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## Approach To The Study Of Vegetable Oils As Collectors: Study Of Collection Power Between Oleic Acid, Linseed Oil And Olive Oil.

BOUKRAA Aissam<sup>1\*</sup>, and BOUHENGUELMustapha<sup>2</sup>.

<sup>1</sup>Laboratory of applied Chemistry and technology of materials (LACTM), University of LarbiBenH'hidi, Oum El-Bouagui – Algeria.

<sup>2</sup>Laboratory of applied Chemistry and technology of materials (LACTM), University of LarbiBenH'hidi, Oum El-Bouagui – Algeria.

### ABSTRACT

Industrial development is always accompanied by the degradation of the environment; this is the case for the flotation of minerals incoming in the composition of phosphate ores. This method uses specific reagents called collector for the purpose of hydrophobizing the inorganic surface to float. To minimize the harmful effects of synthesized collectors, one resorts to the use of two vegetable oils known for their nutritional and therapeutic interest and even for their high saturated and unsaturated fatty acids known as anionic collectors and float well carbonates mineral sphosphate. Our study, based primarily on the power of collection, is a comparison between our vegetable oils, namely linseed oil and olive oil, and a pure fatty acid which is oleic acid in terms of collection power. Our research aims to characterize the materials by using infra red spectroscopy only because it can easily identify the characteristic peaks that we want to detect. The second goal is to study the influence of all parameters on the adsorption of anionic collectors. The originality of this work is to study vegetable oils as collectors by comparing the results with those made with pure acids incoming in these oils. The results show on one hand that the adsorption is promoted in an acidic medium and ends its maximum after 2 minutes at a temperature of 60°C and a concentration not exceeding 0.1 g/l. On the other hand, the approach made by the use of vegetable oils instead of acids incoming in the formation of these oils showed two important things: the unsaturation is a very important parameter in the collecting efficiency; the collector contains more unsaturated bonds is very powerful. The siccativity, too, plays a big role in adsorption. Then, the final result is that the olive oil shows high adsorption efficiency because it contains a large quantity of oleic acid and some small percentages of linoleic acid (2 unsaturations) and linolenic acid (3 unsaturations). Olive oil has another feature that prevents oxidation of its double bonds, a property that we can not find in linseed oil. This property is guaranteed by the phenolic compounds protecting the oxidation of double bond.

**Keywords:** Adsorption, Collectors, Vegetable oils, Phosphate ores, Carbonates

*\*Corresponding author*

## INTRODUCTION

It has long been recognized that unsaturated fatty acids are generally the best flotation collectors for their saturated counterparts. From the study of palmitic acid collecting properties, oleic, linoleic and linolenic on ilmenite, rutile, hematite and magnetite, Hukki and Vartiainen concluded that power accumulator of fatty acids increased in function of unsaturated hydrocarbon chain [1].

Sun, Snow, and Purcel studied the properties collection of unsaturated fatty acids as collectors for phosphate ores and concluded that the power increases with increasing collect unsaturated hydrocarbon chain of up to two double bonds [2].

They worked on the collection of fatty acids properties considered collectors of phosphate ores and concluded that the collecting power increases with the increase in unsaturated carbon chain.

Sun work studying the collection power of the C18 fatty acids of 37 minerals showed that the collecting power of these acids increases in the order:

Stearic → oleic → linoleic → linolenic.

Hukki and Vartiainen, showed that linolenic acid was higher powerful collector than the oleic acid and linoleic acid as collector magnetite. They also found that the ricinoleic acid was a more effective collector for the other mineral.

Seeking to explain the superiority of unsaturated acids, the authors estimated the effects of the critical micelle concentration, surface activity, and hydrolysis. It was concluded that surface activity decreases and increases critical micelle concentration in the case of unsaturated acids increases. In view of the superiority of the unsaturated acids as collectors for many minerals, attention has been directed to the use of fatty acid materials such as crude oils and oils of high linseed which contain significant amounts of these acids. Our study aims to determine the effect of unsaturation of the hydrocarbon chain of the fatty acids on the collection of properties in the calcite, and provides comparable test work with natural products rich in unsaturated acids [3,5].

## METHODOLOGY

The qualitative study of adsorption of collectors on mineral surfaces is a key factor for the development of enrichment technology and concentration of ores by flotation [6, 9].

The surfaces of mineral oxides and silicates can adsorb charged collector having charge of opposite sign on the pole portion. Hydrophobicity of the flotation surface is due to the great length of hydrocarbon chain of the collectors used and the concentration of these collectors must remain low enough to avoid the formation of micelles of surface.

In our study, we carried out an experiment at a concentration of 500 mg/l in acidic or weakly acidic medium [10, 11]. The acidic medium of good flotation of calcite is created by the phosphoric acid which plays the role of a regulator and a depressant simultaneously. Calcite treated under the conditions described above with or under hot water washing under go filtration and drying at room temperature followed by infrared spectroscopic examination [12].

The quantitative study is based on the formation of a complex extractable with an organic solvent and is based on the spectrophotometric assay of a complex surfactant-methylene blue. We have, therefore, to introduce into a separatory funnel, 5 ml of 0.1 M NaOH, 5 ml of methylene blue (0.025%) by adding 10 ml of chloroform. Shaken for 2 minutes and allowed to stand for extracting the chloroform solution. This extraction 10 ml portions of chloroform was repeated twice more until the formation of a colorless chloroform portion. In a second separating funnel, we introduce the test while adding 50 ml of distilled water, salt to extract the fatty acid, 40 ml of 25% H<sub>2</sub>SO<sub>4</sub> and finally 10 ml of chloroform. The contents were stirred and allowed to stand. Were separated after the lower layer of chloroform in a 100 ml beaker by adding Na<sub>2</sub>SO<sub>4</sub> to wash the chloroform solution. We must make two additional chloroform extractions and recovered in the 100 ml

beaker. The amount recovered is treated with chloroform phase of the first bulb. Shaken well for 5 minutes then recovered chloroform phase into a 25 ml volumetric flask containing 2 ml of acetone. After the stirring, proceeds to read in a spectrophotometer at the wavelength 650 nm [12].

## Materials

### Identification of oleic acid

Carboxylic acid dimers show a broad and intense absorption due to the elongation of the OH bond between  $2500$  and  $3300\text{cm}^{-1}$ . The band is centered on  $3000\text{cm}^{-1}$ . Weaker CH bands are often superimposed on the broad OH band link between  $2855$  and  $2950\text{cm}^{-1}$ . Group C=O in carboxylic acid dimer absorbs between  $1706$  and  $1720\text{cm}^{-1}$ , which is our case, where the spectrum shows an intense peak at  $1700\text{cm}^{-1}$ . The carboxylate ion gives rise to two bands: a strong band of asymmetric stretching  $1650$  and  $1550\text{cm}^{-1}$  and a weaker symmetrical band around  $1400\text{cm}^{-1}$  (Figure 1).

### Characterization of olive oil by IR spectroscopy

Observable bands in the region  $3000$ - $2800\text{cm}^{-1}$  are attributable to stretching vibrations of the C-H bond of the  $\text{CH}_2$  and  $\text{CH}_3$  groups. Two intense bands at  $2924$  and  $2853\text{cm}^{-1}$  attributable respectively to the vibrations of symmetric and asymmetric elongation of  $\text{CH}_2$ . Another medium intensity band observable in  $2953\text{cm}^{-1}$  is due to the vibration of asymmetric elongation of  $\text{CH}_3$ . In the low frequency region, only the  $\text{CH}_2$  deformation vibration is observable. The bands  $1458$  and  $1232\text{cm}^{-1}$  are attributable to shearing deformation vibrations out of the plane. A low intensity band is observable to  $3008\text{cm}^{-1}$  and the band situated around  $724\text{cm}^{-1}$  are due to vibration elongation "cis" group=C-H.

The most intense band of the spectrum is observed around  $1750\text{cm}^{-1}$ . This band is due to the stretching vibration of C = O group, characteristic of esters. The intensity of this peak is inversely proportional to the number of carbon atoms (the carbon chain length).

The low frequency region often contains bands of low intensity is  $1150\text{cm}^{-1}$ ; this band is due to the stretching vibration of C-O group of esters (Figure 2).

### Linseed oil characterization by IR spectroscopy

Our FTIR spectrum shows a medium intensity peak at  $720\text{cm}^{-1}$  corresponding to the band of the double bonds in the *cis* configuration (Z). In contrast, the spectrum shows no peak characteristic of the CH of the double bonds in the *trans* configuration (E) to  $970\text{cm}^{-1}$ . Therefore, all double bonds of linseed oil are in the "cis configuration". Also, the spectrum clearly stands a very strong band at  $1750\text{cm}^{-1}$  indicating the existence of the link C=O (Figure 3).

### Identification of pure calcite by IR spectroscopy

The calcite used in the investigation was marble from Djebel el Onk, Tebessa, Algeria. Hexagonal and rhombohedra carbonates give an intensive broad absorption in the region  $1400$ - $1560\text{cm}^{-1}$ . The doublet  $871\text{cm}^{-1}$  and  $848\text{cm}^{-1}$  is a characteristic of aragonite which has the chemical composition and crystal structure similar to those of calcite (Figure 4).

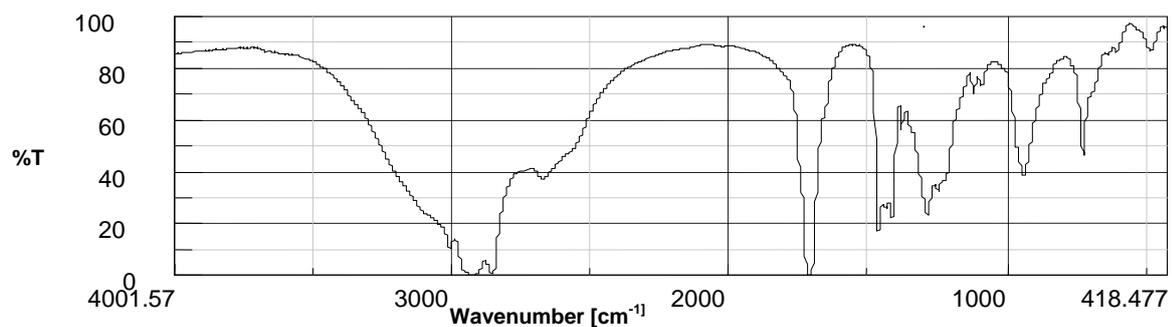


Figure1: FTIR spectrum of oleic acid

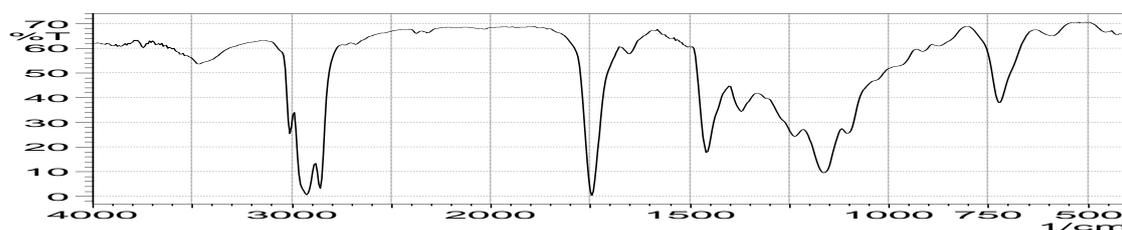


Figure 2: FTIR spectrum of olive oil.

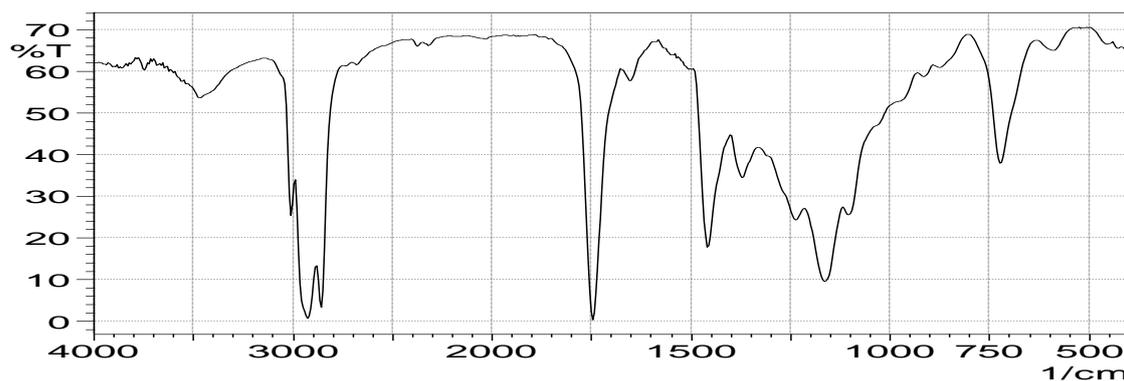


Figure 3: FTIR spectrum of linseed oil.

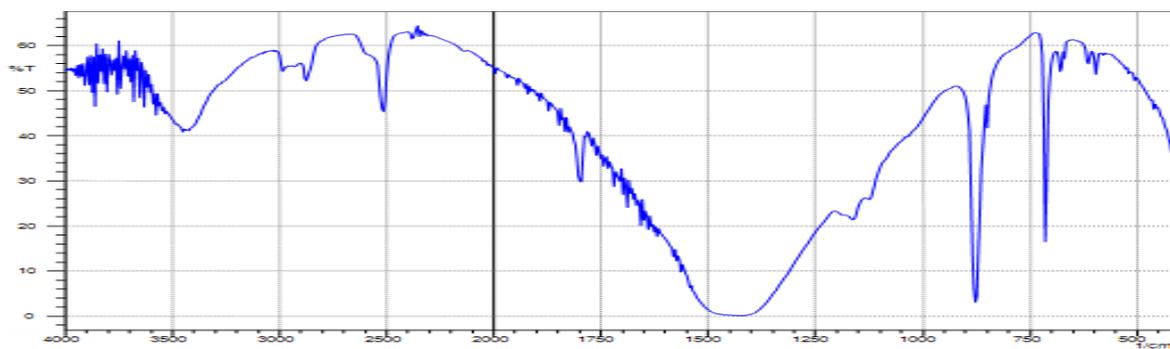


Figure 4: FTIR spectrum of pure calcite.

## DISCUSSION OF RESULTS

### Qualitative Study of adsorption of oleic acid on the calcite by IR spectroscopy

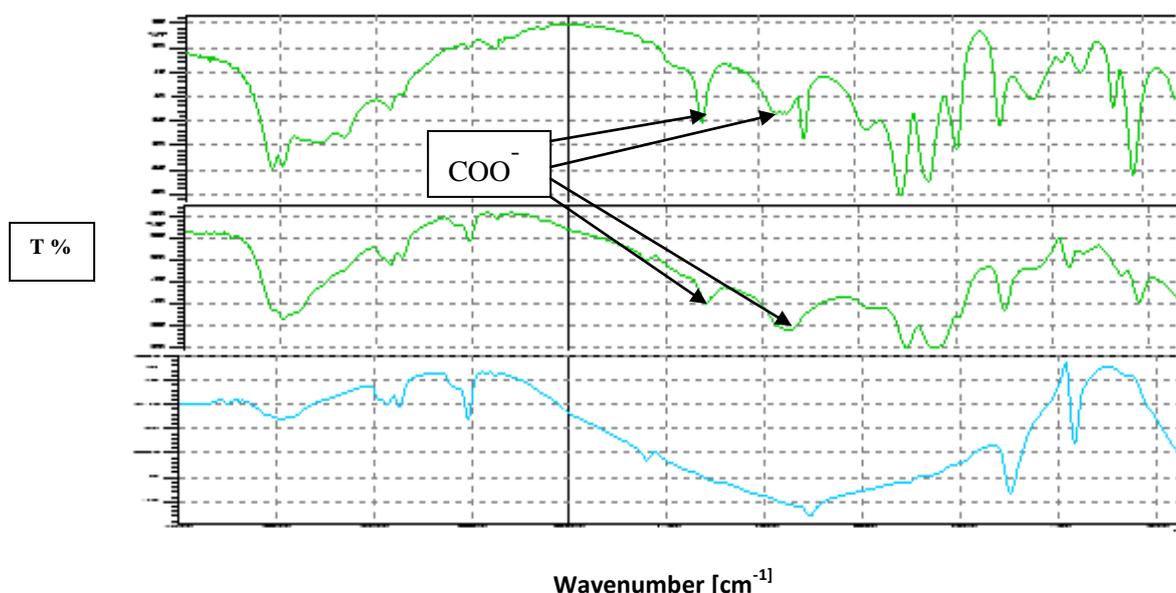
The peaks  $474\text{ cm}^{-1}$  and  $1099\text{ cm}^{-1}$  may be attributed to the anion  $\text{PO}_4^{3-}$ . The peaks pointing to  $2925\text{ cm}^{-1}$ ,  $2854\text{ cm}^{-1}$  and the peak lying around  $2500\text{ cm}^{-1}$  can be attributed to CH oleic acid. The intense peak at  $1650\text{ cm}^{-1}$  and the two peaks at about  $1420\text{ cm}^{-1}$  and  $1480\text{ cm}^{-1}$  are characteristic of the anion  $\text{COO}^-$ . After washing with hot water for 2 minutes, we see that the peaks located at  $1650\text{ cm}^{-1}$ ,  $1420\text{ cm}^{-1}$  and  $1480\text{ cm}^{-1}$  characterizing the ionic form, begin to disappear while losing their intensities in a progressive manner. After a second washing with hot water, no trace of oleic acid is observed. (Figure6)

### Adsorption of linseed oil on calcite

Diagnosis by IR spectroscopy shows the peaks  $474\text{ cm}^{-1}$  and  $1099\text{ cm}^{-1}$  attributed to the anion  $\text{PO}_4^{3-}$ . The peaks pointing to  $2925\text{ cm}^{-1}$ ,  $2854\text{ cm}^{-1}$  and  $2500\text{ cm}^{-1}$  can be attributed to CH oleic acid. The intense peak at  $1650\text{ cm}^{-1}$  and the two peaks at about  $1420\text{ cm}^{-1}$  and  $1480\text{ cm}^{-1}$  characteristic of the  $\text{COO}^-$  anion. After washing with hot water for 2 minutes, we see that the peaks located at  $1650\text{ cm}^{-1}$ ,  $1420\text{ cm}^{-1}$  and  $1480\text{ cm}^{-1}$  characterizing the ionic form, begin to disappear while losing their intensities in a progressive manner. After a second washing with hot water, no trace of oleic acid is observed. So we can conclude that only the reactivity of the acid function comes into play: no trace of the double bond. (Figure7)

### Adsorption of olive oil on calcite

Diagnosis by IR spectroscopy shows the peaks  $474\text{ cm}^{-1}$  and  $1099\text{ cm}^{-1}$  attributed to the anion  $\text{PO}_4^{3-}$ . The peaks pointing to  $2925\text{ cm}^{-1}$ ,  $2854\text{ cm}^{-1}$  and the peak lying around  $2500\text{ cm}^{-1}$  can be attributed to CH oleic acid. The intensive peak at  $1650\text{ cm}^{-1}$  and two peaks at around  $1420\text{ cm}^{-1}$  and  $1480\text{ cm}^{-1}$  characteristic of the  $\text{COO}^-$  anion. The spectrum shows a moderately intense peak around  $720\text{ cm}^{-1}$  which attributed to the double C = C bond forming fatty acids in olive oil. After two washes with hot water, we see that the peaks located at  $1650\text{ cm}^{-1}$ ,  $1420\text{ cm}^{-1}$  and  $1480\text{ cm}^{-1}$  characterizing the ionic form and the peak of the C = C double bond remain unchanged. After the third wash with hot water, the peaks located above begin to disappear while losing their intensities in a progressive manner. We can easily notice that the peak characterizing the rhombohedra carbonates began to appear which supports our hypothesis about the nature of pic  $720\text{ cm}^{-1}$ . Therefore, it can be concluded that the reactivity of the acid as well as the function of the double bond C = C are involved. (Fig 8)



**Figure:6/ A:** FTIR spectrum of calcite treated by oleic acid (C= 500mg/l, pH= 4.8, T= (60°C, 80°C)). **B:** FTIR spectrum of calcite treated by oleic acid after first washing by hot water (pH= 4.8, T= (60°C,

80°C)). C: FTIR spectrum of calcite treated by oleic acid after second washing by hot water. (pH= 4.8, T= (60°C, 80°C)).

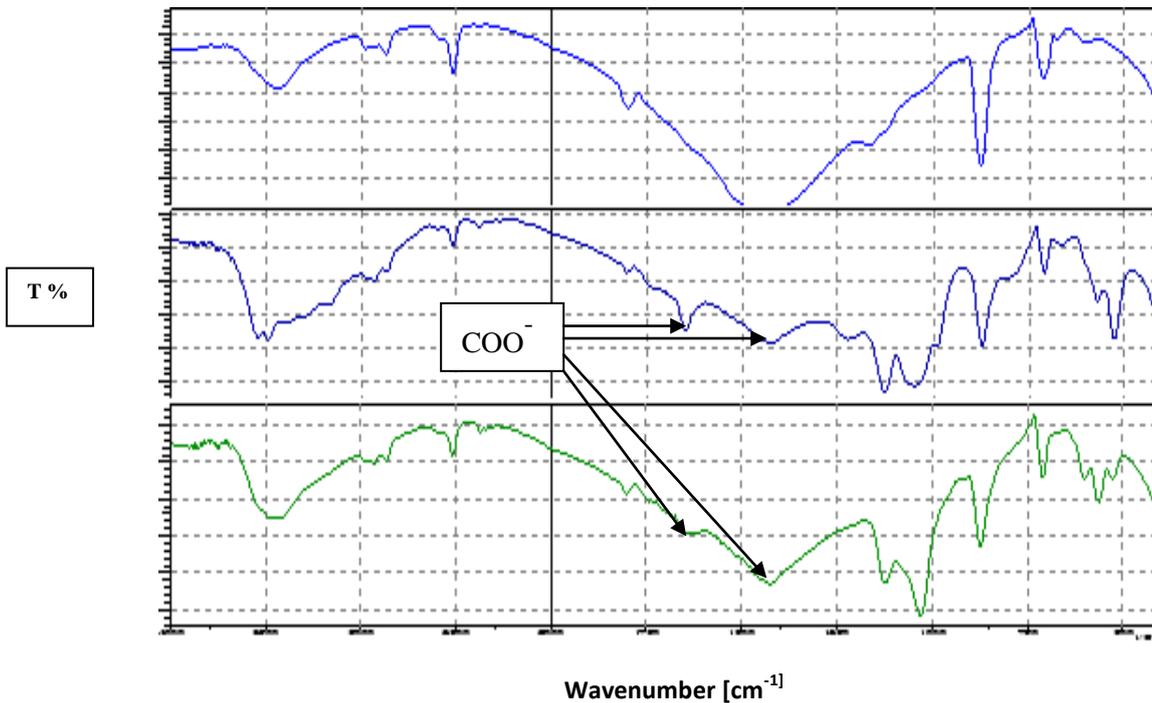


Figure:7/ A: FTIR spectrum of pure calcite. B: FTIR spectrum of calcite treated by linseed oil (C= 500mg/l, pH= 4.8, T= (60°C, 80°C)). C: FTIR spectrum of calcite treated by linseed oil after first washing by hot water. (pH= 4.8, T= (60°C, 80°C)).

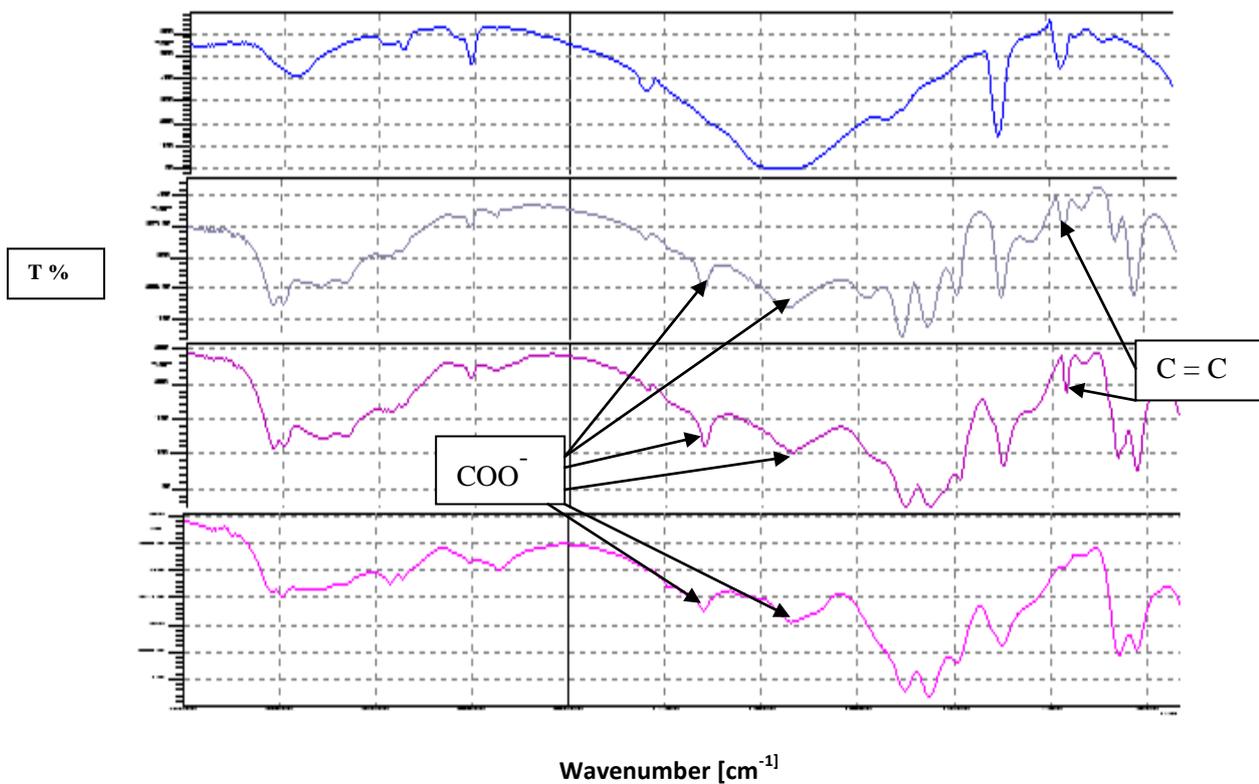


Fig.8 : A/ FTIR spectrum of pure calcite. B/FTIR spectrum of calcite treated by olive oil (C= 500mg/l, pH= 4.8, T=60°C, 80°C). C/FTIR spectrum of calcite treated by olive oil after first washing by hot water (P<sup>H</sup>= 4.8, t =2 min,

T= 60°C, 80°C). D/ FTIR spectrum of calcite treated by olive oil after third washing by hot water ( $p^H= 4.8$ , T=60°C, 80°C, t =2 min).

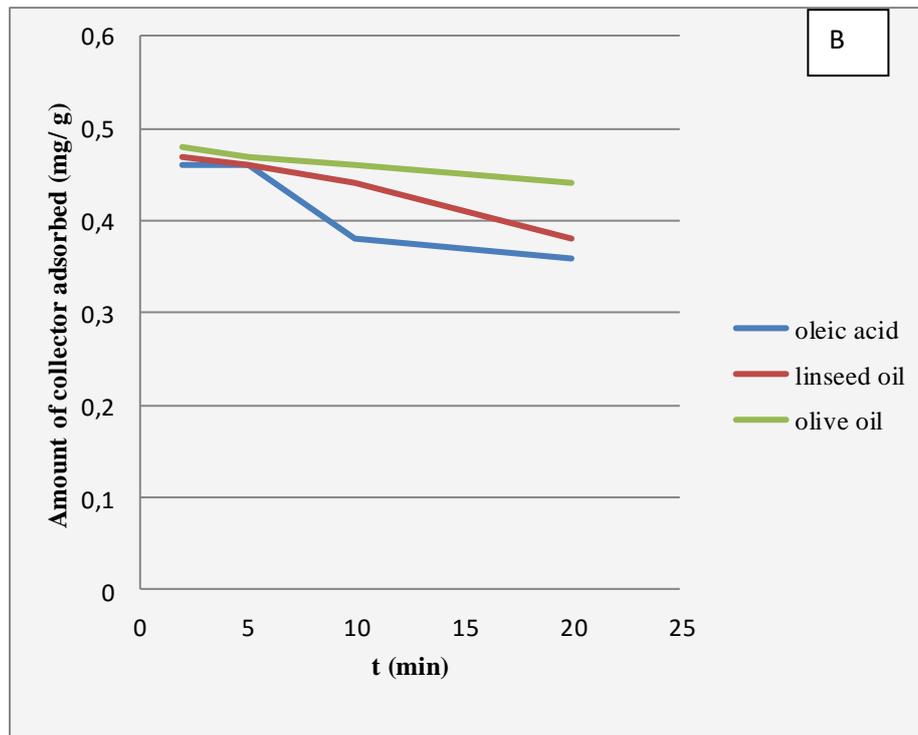
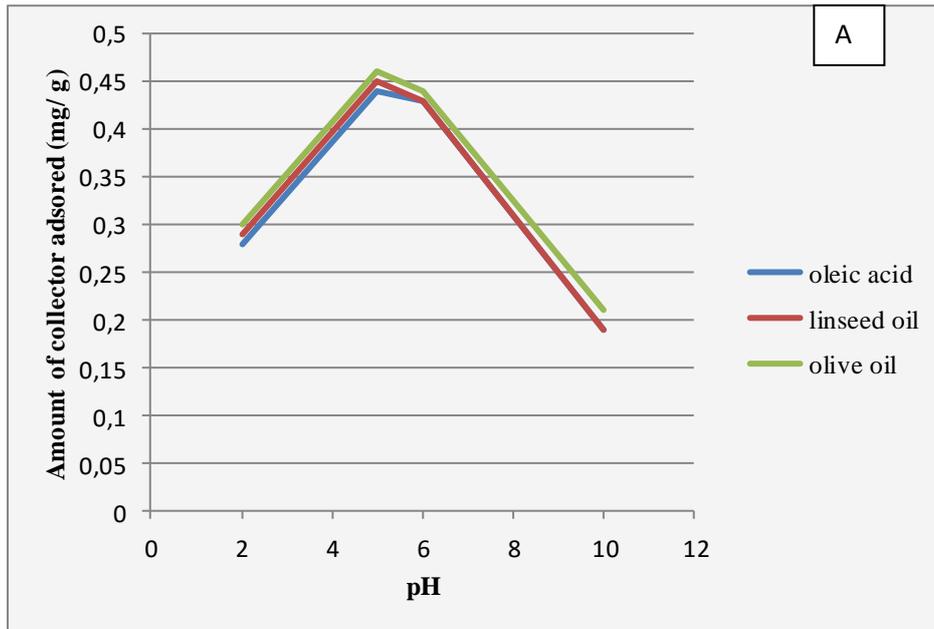
### Quantitative Study of adsorption of anionic collectors on surface of calcite

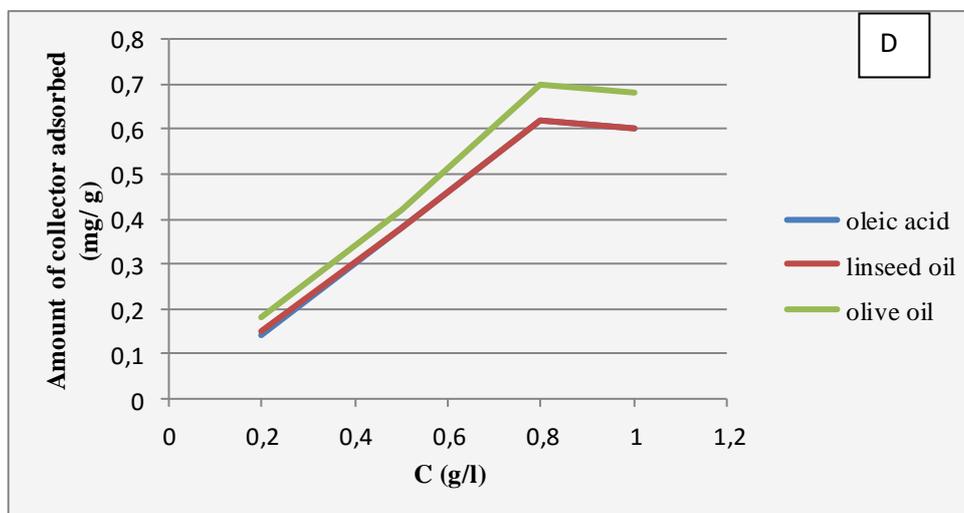
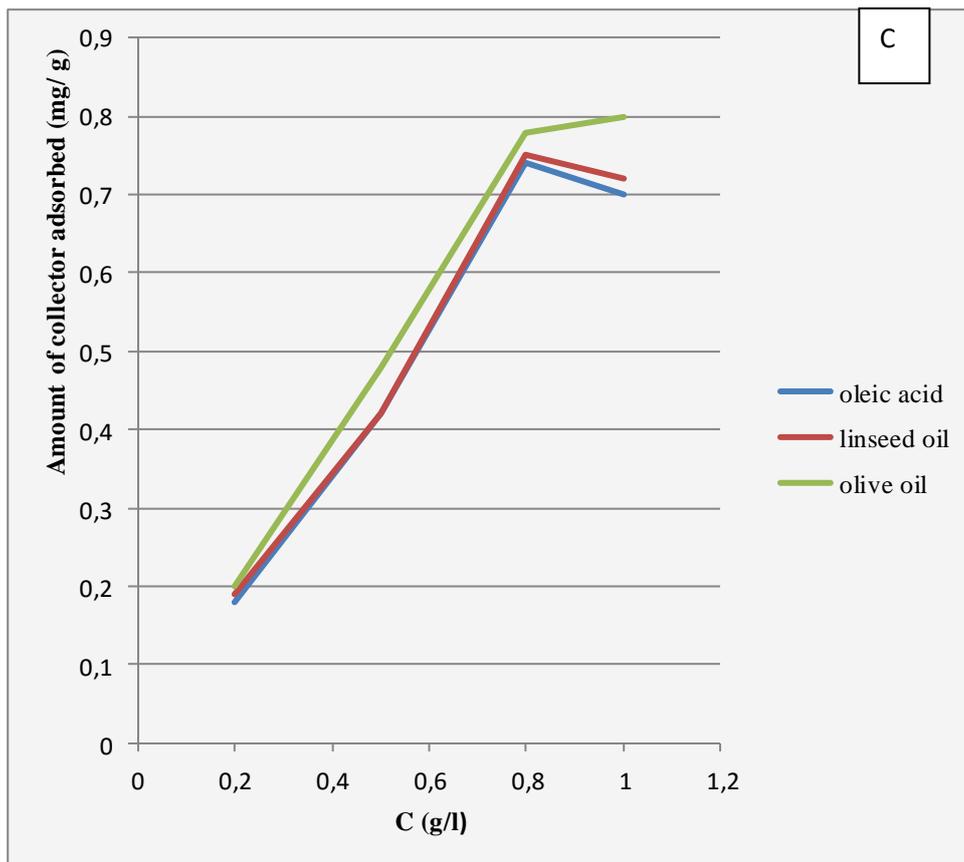
Adsorption of Na-oleate, Na-linoleate and Na-linolineate on calcite is pH dependent. The data presented in Fig12A illustrate the effect of pH at different levels. The formation of Ca-oleate, Ca-linoleate and Ca-linolineate first increases with increasing the concentration of Na-oleate, Na-linoleate and Na-linolineate. At low pH, Adsorption of Na-oleate on calcite increases and becomes maximum. Beyond this maximum, adsorption decreases rapidly as the concentration of Na-oleate, Na-linoleate and Na-linolineate increases. This result indicates that the formation of Ca-oleate, Ca-linoleate and Ca-linolineate decreases at high pH values with respect to low pH values obtained in this study.

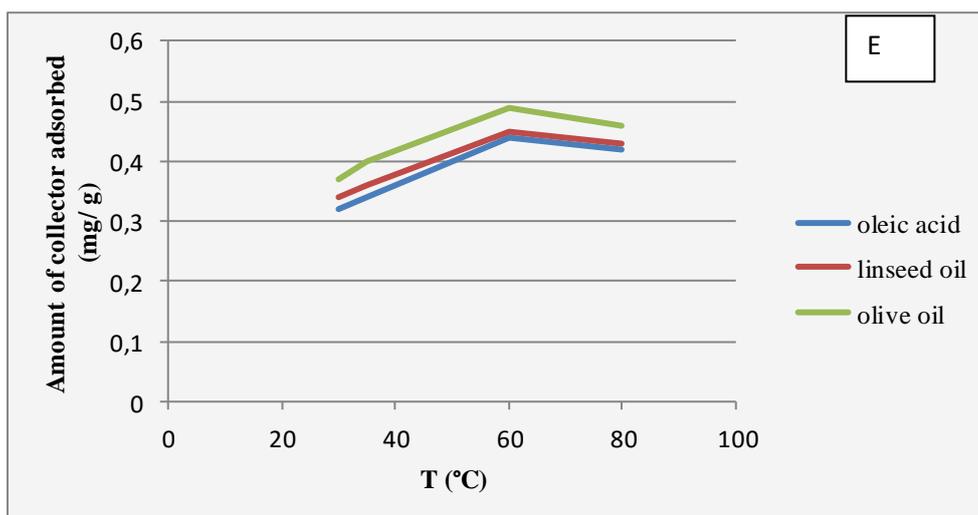
The effect of contact time on Adsorption on the calcite surface is shown in Figure12 B. The adsorption rate of Na-oleate, Na-linoleate and Na-linolineate on calcite initially increases with time. After the first 2 minutes, the amount adsorbed on calcite for an initial concentration of 0.5 g / l was almost 89%. The optimum adsorption was created within 2 min. After this time, the optimum amount adsorbed on calcite decreases. This indicates that the calcite surface was saturated with Na-oleate, Na-linoleate and Na-linolineate therefore beyond 2 min desorption of Na-oleate, Na-linoleate and Na-linolineate on the calcite surface occurs.(Figure12B).

Figure12 C shows that adsorption of Na-oleate, Na-linoleate and Na-linolineate on calcite increases as the initial concentration increases at pH 5 and pH 9. At low pH 5, the adsorption on calcite increases and maximal adsorption was observed at concentration of 0.8g/l. Beyond this maximum, adsorption decreases rapidly as the concentration increases. At pH 9 there was also a sharp increase in the adsorption of collector on calcite, also maximum adsorption was observed at concentration 0.8 g / l at pH 5 and pH 9. In aqueous solution, Na-oleate Na-linoleate and Na-linolineate are molecularly dispersed at low concentrations. However, when a certain critical concentration is reached, the surfactant molecules form micelles. (Figure12 D)

Figure12 D shows the amount of Na-oleate adsorbed on calcite in the formation of Ca-oleate. This study was carried out at a concentration of Na-oleate 0.5 g/l. The ranges of the temperatures were between 30 and 80°C. A concentration of collector 0.5g/l, the amount of collector adsorbed on calcite gradually increases as the temperature increases from 30 to 35°C. The optimum temperature of the adsorption was observed at 60°C. In addition to the optimum temperature there was a small decrease to 80°C followed by desorption when the temperature increases. (Figure 12E)







**Figure12A:**Influence of pH on adsorption on calcite. (T=60°C, t =2min, C= 0, 5g/l.)/**Figure12B:**Influence of contact time on adsorption on calcite. (T=60°C, pH = 5, C= 0, 5g/l)/**Figure12C:**Influence of initial concentration on adsorption on calcite.(T=60°C, pH = 5, t= 2min.)/**Figure12D:**Influence of initial concentration on adsorption on calcite. (T=60°C, pH = 9, t= 2min.)/ **Figure12 E:**Influence of temperature on adsorption on calcite. (T=60°C, t =2min, C= 0, 5g/l.)

### Interpretation of results

In order to clarify the mechanism of adsorption of oleic acid on the calcite, it is necessary to recall certain features of this collector. Because of the double bond between C<sub>9</sub> and C<sub>10</sub> with the *cis configuration*, the carbon chain is curved. It follows that the length of the molecule is about 14 Å, while the lipophilic group of the corresponding saturated fatty acid, stearic acid, is about 23 Å. If we consider a section perpendicular to the molecule, the geometric dimensions are 20.4 Å. Along a plane parallel to the terminal carbon of the carboxyl group, the area occupied by the latter is 24.2 Å. Most authors agree that the diameter of the carboxylic group of oleic acid is about 4.2 Å. When the adsorption of collector on mineral surface, it is appropriate to distinguish three types of attraction power: The interaction of the polar group collector with the surface of the mineral, the interaction between the polar groups of the ion collector and the energy of association of non-polar groups of the carbon chain.

The examination of the isotherms obtained shows that Adsorption is highly pH dependent.

At PH = 9, all acids are completely dissociated. All acids have indeed a characteristic peak at 1704cm<sup>-1</sup> to the "Stretching mode" of the carbonyl group. Ionization of this group slid this peak to a lower wave number, between 1600 cm<sup>-1</sup> and 1420 cm<sup>-1</sup> and 1480 cm<sup>-1</sup> and 1420 cm<sup>-1</sup> assigned to the respective "Stretching mode" and antisymmetric of the carbonyl group.

At pH = 5, only a part of the oleic acid is dissociated. In this acidity range, oleates ions are adsorbed by electrostatic attraction in the *Stern layer* and can change the sign of the surface charge. In addition, the presence of oleic acid gives rise to a physical adsorption in multilayers. It does not necessarily form a monolayer followed by a second layer. The multilayer adsorption can then take place before all the possible sites are filled. At this pH, the adsorbed species can not be easily washed. This behavior is due to the presence of free oleic acid, which is highly soluble in water, is maintained at the surface by hydrogen bonding enhanced by the acidity of the environment.

In conclusion, the decrease in pH is associated with an increase of adsorption of oleic acid and a strengthening of the flotation. In basic medium, oleates ions are easily desorbed from the surface of the mineral and the flotation is deteriorated.

The decrease in the formation of Ca-oleate, Ca-linoleate and Ca-linoleate at pH values above can probably be due to the increase of electrostatic repulsion between the micelles. As this study shows that critical micelle concentration changes at high pH values, since a change in the CMC was observed at pH 9 and pH 10 with respect to the value obtained at pH 4 and pH 6.

The adsorption of Na-oleate on calcite is temperature dependent. Decreasing the adsorption of oleate to calcite at a temperature as shown in Figure 7 may be associated with an increase in solubility. In Adsorption, the temperature should not only affect the adsorption process, but also the solubility of the adsorbate. Since the solubility of a substance determines its chemical potential, which in turn controls adsorption, solubility is a factor that can not be ignored in any investigation of Adsorption solutions.

The decrease of adsorption with temperature increase can also be attributed to weak attractive forces between oleate, linoleate and linoleate and calcite due to the improvement of thermal energies of the adsorbate; making them attractive forces between oleate and calcite insufficient to maintain oleate binding site. This could lead to a desorption or bounce oleate on the surface of calcite instead of collision by combining with it.

The results of the flotation tests using oleic acid, linseed oil and olive oil show that the latter has the largest collection of power. We can easily conclude that the increase ordered in fatty acids gathering powers C18 is due to oxidisability double bonds. The double bonds of linoleic acid can undergo oxidation as a result of ventilation in the flotation cell and the oxidation may be the reason of linolenic acid and linoleic appearing less than or at least for the anomalous results.

Hydrolysis of soap solutions, either to form acid soaps or free acid, can be expected to affect the buoyancy properties. The soaps such as the sodium linoleate which hydrolyze to a lesser degree than sodium oleate may be provided to be upper manifolds.

The collection properties of oleic acid, linoleic and linolenic, do not follow the rule of Hukki and Vartiainen. Then, we can conclude that olive oil is thanks to its property of non-oxidation of the double bonds. This property is due to the existence of anti oxidants [13].

The iodine value of the linseed oil (between 170 and 204) is larger than that of olive oil (between 80 and 88). This index providing information on the number of double bonds indicating that flaxseed oil is siccative while olive oil is non-siccative. If we know that the siccativity is the oxidation of unsaturated fatty acids contained in binders such phenomenon in the presence of oxygen in the air oils, hydroperoxides are formed and covalent bonds are established between the acid chains fat [14].

## CONCLUSION

Completion of this work is the study of the effect of unsaturation on flotation performance while relying on comparing the characteristics of three collectors: the first is a pure fatty acid and the other two are essential oils high in saturated and unsaturated fatty acids. To understand the influence of the characteristics of each collector was used, first, to study the factors that influence on the adsorption of oleic acid known calcite where the results were satisfactory. Secondly, we tried to make an approach aimed to give a strategy helping to understand the characteristics of essential oils to recommend after as collectors.

First, the study began with characterization by IR spectroscopy to target isomerism unsaturations where the diagnosis showed isomerism "cis" for fatty acids forming the structure of each oil. Secondly, it was the study of three main indices that can give valuable information regarding each oil; three indices giving richness in fatty acids (iodine value), free fatty acid rich (acid number) and finally the index that provides information on the saponification of fatty acids of both oils.

Initial results have shown that linseed oil is siccative while olive oil is non-siccative. This property indicates that the siccativity is the cause of the fatty acid oxidation when exposed to air, oxygen reacts with them leading to chain reactions giving hydroperoxides.

However, virgin olive oil resists oxidative deterioration due to its lower composition of polyunsaturated fatty acids and the presence of phenolic antioxidants comprising polyphenols and tocopherols [14].

Adsorption tests have shown that the fatty acid collecting properties C18 unsaturated increased on calcite is associated with the oxidizability of the double bond, the degree of hydrolysis of the fatty acid soap solutions and the critical micellar concentrations solutions of fatty acids.

At the end of our work, we hope that the results are the first step for further studies aimed at treating vegetable oils as collectors taking this study as a starting point.

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