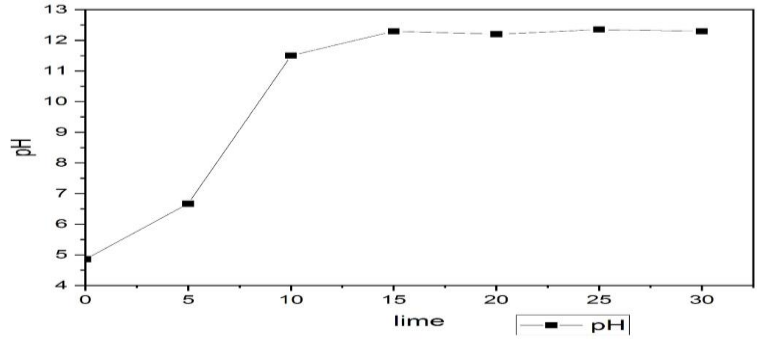

Figure 7: pH evolution based on the dose of lime added.

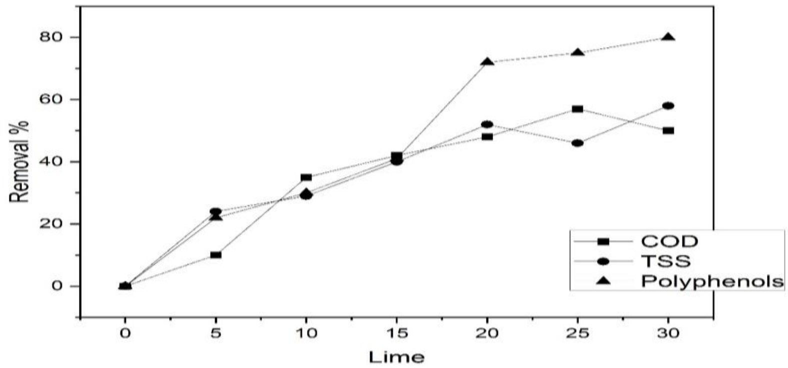

Figure 8: Evolution of the percentage (%) reduction in TSS, COD, polyphenols in terms of lime coagulation.

3.2.3. The combination of aluminum sulfate and 20g/l lime

In this step, the coagulation technique using aluminum sulfate coagulant was applied on olive mills wastewaters treated with a dose of lime equal to 20 g / L. The first parameter examined is the pH; increasing doses of aluminum sulfate did not affect the pH figure 9 illustrates that the pH stabilizes at 11.8 after adding 1 g/l of aluminum sulfate. Regarding the other parameters (figure 10), the 2.5g/l dose of aluminum sulfate was the optimal dose where it reduced almost 45% of the COD, 65% of the TSS, and 63 % of polyphenols, and the sludge produced was 31g/l.

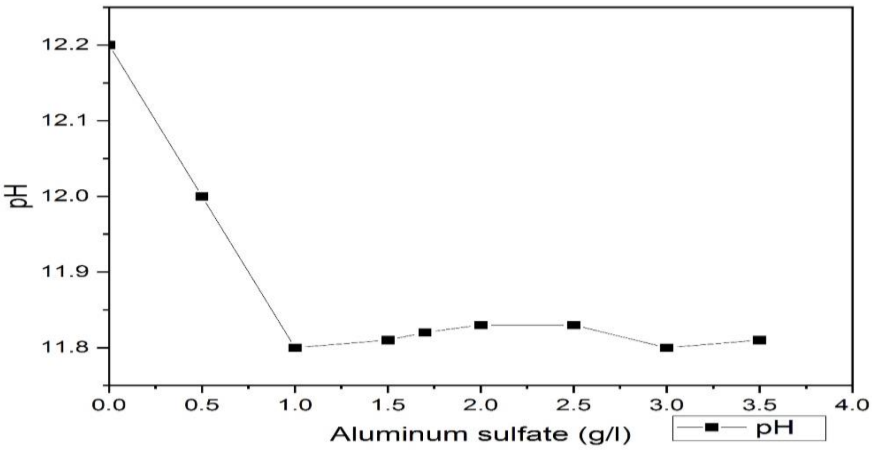

Figure 9: The pH evolution in terms of the variation in concentration of aluminum sulfate and lime (20g/l).

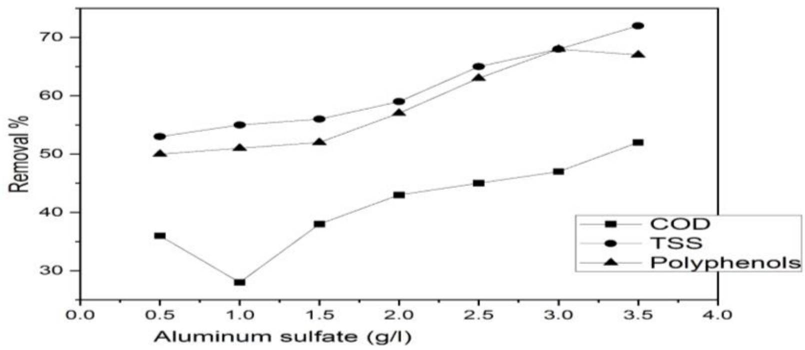

Figure 10: Aluminum sulfate variation with a constant dose of lime (20 g /l).

3.2.4. The combination of lime and 1.7g/L of aluminum sulfate

The reverse operation of the last step was performed. In this step, the dose of aluminum sulfate coagulant was set at 1.7 g/L and increased the dose of lime. Based on figure 11, the increasing doses of lime were accompanied by an increase in pH; around 15 g/l of the lime, it stabilized at 12. Figure 12 shows that the best dose of removal remains 20 g/l with a yield of 72%, 64%, and 62% for TSS, COD, and polyphenols, respectively. Moreover, the pH correction did not influence the removal efficiency of COD and polyphenols, unlike it increases the reduction rate of TSS. The sludge produced was 29 g/l.

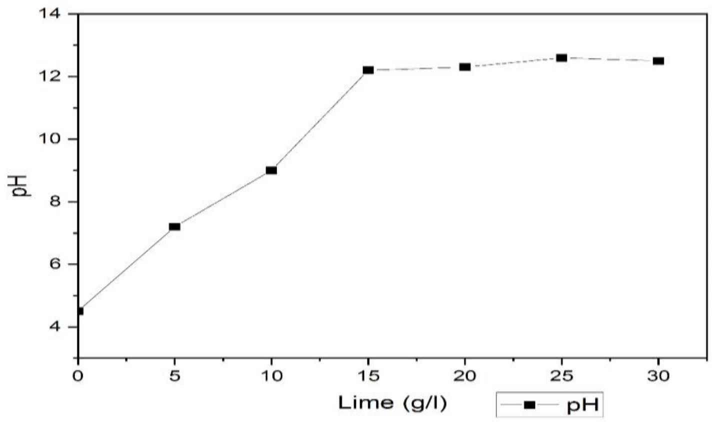

Figure 11 : The pH evolution in terms of the variation in the concentration of lime and aluminum sulfate (1.7 g/l).

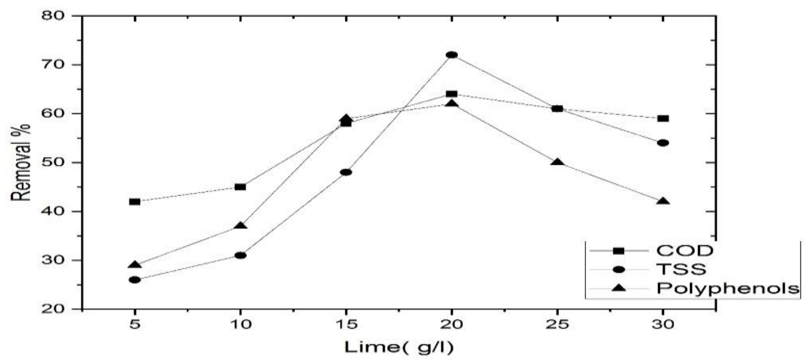

Figure 12: Lime variation with a constant dose of aluminum sulfate (1.7g/l).

The following table combines the results obtained in the various analysis carried out during this study. According to **table 2**, the best treatment performed was combining a dose of 1.7 g/l of aluminum sulfate and 20 g/l of lime.

Table 2: Summary table of the results obtained.

The coagulant	The optimal dose	pH	The percentage removal of COD	The percentage removal of TSS	The percentage removal of polyphenol	Sludge produced
Lime	20 g/l	PH increase from 4.86 to 12.3	52%	48%	72%	25g/l
Aluminum sulfate	1,7 g/l	Decrease in pH from 4.86 to 3.4	58%	23%	24%	21g/l
20g / l of lime + aluminum sulfate	20 g / l of lime + 2.5 g / l of aluminum sulfate	Low pH variation from 12.2 to 11.8	45%	65%	63%	31 g/l
1.7 g / l of aluminum sulfate + lime	20 g / l of lime + 1.7 g / l of aluminum sulfate	PH increase from 4.56 to 12.2	64%	72%	62%	29 g/l

3.3. Germination test

To valorize the OOMW treated and test the efficiency of the treatment process adopted, we decide to use the OOMW treated in irrigation and go through the germination test.

The experiment was conducted in plastic sprouting pots. The experimental device adopted (figure 13) is composed of:

- A control pot: the irrigation is by mineral water.
- Two pots irrigate by the OOMW treated with lime
- Two pots irrigate by the OOMW treated with aluminum sulfate.
- Two pots irrigate by the OOMW with lime and aluminum sulfate.
- Two pots irrigate by the raw OOMW.
- Two pots irrigate with distilled water.

(a) (b)

Figure 13: Seed germination pots, ((a) : first day and (b): after seven days).

Each pot contains 20 g of well-fertilized soil and a cucumber seed; the choice of seed type is based on the number of germination days which varies between 3 and 5 days. Each day, we rinse the pots by 5ml/pot and measure the hypocotyl. Figure 14 illustrates the results obtained; we notice the formation of tigers of different sizes in all pots except pot irrigated by the raw OOMW; this absence is due to the clogging of the soil by the phenols.

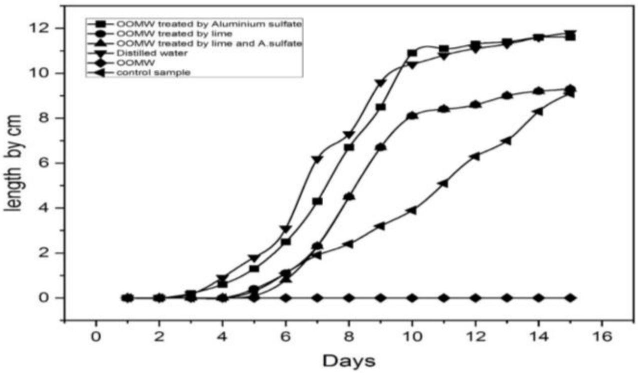

Figure 14: Variation of the size of the hypocotyl according to the days.

4. Conclusion

This study aims to reduce the organic matter and phenols that characterize the olive oil mill wastewaters and valorize the OOMW treated in the irrigation.

The results obtained in the laboratory make the following conclusions:

- The addition of 1.7 g/l of aluminum sulfate eliminates 58 % of COD, 23 % of TSS, and 24 % phenols in the OOWM.
- The treatment of the OOMW by 20 g/l of the lime eliminates 52 % of COD, 48 % of TSS, and 72 % of phenols.
- the combination of 1.7 g/l aluminum sulfate and 20 g/l lime can eliminate 64% of COD, 72% of TSS, and 62% phenols.
- The treatment based on aluminum sulfate alone generates a small amount of sludge (21 g/l) than other tests.
- THE OOMW treated may be used fin the agriculture irrigation according to the germination test.

References

[1] R. Aharonov-Nadborny, L. Tsechansky, M. Ravi, E.R. Graber. Impact of spreading olive mill wastewater on agricultural soils for leaching of metal micronutrients and cations. *Chemosphere*. 179 (2017) 213-221.

[2] A. Suna Erses Yay, H. Volkan Oral, T. Turgut Onay, O. Yenigün. A study on olive oil mill wastewater management in Turkey: A questionnaire and experimental approach. *Resour. Conserv. Recy.* 60 (2012) 64-71.

[3] M.O.J. zam, S.A. Hazaimeh. Olive mill wastewater treatment and valorization by extraction/concentration of hydroxy-tyrosol and other natural phenols. *Process Safety and Environmental Protection*, 148 (2021) 495–523.

[4] S. Dermeche, M. Nadour, C. Larroche, F. Moulti-Mati, P. Michaud. Olive mill wastes: Biochemical characterizations and valorization strategies. *Process Biochem*. 48(2013) 1532-1552.

[5] A. RANALLI Olive oil mill effluent: Proposals for its treatment. References to the Italian regulations on the subject. First part. *Olivae*, 37(1991a)., 30-39.

[6] RANALLI A.,). The effluent of olive oil mills: proposals for its treatment. References to the Italian regulations on the subject. Third part. *Olivae*, 39(1991b), 18-34.

[7] M.Chatoui, S. Lahsaini, A. Aguelmous, S. Souabi, M.A. Bahlaoui, & A. Jada. Removal of oil and grease from vegetable oil refinery wastewaters by coagulation-flocculation process. *Moroccan Journal of Chemistry*, 5(2017), 4–683.
[8] G. Sbai, M. Loukili. (2015). Treatment Of Margins by a Procedure Coupling Flocculation Coagulation and The Electrochemical Path. *European Scientific Journal*, 11(2015) 158-169. c
[9] M. Achak, N. Ouazzani, A. Yaacoubi, L. Mandi. Characterization of vegetable waters from a modern oil mill and tests of their treatment by coagulation-flocculation with lime and aluminum sulfate Modern olive mill effluent characterization and their treatment by coagulation-flocculation use. *Journal of Water Science*, 21(2008)53–67.
[10] E. Eroğlu, L Eroğlu, U. Gündüz, M. Yücel, M. Effect of clay pretreatment on photofermentative hydrogen production from olive mill wastewater. *Bioresource Technology*, 99(2008) 6799–6808.
[11] I.A. Aneyo, F. Doherty, O.A. Adebesin, M.O. Hammed. Biodegradation of Pollutants in Wastewater from Pharmaceutical, Textile and Local Dye Effluent in Lagos, Nigeria. *Journal of Health and Pollution*, 6(2016) 34–42.
[12] DI Giovacchino., A. Mascolo, L. Seguetti. *Sostanze Grasse*, (1988) 71-587.
[13] K. AL-Mallah, M. Azzam, N. Abu-lail. Olive mill effluent (OME) wastewater post-treatment using activated clay. *Separation and Purification Technology*, 20(2000) 225-234.
[14] B. Lekhlif, L. Oudrhiri, F. Zidane, P. Drogui, J.F. Blais. Study of the electrocoagulation of electroplating industry wastewaters charged by nickel (II) and chromium (VI*). Journal of Materials and Environmental Science*, 5(2014)111–120.
[15] A.P. BLACK, D.G. Willems. Electrophoretic studies of coagulation for removal of organic color. *J. Am. Water Works Assoc.*, (1961) 53-589.