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Treatment Of Olive Oil Mill Wastewaters By A Bio Flocculent Extracted From The Cactus Powder Solution (*Opuntia ficus indica*).

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ABSTRACT

The objective of our work is to use a new biodegradable flocculent extracted from the cactus powder solution (Opuntia ficus indica), in order to study the decrease of the organic load and the polyphenols by using coagulation-flocculation process. The coagulation tests were carried out using a jar test set consisting of a series of six beakers. The series contains a suspension witness without addition of coagulant as well as the same suspension subjected to increasing doses of the lime alone and of the lime combined with the cactus powder solution. The coagulation-flocculation tests show that the application of the cactus powder at a dose of 6 ml carried out under slow stirring at 60 rpm for 20 min and at a pH between 6.20 and 7.05 allows to eliminate 80 % of the COD, 45% of the TSS and 44 % of polyphenols, while application of lime at a dose of 20 g / L remove 40%, 71% and 46% of COD, polyphenols and TSS respectively. The combination of 6 ml of cactus powder and 15 g/ L of lime reduces 66% of TSS, 71.3% of COD, and 55% of polyphenols. All the results show that the best coagulation-flocculation treatment is obtained by the Combination of 6 ml of cactus powder and 15 g / L of lime.
Keywords: Olive oil mill wastewater, Opuntia ficus indica, coagulation-floculation, Cactus, polyphenols, bio-floculent, Lime

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INTRODUCTION

The treatment of liquid effluents from olive oil mills is one of the most important environmental problems. To reduce their negative effects, several purification processes are implemented. [1,2], have been used for the valorization and treatment of Olive oil mill wastewaters.

Conventional aerobic or anaerobic biological treatments prove to be very difficult because of the high contents of olive oil mill wastewaters (OMW) in suspended matter and organic substances such as polyphenols, sugars, organic acids and tannins. In addition to research conducted on the treatment of OMW, valorization studies have been carried out such as anaerobic digestion to produce bio methane which is a well-established and widely studied technique [3] and [4].It transforms about 80% of organic substances into biogas (65 to 70% methane).

This process has the advantage over conventional aerobic processes but remains very expensive.

On the other hand, several known physicochemical technologies have already proved their worth in the field of treatment of these effluents among them the coagulation-flocculation technique, which is considered as a pretreatment for industrial effluents [5].

The purpose of the coagulation-flocculation technique is destabilizing of the suspended particles by the injection and rapid dispersion of chemicals in order to favor their agglomeration and allow their settling. The most difficult suspended particles in the water to be treated are those with very small size (colloidal particles causing turbidity) and those that are dissolved (organic materials causing coloring). These colloids usually carry a negative electrical charge which prevents the particles from agglomerating together to form larger particles (flocks) and facilitate their removal by sedimentation and filtration. This method makes it possible to increase the effectiveness of secondary treatments [6].

The coagulation-flocculation process involves several chemical agents, including coagulants and flocculants. These synthetic products have harmful effects on human health and the environment; however the search for alternative products becomes a crucial necessity. In order to replace these chemicals and reduce the cost of treatment of industrial effluents, biological coagulants have been proposed. Previous studies have shown the efficacy of chitosan as coagulant [7] or flocculent [8]. The seed of Moringa oleifera has been known for decades Coagulation properties [9]. Recently, other biological extracted products have been proposed [10].

Our goal is to improve the coagulation - flocculation technique by introducing for the first time in our study a biodegradable natural flocculent extracted from Moroccan cactus from the Fez region (Opuntia Ficus Indica). This bio- flocculent is used for the treatment of olive oil mill wastewaters loaded with organic matter. Moreover, this process becomes profitable and enters the sustainable development in areas where the cactus is grown in large quantities.

MATERIALS AND METHODS

Collection of olive oil mill wastewaters samples

The OMW used were taken from a modern oil mill in a three-phase system in Meknes. During the 2016-2017 olive growing season. No chemical additives are used during the production of olive oil.

The analytical results and their interpretation depend essentially on the method of sampling, conditioning and storage time. To do this, our samples were taken in clean containers rinsed several times with the olive oil mill wastewaters to be analyzed and then closed hermetically without leaving any air bubbles in the bottle. Then transported immediately to the laboratory, one part was used for physicochemical analysis and the other was stored in the dark at 4°C until further use.

Preparation of coagulant and bio- flocculent

Preparation of the flocculent: the bio- flocculent used in our experiments is extracted from the racket of the prickly pear (Opuntia ficus indica). This cactus grows in abundance in Morocco has been collected in the vicinity of the city of Fez.

For the production of the powder we have followed the following steps:

- The racket is carefully cleaned with water. (Photo 1)
- The vegetable part is dried beforehand in an oven at a temperature of 60 ºC for 24 h.
- The grinding of the vegetable part was carried out by means of a grinder and then sieved to obtain particles of very fine powder. (Photo 3)

The product obtained is a green coloring powder. Afterwards, 5 g of cactus powder are introduced into an Erlenmeyer flask in 1 L of distilled water and then homogenized by stirring for 20 minutes.

Photo 1: Clean racket

Photo 2: Racket before drying

Photo 3: Cactus powder

Elemental Composition of Cactus Powder

The elemental composition of the cactus powder is according to Table 1. The initial pH of the cactus powder mixed in distilled water was 6.5 (slightly acid).

Table 1: Elemental composition of the cactus powder

Minerals	Percentage% in cactus powder
Azote	2.3
Carbone	29.4
Ca++	7.27
Mg++	1.66
K+	1.66
Hydrogen	1.7

Jar test:

The coagulation-flocculation tests were carried out in the laboratory at ambient temperature with samples of olive oil mill wastewaters from the 2016/2017 olive-growing campaign using a Jar -test system, Model JLT6 Leachingtest.

First, lime as a coagulant is introduced into a series of six one-liter beakers containing 500 mL of olive oil mill wastewaters diluted at 50% for 3 minutes at a very rapid rate (130 rpm) and the pH was adjusted by NaOH.Thereafter, to trigger the flocculation mechanism and to accelerate the decantation of the suspended matter, we have added the previously prepared cactus powder in solution. The flocculent is added under slow stirring atV= 60 rpm for 20 min. After one hour of settling, the stirrers were turn off and the flocks allowed settling for one hour, then the supernatant was taken in order to be analyzed.

Photo 4: Jar test

Following the same stirring conditions, the same series of beakers containing the same slurry of the olive oil mill wastewaters (500 mL) is subjected to increasing doses of quick lime, doses of 0 to 30 g/L. The flakes are left standing for one hour and the supernatant is siphoned for analysis. The influence of the combination of the two coagulants was also studied on the same suspension of the OMW and under the same agitation conditions by the addition of: increasing doses of the solution of the cactus powder which range from 0 to 10 ml with fixing of the lime concentration to 15 g /L.

The doses of the cactus powder used range from 0 to 10 ml with adjustment of the pH.

Physicochemical parameters of the olive oil mill wastewaters studied:

The hydrogen potential (pH) was measured by a pH meter (pH meter HANNA Instruments); the electrical conductivity (CE) was measured using a conductivity meter (EC214 HANNA Instruments); the suspended matters (TSS) are determined by filtration on membranes with 0.45 µm pore diameter (AFNOR T 90-105).

Chemical oxygen demand (COD) was determined according to the standard method (APHA 1992) by oxidation of the organic matter contained in the sample at 150 °C. By an excess of potassium dichromate in an acid medium and in the presence of sulfate of silver. The excess of potassium dichromate is measured by colorimetry at 620 nm.The concentration of the total polyphenols was determined by spectrophotometry at 720 nm in which the Folin-Ciocalteu reagent was used as a selective reagent. The results are expressed in grams of gallic acid per liter.

RESULTS

Physicochemical characterization of OMW:

Before performing the treatment tests, a characterization of this effluent is necessary. Table 2 shows the various physicochemical parameters of the olive oil mill wastewaters studied.

Table 2: Physicochemical characteristics of the OMW studied

Parameter	OMW raw	OMW diluted 10 times
pH	4.5	4.9
Conductivity (mS/cm)	8.51	9.6
Suspended matters (TSS) (g /L)	5.36	4.86
Chemical oxygen demand (COD)(gO2/L)	70.6	64.31
Polyphenols (g/L)	1.62	1.59

Analysis of these results (Table 2) shows that the effluent is acidic. The high value of the electrical conductivity 8.51 mS/cm; Our results show concordance with those reported by other authors [6], but remains low compared to those found at the effluents of Sidi Kacem which is of the order 23.35 mS/cm [11], this can be explained by the salting done to preserve the olives until trituration. The mean value of the suspended matter is about 5.36 g/L, which is still low compared to that found by the authors of Sidi Kacem, whose value is 9.37 g/L. This difference could explain that our OMW studied are fresh and their values come from a settling basin, which has caused the degradation of the organic matter of the OMW in contact with the light.

The pollutant expressed in terms of chemical oxygen demand (COD) is in the order of 70.6 ± 2.31 g /L. Finally, the phenolic content is about 1.62 ± 0.1 g/L, the phenolic composition of the OMW depends mainly on the diversity, maturity of the olives and climatic conditions, and the processes used to separate the phase aqueous phase of the oily phase [12].

After dilution, the characteristics of the OMW show a small increase in pH and a decrease in conductivity, chemical oxygen demand (COD) and concentration of polyphenols.

Treatment of olive oil mill wastewaters by coagulation-flocculation

Application of cactus powder

Dose Optimization Cactus Powder:

The results of the coagulation tests using the cactus powder are illustrated in figures 1 and 2, the addition of the flocculent is carried out under slow stirring at V= 60 rpm for 20 min. From Figure 1, it can be seen that the gradual addition of the cactus to the diluted OMW caused a small decrease in pH from 4.9 to 4.34.

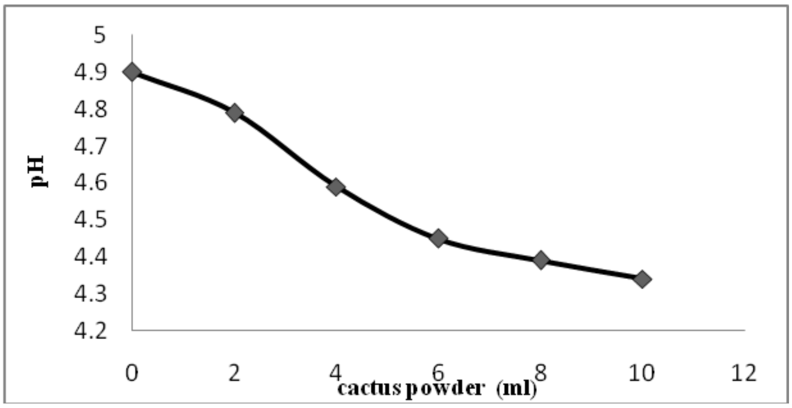


Figure 1: Variation of the pH as a function of the dose of the cactus powder (ml)

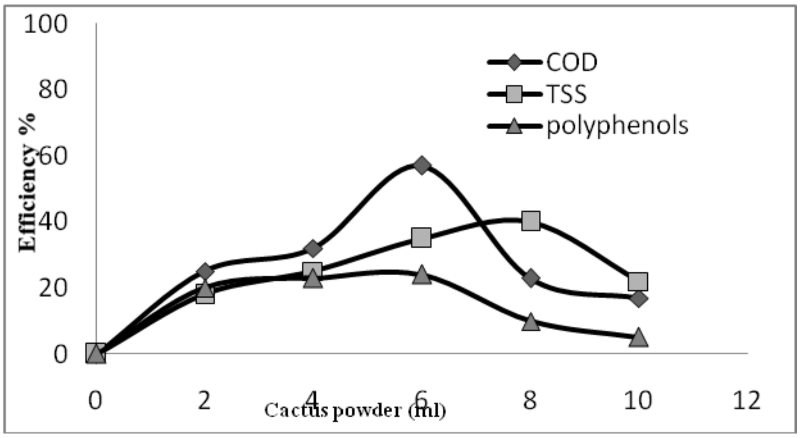


Figure 2: Evolution of the percent reduction (%) of TSS, COD and polyphenols in terms of the dose of cactus powder without pH adjustment.

The dose of 6 ml of cactus powder allows a better removal of COD and polyphenols; it is of the order of (57%) to (24%) respectively. On the other hand, the optimum of the elimination of TSS (40%) is obtained at a dose of 8 ml.

From figures 1 and 2, it is concluded that the obtained pH range does not allow very good eliminations of the polluting charges, in particular for polyphenols.

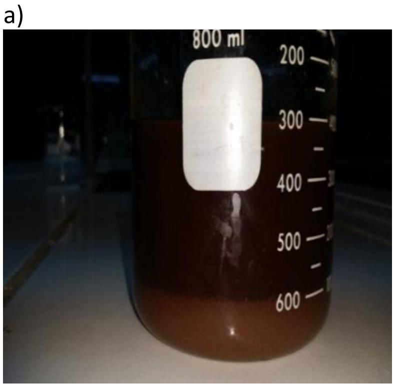
Optimization of the pH with the optimal dose of the cactus powder

In the coagulation-flocculation tests, it is important to adjust the pH since coagulation occurs within a specific pH range for each coagulant and according to the type and characteristic of the effluent to be treated.

The experiments were carried out with different pH values, in order to determine the optimum pH value. The flocculent is added under slow stirring at V= 60 rpm for 20 min. It is noted that the formation of the flocs begins with the addition of the bio flocculent in the various samples (photo 5). The best result was a pH between 6.2 and 7.05.

The optimization of the pH has attracted the attention of [13] who evaluated the purifying power of the solution extracted from Opuntia Ficus Indica racket in the treatment of the tannery effluent the best result obtained at pH 9 and neutral pH where the colloidal particles destabilization occurs.

a)



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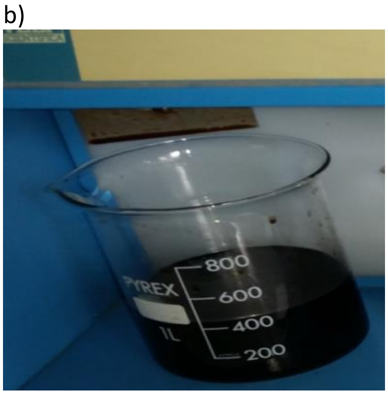

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c) d)

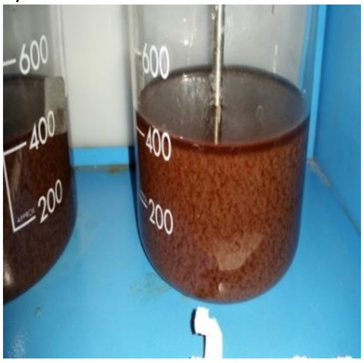

Photo 5: Coagulation steps - flaking: a) crude effluent b) coagulation; c) flocculation d) decanting

The evolution of TSS, COD and polyphenols of OMW as a function of the pH at the optimal concentration of the cactus powder is shown in figure 3.

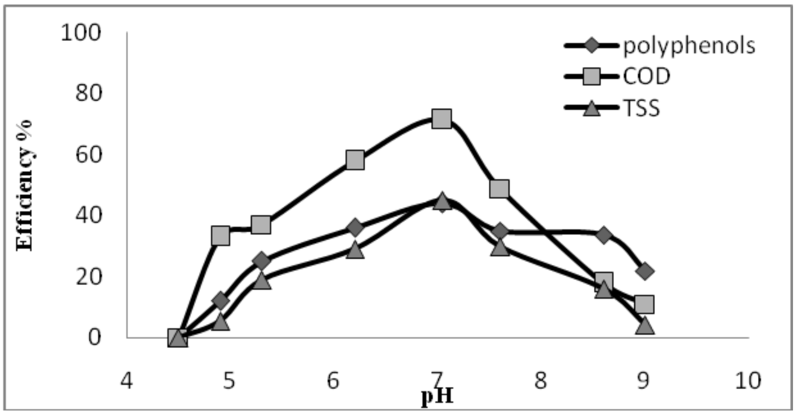

Figure 3: Evolution of the percentage (%) reduction of MES, COD and polyphenols in terms of the coagulation pH by the cactus powder at the optimum dose 6 ml.

The analysis of the results obtained shows that the correction of the pH gives a slight improvement in the elimination of effluent TSS (45%) and COD (71.3%). This could be due to the dominance of colloidal fractions in suspended solids and dissolved fractions of total COD, while the polyphenol abatement rate increases from 24% to 44% for a pH between 6.20-7, 05. This can be attributed to the change in coagulation mechanism.

One of the biggest differences between chemical and natural coagulants-flocculants is in their hydrolytic reaction. The metal salts (alum, ferric chloride) hydrolyze immediately when added to water. The adsorption reactions are very fast and sometimes even of the order of 0.01 seconds. When cationic polymers such as chitosan, cactus powder and Moringa Oleifera when added to water, hydrolytic reactions do not occur. The rate of colloidal adsorption is much slower. The mixing time required is between 2 to 5 seconds [14].

Their mechanism is to neutralize the electric charges of the particles in the water. Then they ensure through their chemical structure, bridging between particles or flocs. They are characterized by the presence of positive charges that can adsorb negatively charged colloids (or flocs). The addition of the cactus in sufficient quantity makes it possible to lower the zeta potential to zero. The mass attraction forces become effective and the polyelectrolyte then acts by mechanical bridging. The longer the organic chain, the better the bridging [15].

Application of lime

The increase in lime concentration leads to an increase in the pH up to 15 g/L of the lime; it is added under slow stirring at V= 60 rpm for 20 min. After the pH stabilizes around 12 as shown in Figure 4.

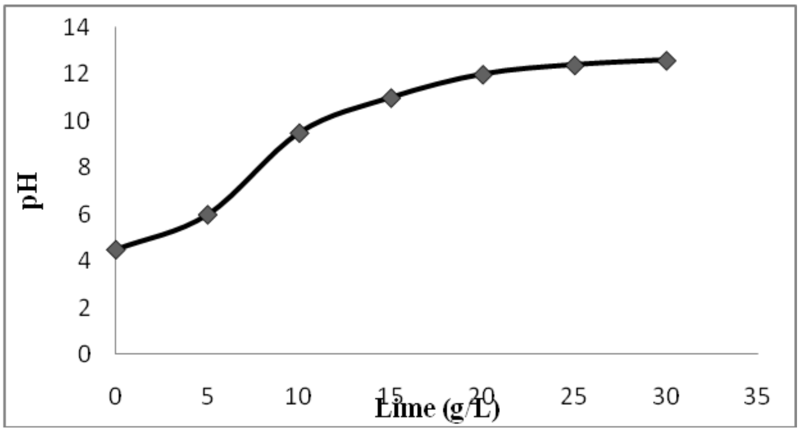

Figure 4: Evolution of the pH according to the dose of the lime added.

Figure 5 shows that for a lime concentration of 20 g/L, the removal of TSS, COD and polyphenols becomes optimal. It is of the order of 46%, 40% and 71% respectively. These results are comparable to those achieved by [6], a COD elimination and polyphenols, of the order of 43% and 75%, respectively.

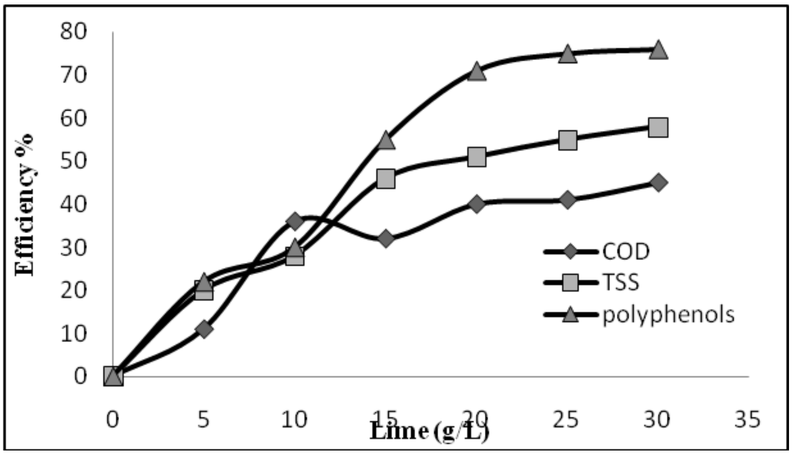

Figure 5: Evolution of percentage (%) reduction of TSS, COD and polyphenols in terms of lime concentration.

This is accomplished by precipitation in the presence of Ca(OH)2 by imprisonment and adsorption of the dissolved material on the flocs. The application of lime at 20 g/L removes 28% of the volatile phenols responsible for the toxicity of OMW and the high concentration of COD, whereas phenols which have two OH functions in the ortho position are eliminated completely, phenols which have an OH function and a carboxylic function are partially removed (vanillic acid, syringic acid). On the other hand, phenols which have either an OH function or a carboxylic function (tyrosol, veratric acid) are not affected by the lime, according to a chromatographic study made by [16].

Application of the combination of lime and cactus powder

Variation of Cactus powder with a constant dose of lime (15 g /L):

The initial pH of cactus powder mixed with distilled water was 6,50 (slightly acid). Figure 6 shows that the addition of the cactus powder results in a small variation in the pH of the mixture. It was found that the increase in cactus doses from 2 to 10 ml had a marginal effect on the final pH of the mixture with values that range from 12,60 to 11,73. The coagulant is added under a very fast speed (130 rpm) for 3 min and the flocculent under slow stirring at V= 60 rpm for 20 min.

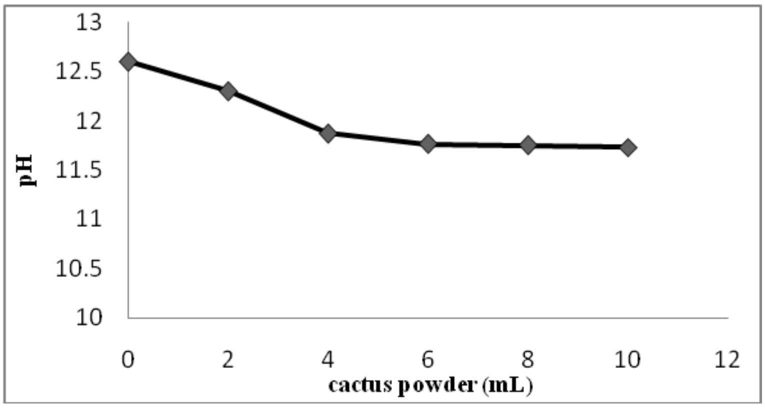

Figure 6: Variation of the pH according to the dose of powder of the added cactus (lime 15 g/L).

The lime dose was set at 15 g/L instead of the optimum dose of 20 g/L to minimize the amount of sludge produced. The elimination of TSS, COD and polyphenols is calculated relative to the diluted marginal contents at initial pH 4.9.

Figure 7 indicates that the optimum coagulation treatment is around 6 ml of the cactus powder. At this concentration, a very large reduction of the order of 49%, 71.3% and 30% of TSS, COD and polyphenols respectively is obtained.

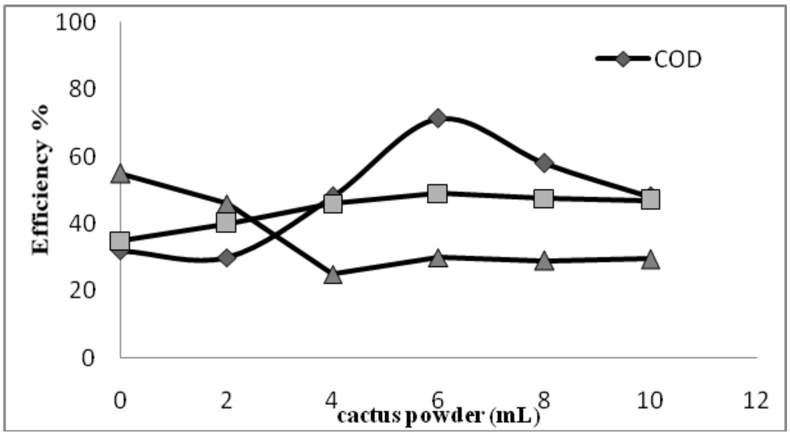

Figure 7: Evolution of percentage (%) reduction of TSS, COD, polyphenols in terms of the of cactus powder dose (lime 15 g/L)

The comparison between coagulation by lime alone (figure 4) and lime-adjusted cactus powder (figure. 6) shows that the correction of the pH by lime does not affect the rate of reduction of COD and polyphenols but improves the reduction of TSS by a percentage of 14%.

Variation of lime combined with a constant dose of cactus powder (6ml)

The increase in the concentration of the lime leads to a continuous increase of the pH up to a dose of 15 g/L of lime, where the pH stabilizes around 12 as shown in figure. 8. The coagulant is added for 3 minutes with a very fast speed (130 rpm) and the flocculent under a slow stirring V= 60 rpm for 20 min.

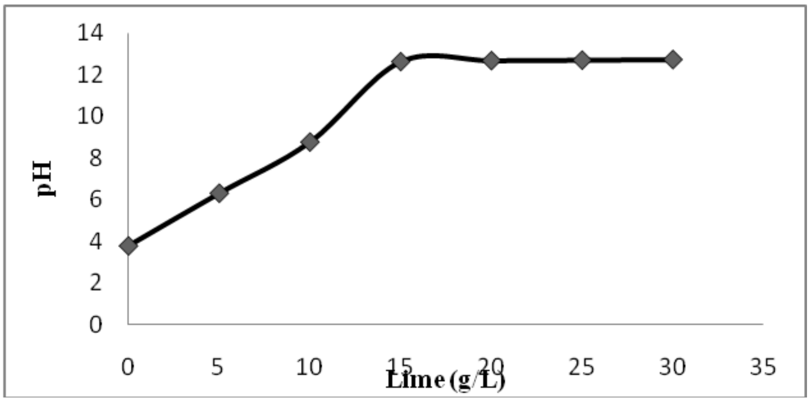

Figure 8: Evolution of pH in terms of the added lime dose (Cactus powder dose = 6ml).

The results of this combination show a significant change in pH from a dose of 10 g/L of lime (Figure 8) and a very large elimination of TSS (66,5%), thus reducing COD and polyphenols of the order of 80% and 55% respectively at a dose of 15 g/L of the lime (Figure 9).

From the experimental results, it is noted that the comparison between coagulation by the cactus powder (Figure 3) alone and the lime with the cactus powder (Figure 8) shows that the correction of the pH by the lime does not affect the reduction rate of COD and polyphenols but improved the reduction of TSS by a percentage of 43% .As the comparison between coagulation by lime alone at a dose of 20 g /L (Figure 5) and lime with cactus powder (Figure 8) shows that the pH correction by lime does not affect the rate of reduction of COD and polyphenols but improves the reduction of TSS by a percentage of 20.5%.

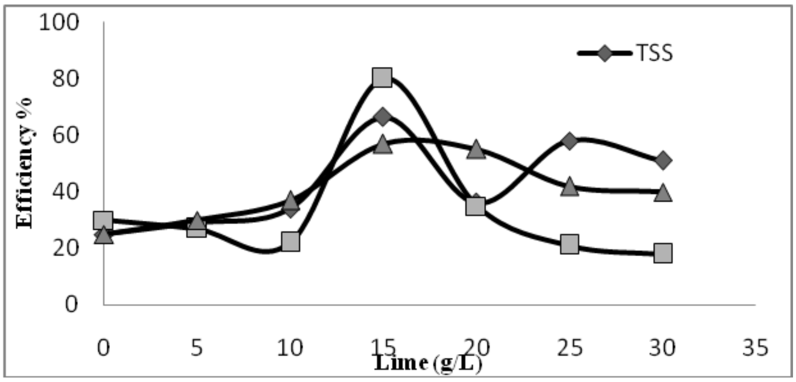

Figure 9: Evolution of percentage (%) reduction of TSS, COD and Polyphenols according to the concentration of lime added (cactus powder = 6ml)

From the results obtained, it is illustrated that the correction of the pH by the lime for the two combinations does not affect the reduction of the COD and the polyphenols by coagulation-flocculation. The concentration of COD remains constant in all cases of treatment. Considering that the interest of coagulation is mainly concerned with the separation of fine or extra fine particles and colloids from the interstitial phase by precipitation [17].

The comparison between the two combinations for TSS reduction suggests that the best combination is obtained for a dose of 6 ml of cactus powder and 15 g/L of lime. As in the case of the reduction of polyphenols.

In summary, the results obtained show that treatment with the combination of 6 ml of cactus powder with 15 g/L of lime is the best coagulation-flocculation treatment which gives better removal of the colloidal particles causing turbidity, a good reduction of organic matter causing staining and toxic substances responsible for the inhibitory effect of olive oil mill wastewaters.

Production of sludge

The coagulation-flocculation treatment, using cactus powder alone, lime alone and lime combination and cactus powder, generate a solid precipitate called "sludge".

The sludge produced is determined by measuring the weight of the solid precipitate remaining in a beaker after coagulation and by three repetitions. The beaker containing the precipitate is dried in an oven at 100 ° C. for 4 h [18] and weighed. The quantity of sludge produced is calculated according to the following formula:

$$\text{Produced Sludge (g/L)} = \frac{P_1 - P_0}{V}$$

P1: weight of the beaker with solid precipitate (g)
P0: weight of empty beaker (g)
V: volume of the test portion (L).

The coagulation-flocculation of the olive oil mill wastewaters allows eliminating a good part of the polluting charges of the OMW, but it generates a physicochemical mud that will have to be dried and eliminated thereafter. The amount of sludge produced by the various coagulants is shown in Table 3.

Table 3: Sludge produced (g /L) by the different coagulants and percentage of abatement of each parameter

Cactus Powder (ml)	Lime (g/L)	pH	Rate	COD (%)	Polyphenols (%)	TSS (%)	Produced sludge (g/L)
6	0	6,20-7,05	60 rpm for 20 min	71,3 %	44%	45 %	26
6	15	12.60	60 rpm for 20 min	80 %	55 %	66.5 %	40
10	15	11,73	60 rpm for 20 min	33 %	30 %	49 %	30

The results show that the application of cactus powder alone generates only a small quantity of the sludge and allows a rate of reduction of the TSS (45%) with optimization of the pH.

According to the results, the physicochemical treatment system applied to oil mill effluents shows that the best removal rate of TSS 66.5%, COD 80% and polyphenols 55% is given by a dose of 6 ml of cactus powder and 15 g /L of lime. These results in terms of COD reduction are consistent with those of [19] who obtained 75% COD removal from tannery effluents using the cactus as a powder as coagulant.

The plant we evaluated (Opuntia ficus indica) was used by [13] as a juice flocculent to reduce COD of textile effluents, the result was a reduction of 88.6%.In the work of [20] who used a treatment based on coagulation with lime, followed by flocculation with Cactus powder obtained 99% reduction in TSS wastewater loaded with zinc ions and suspended solids.[21] Sought to determine the removal of COD from textile effluents by using the mucilage cactus combined with aluminum sulfate as a coagulant and found an elimination rate of 88.76%.

In some treatments, Opuntia ficus indica has been evaluated as coagulant in the elimination of effluent turbidity [22, 23], as well as in the reduction of the bacterium [24].The choice of l the combination of 6 ml of cactus powder with a dose of 15 g/L of lime as the best coagulants for the treatment of olive oil mill wastewaters present almost the same quantities of sludge. The quantity of sludge produced in the combination of lime and cactus powder is 40 g/L.

The sludge produced contains, in addition to an amount of chemical reagents used in the form of a precipitate, a particulate and colloidal fraction which can be removed from the OMW, in particular organic matter and polyphenols (toxic substances). In the case of cactus powder the recovered sludge will be biodegradable and free from chemical polymers. As regards discharge, it may encounter problems of dryness which may be imposed on products received in discharge.

CONCLUSION

This work presents the possibility of introducing a new biodegradable reagent in the process of physicochemical treatment by coagulation flocculation process. We have tried by this work to replace some inorganic coagulants widely applied in the field of water treatment and having disadvantages on the environment and in particular human health.

The benefits of cactus powder treatment (Opuntia ficus indica) will be numerous. In addition, this process will be cost-effective and will introduce sustainable development in areas where cactus is grown on a large scale. Other advantages include changes in the physicochemical properties of the treated sample and recovered sludge which is biodegradable and free of iron or aluminum. The cactus powder will therefore have a strong possibility of being an alternative to chemical coagulants and flocculants. The sludge produced in the process can be used to produce biogas, using methanisation process.

In addition, compliance with Law 36-15 on the rational and sustainable use and better quantitative and qualitative use of water to ensure the protection and safety of people for the good of our environment.

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