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Phosphate Froth Flotation Using Sesame Oil as a Collector

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Abstract

Sedimentary phosphate deposits are the most important phosphorus source in Egypt. Most of these deposits having complex chemical and mineralogical compositions. The beneficiation of phosphate deposits containing carbonate and silicate gangues by conventional techniques such as physical separation methods or flotation is very difficult due to the similarities in physico-chemical properties of constituent minerals present in the system. The low-grade sedimentary phosphate deposits, abundant in silicate and carbonate gangue minerals, exhibits a poor processability. Sesame oil has been proved to be an efficient collector for achieving ambient temperature flotation of the sedimentary phosphate deposits used in this study, instead of high-cost reagents, which are usually made abroad. The direct froth flotation was investigated to technique has been adopted to upgrade the East Sebaiya phosphate deposits to ascertain the excellent collecting performance of sesame oil which would impart a good level of hydrophobicity to calcite. Prior to flotation experiments, a feed flotation was prepared by washing and desliming operations to eliminate fine materials. In flotation experiments, the effect of the parameters, collector (sesame oil) quantity, silica and calcite depressor (cornstarch) quantity, particle size, pH of the pulp, air superficial velocity, pulp temperature and flotation time were investigated. Consequently, a required high quality of phosphate concentrates containing 32.77% P_2O_5 was obtained, with a recovery of 94.7% from a feed sample containing about 23.48% P_2O_5 and 44.84% CaO. Scanning electron microscopy (SEM) of the flotation products confirmed that the majority of silicate and carbonate gangues were effectively removed from the concentrate.

Keywords: Egypt; East Sebaiya; Sedimentary phosphate deposits; Froth flotation; Collector; Sesame oil; Corn starch.
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1. Introduction

Phosphate deposits are a vital nonrenewable and strategic resource widely used in manufacturing fertilizers, detergents, pesticides, animal fodder, and other phosphorous-based chemicals [1]. More than 75% of the phosphate resources in the world are distributed as sedimentary deposits [2]. Among these, the majority is a sedimentary phosphate deposit characterized by a low-grade and a cryptocrystalline structure. They coexist with silicate and carbonate gangues such as quartz, dolomite, calcite, etc., and thus have a poor processability [3]. Therefore, the beneficiation and upgrade of this kind of sedimentary phosphate deposits is of great significance to meet the marketable requirements of the phosphate industry and to further alleviate the resource scarcity in the world. Froth flotation is considered as the most effective process for the beneficiation of the sedimentary phosphate deposits, due to the high efficiency of removing silicate and carbonate gangue minerals [4,5]. The direct fatty acid flotation of the phosphate deposits with carbonate gangue depression is one of the promising selective separation techniques that has been tried by several investigations. In the meantime, great efforts have been paid to the direct flotation process with anionic collectors that impart a better filtration performance of the corresponding froth products. Fatty acids are the main traditional anionic collectors used for the flotation of non-sulfide deposits [6]. However, their application suffers from sensitivity to slimes and ions, an increased collector price, relatively high consumption due to their very low solubility in water, and a high temperature requirement [7]. Flotation operations are generally carried out at room temperatures, or at room temperature less than30 °C. An increasing operation temperature would incur expensive flotation separation, especially for the separation of silicate and carbonate gangues in the direct flotation process of sedimentary phosphate deposits [8]. Therefore, searching for collectors which can achieve the ambient flotation of phosphate deposits is a future direction for improving the flotation separation efficiency of phosphate deposits. Vegetable oils have recently been investigated as an economical and environmentally friendly alternative collector in selective flotation. Such vegetable oils include soybean oil [9,10], canola and palm oils [11], jojoba oil [12], etc. Sesame oil has an advantage of containing a relatively high level of unsaturated compounds, especially polyunsaturated fatty acids (linoleic acid and linolenic acid). This unique feature of sesame oil results in an excellent solubility in pulp, without the need to raise the flotation temperature.

Lima et al. [13], in his work for the characterization of extracting pequi's yellow pulp oil, found that the fruit pulp is rich in lipids, corresponding to 33+4% of its composition. The results indicate that, in the yellow pulp, unsaturated fatty acids predominate (61.35% of the total). Branda˜o *et al.* [14] performed micro flotation tests in a Hallimond tube with pure apatite, using as a collector the sodium salts of palmitic, stearic, oleic, linoleic and linolenic fatty acids, as a function of pH. The results showed that the unsaturated fatty acids (linoleic, oleic and linolenic) exhibited superior performance compared to the saturated acids. Therefore, the pequi's fatty acid composition suggests its potential as a collector because, as described by Lima *et al.* [13], unsaturated fatty acids predominate in pequi's yellow pulp.

Ashraf Alsafasfeh and Lana Alagha (2017) [15] studied the recovery of phosphate minerals from plant tailings using direct froth flotation to upgrade the P_2O_5 content, using sodium oleate, as anionic collector, methyl isobutyl carbinol (MIBC) as a frother and sodium silicate as a depressor. The study showed that the pH value impacted the flotation performance. The recovery and grade of P_2O_5 in the concentrate products improved when the pH was increased to 9 as compared to natural pH of 6.87 when using sodium oleate collector and sodium silicate depressor at 60% feed solids and 10 min of pulp residence time. A final concentrate of 28.4% P_2O_5 with accumulated recovery of 73.86% was obtained.

Haifa Boujlel [16] investigated the beneficiation of the low-grade phosphate ore of the Tozeur-Nefta deposit of P_2O_5 (12.0%) and MgO (4.9%) and high amounts of CaO (40.7%) and SiO_2 (20.5%), using scrubbing-attrition, ball grinding and anionic/cationic reverse flotation in order to separate phosphate-rich particles from their gangue. Scrubbing-attrition, grinding and reverse flotation methods were applied to the +71µm fraction. Scrubbing-attrition tests of the 71–315 µm fractions have helped to improve the P_2O_5 grade to 15.5%. Ball-grinding tests were used to reduce the coarse fraction +315 µm. Grounded materials were sieved to 71–315 µm and combined with the scrubbed fractional in the flotation feed. Reverse-flotation tests of the phosphate-rich fraction (71–315 µm) have helped to improve the P_2O_5 grade to 27.1%, with a recovery rate of 92.4%.

In this work, the amenability of upgrading Egyptian phosphate deposits in Nile valley has been studied using sesame oil as an economically and environmentally friendly alternative collector through the flotation process to decrease the content of silicate and carbonate impurities to produce marketable phosphate grade (P_2O_5% ≥30%).

2. Materials and Methods

2.1. Materials

1.1.1. Sedimentary Phosphate Ore

The sedimentary phosphate ore sample was collected from East Sebaiya localities, Nile Valley, Egypt. The samples have been analyzed in the central laboratories of the Egyptian mineral resources authority (EMRA) by XRF using the Philips X-unique-II Spectrometer. Another sample thereof was also subjected to mineral identification in the labs of the (EMRA) using the data of the powder pattern of the ASTM on cobalt radiation target with a Fe filter at 30 kV and 20 mA. A 'Philips' X-ray diffractometer (PW 1730) was used. The scanning was limited from 2θ=1 to 2θ=80-degree range. SEM was used to investigate the surface morphology of solid samples before and after floatation experiments using (SEM, JSM-5510LV, Japan Electron Optics Laboratory, Tokyo, Japan) in central laboratories of King Faisal Bin Abdul-Aziz University, Saudi Arabia.

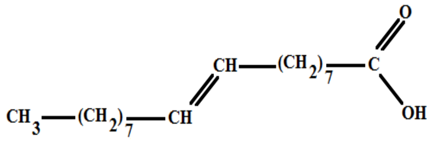
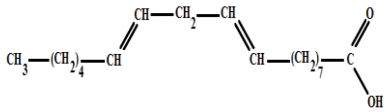
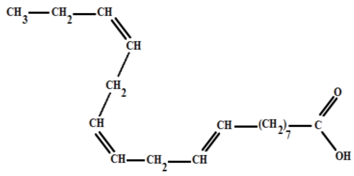
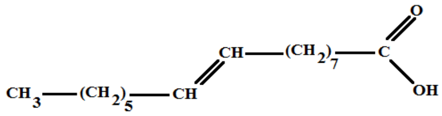
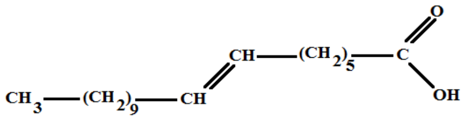
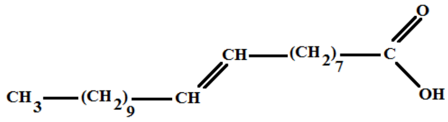
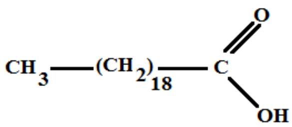
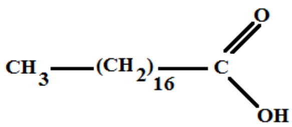
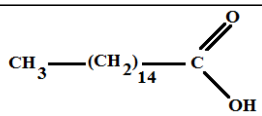
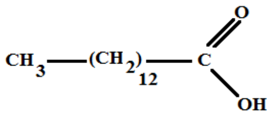
2.2. Reagents

Sesame oil was saponified with standard aqueous sodium hydroxide solution 0.5 N before used as a collector for the flotation experiments in this study, due to it contains many of the fatty acids (85%) are esterified to glycerol. The Cornstarch powder was gelatinized before using as silica depressor and NaOH was used as pH modifier. Sesame oil of (iodine value 123 g/100g) was purchased from the local market. Its components were analyzed by gas chromatography (GC Hewlett–Packard 5890-II gas chromatograph equipped with a FID, and a 400-65 HT (15 m 0.25 mm ID, 0.1 ml film) from Quardrex (Folsom, CA, USA) and are listed in Table (1). Sesame oil is composed of the following fatty acids: linoleic acid (41.32% of total), linolenic (3.5%), oleic acid (39.92%), palmitic acid (8.55%), stearic acid (5.45%) and others small amounts (1.26% of total). All of the reagents except the sesame oil were analytical grade. Table (2) shows the chemical structure formula of more polyunsaturated fatty acids confined in the vegetable oil adopted by Lima *et al*, (2007) [13].

Table (1): The main components of sesame oil (wt.%).

Fatty acid	Linoleic	Linolenic	Oleic	Palmitic	Stearic	Others
Content %	41.32	3.50	39.92	8.55	5.45	1.26

Table (2): Chemical composition of poly saturated and unsaturated fatty acids.

Fatty acid	Chemical structural formulae
Oleic - ω9(C18:1)	
Linoleic - ω6,9(C18:2)	
Linolenic - ω3,6,9(C18:3)	
Palmitoleic-ω7 (C16:1)	
Cis-Vaccenic-ω7 (C18:1)	
Gadoleic (C20:1)	
Arachidic (C20)	
Stearic (C18)	
Palmitic (C16)	
Myristic (C14)	

2.2.1. Oil saponification procedure [17]

Vegetable oils which were initially insoluble in aqueous medium were saponified in order to make them soluble. The method used consists of ester hydrolysis in basic medium, which causes the oil to transform in soap. Saponification value is the number of milligrams of lye (sodium hydroxide) required to completely saponify one gram of a specific fat, or the number of milligrams of potassium hydroxide required to neutralize the free fatty acids present in one gram of fat. Sodium hydroxide should be dissolved in water; also, the hydrolysis of fat is needed to water. Using too much water may produce soft bars of soap, may demand extra drying time. Because the water is used to dissolve the lye, the amount of lye (sodium hydroxide) will determine the amount of water.

To calculate the correct amount of water, first determine the total amount of lye (sodium hydroxide). Divide the amount of lye by 0.3 and then subtract the amount of lye (sodium hydroxide) from the result.

1. (Amount of fat) × (Saponification value of the fat) = (Amount of lye)
2. (Amount of lye) ÷ 0.3 = (Total weight of the lye /water solution)
3. (Total weight of lye water solution) − (Amount of lye) = (Amount of water)

Saponification value of making sesame oil soap with (sodium hydroxide =0.1336) and with caustic potash (potassium hydroxide= 0.1882)

To make just 200g of sesame oil soap:

1. 200 g × 0.1336=26.72 g sodium hydroxide as lye required for saponification.
2. 26.72÷ 0.3 =89 g weight of sodium hydroxide / water solution.
3. 89-26.72=62.34 g of water required for hydrolysis of fat.

It should be pointed out that the saponification process always measures by weight, such as by pounds, ounces, or grams not by volume and the same unit of measure must be used for all ingredients.

2.2.2. Gelatinization of depressor

The depressor acts as an inhibitor of flotation in a mineral, and this happens by adsorption of reagent onto mineral surface, preventing the collector adsorption or inducing strong hydrophilic properties on the mineral surface The depressors were solubilized or gelatinized with 1N sodium hydroxide solutions (depressor: NaOH ratio= 4:1 w/w) added to depressor suspensions in water (10% w/w), under magnetic stirring for 20 min, followed by distilled water addition to yield a concentration of 1% w/w. Gelatinization process occurs without heating a starch suspension in water above 56°C to avoid weakens of the inter-granule hydrogen bonds, where the heating causes swelling of the granules, loss of birefringence and increase of the clarity and viscosity of the solution [18]. Corn starch solutions should not be stored for long periods of time due to retrogradation, a spontaneous phenomenon that causes opalescence, turbidity, decrease in viscosity and, finally, precipitation. The predominate polysaccharides in starch amylopectin retrogrades only 10% within 100 days, while the retrogradation of amylose starts in only four to five hours and is favored by low temperatures [19].

2.3. Methods

2.3.1. Sample preparation

The 30 kg phosphate sample was subjected to primary crushing leading to a product of 100% - 6.5 mm, then to secondary crushing leading to a product of -2mm particle size. Sampling of the crushed product was conducted by a "Denver" Jones riffle Splitter to about 5 kg batches. Identical sample of 500g was separated for wet size analysis and distribution. Another 300g batch was finely ground to-75 µm, in a laboratory analytical mill, for chemical analysis, XRD and SEM analysis for characterization studies of mineral surface chemistry to improve flotation process and provide information on reagent adsorption on mineral surface such as reaction, product and mechanism**.**

2.3.2. Wet size analysis of sedimentary phosphate ore

As long as the flotation technique used to enrich phosphate ore is a wet process, the size analysis was conducted on a wet base by mixing 500 g of slurry phosphate ore sample of particle size more than 500 µm with water for 10 minutes at 1:3 S/L ratio and then pass onto a series of sieves of (≤1000, 500, 500-300, 300-150, 150-100, 100-75, 75-49 µm) sieve opening. The remaining amount of phosphate ore of each size fraction was dried in a laboratory oven at 100 °C for 2 hours, weighted and a sample is taken for P_2O_5 determination. The obtained results were used to determine the most suitable fraction size of the experimental work.

2.3.3. Zeta potential experiments

Zeta potential measurements were performed on pure mineral samples (apatite and quartz and clay mineral) with a Brook Haven Instruments Corporation zeta-plus analyzer in central laboratories of King Faisal University, Saudi Arabia. The experiments were conducted at room temperature and atmosphere and a 1 mM KCl solution was used. A 0.5 g of -45 µm raw sample was mixed in an 80 ml 1 mM KCl solution. The prepared mineral suspension was agitated using an IKA RW20 mechanical stirrer (IKA Instruments, Wilmington, NC, USA) for 45 min at a constant agitation rate of 250 RPM. The suspensions were allowed to settle overnight. A NaOH solution was used to adjust the pH value between pH 2 to 12 of pure apatite, quartz and clay mineral. The mineral suspension was poured into a cell for zeta potential measurements. The supernatant liquid was measured for the final pH.

2. Flotation Experiments.

The flotation tests were performed in a conventional "Denver D-12" sub-aeration flotation machine with 1.0-liter capacity cell in the central laboratories of the Egyptian mineral resources authority (EMRA), The desired amount of water was added to the 1-liter flotation cell. Then 1 kg of phosphate ore having a particle size in the range of 100 -75 µm assaying 21.66 % P_2O_5 was introduced. The pulp was mixed for 2 minutes by machine impeller itself at 2000 r.p.m with the air valve closed at 2.0 cm/s to adjust the pulp density of about (1:3) S/L to improve the dispersion of reagents, which results in a more mechanical spreading of fatty acid droplets onto the surface of the phosphate particles [20, 21]. This speed was maintained constant for all experiments, while changing the air superficial velocity from 2.0 cm/s to 1.6 cm/s during the experimental work. The pH of pulp was measured, and the necessary amount of sodium hydroxide was added to reach the desired pH in 2 minutes conditioning time. Then the required amount of collector was added. After 2 minutes as conditioning time, a measured amount of depressor was added, and the pH was adjusted again. When the conditioning time finished, the air valve is opened. Phosphate concentrate was filtered, dried, weighted and analyzed for P_2O_5. Then, the recovery of P_2O_5 was calculated. In the course of the flotation experiments, the effect of (collector and depressor quantities, pulp pH value air superficial velocity, temperature and flotation time) on the grade and recovery of P_2O_5% of the concentrated phosphate were studied.

2.1. Theory of phosphate flotation

Froth flotation is one of the most widely used mineral separation techniques. Selectivity in a froth flotation process depends on the ability to selectively induce hydrophobicity on one mineral while the other gangue minerals remain hydrophilic. The hydrophobic minerals attach to air bubbles in the flotation cell, rise to the top of the cell, and concentrate in the froth phase. The hydrophilic gangue stays in pulp phase and exits the bottom of the flotation cell in the tailings. Sparingly soluble minerals are hydrophilic. Selective hydrophobization of the desired mineral by various reagents is critical in determining the effectiveness of the separation process. The separation of sparingly soluble minerals from oxides and silicate minerals has been successfully carried out by flotation method. However, separation of phosphate from carbonates (e.g., Calcite, dolomite, etc.) Is found to be difficult due to their similar surface properties [22]. The type of phosphate deposit affects the flotation performance. Sedimentary deposits of phosphate ores can be treated by flotation when the gangue consists essentially of siliceous materials, as the phosphatic sandstone in Central Florida. The sedimentary phosphates with high carbonates (e.g., Southern Florida and Mediterranean area), however, are not easily floated. The grade and recovery of the valuable minerals have usually been used to evaluate the selectivity of the separation process for determining the optimum conditions.

$$Recovery\,\% = \frac{weight\ of\ concentrate}{Total\ weight\ of\ experimental\ sample}\,\boldsymbol{x}100 \quad (1)$$

3. Results and Discussions

3.1. Mineral composition and characterization

The chemical analysis of samples, using XRF, investigated the results of which are shown in Table (3). The main chemical composition of the raw ore was a typical calcareous and siliceous phosphate ore characterized by a low-grade of (23.48%) P_2O_5, with a relatively content of CaO (44.83%), SiO_2 (12.81%) and lower content of MgO (0.51%). The loss on ignition (L.O.I) is (9.21%) as a result of decomposition of apatite and calcite upon heating. The obtained X-ray diffraction pattern of the studied sample from East Sebaiya, the Nile valley area which is shown in Fig (1) indicates that the mineral composition involves the apatite mineral francolite which represents the main component associated with calcium hydrogen phosphate hydrate $CaHPO_4\ (H_2O)_2$, quartz, SiO_2 and calcite, $CaCO_3$. The REEs and U distribution on the ore are represented in Table (4).

Table (3): The chemical compositions of the phosphate ore by X-ray fluorescence analysis (wt. %).

Component	P_2O_5	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO
Content (%)	23.48	44.84	12.81	0.80	2.0	0.51
Component	TiO_2	Na_2O	Cl	F	SO_4^{--}	L.O.I
Content (%)	0.07	0.24	<0.01	3.01	3.03	9.21

Table (4): REEs and U Distribution in phosphate ore from East Seabiya.

Element	Content, ppm
La	42
Ce	26
Pr	2.7
Nd	9.8
Sm	4.5
Eu	0.1
Gd	4.5
Tb	0.8
Dy	5.3
Ho	0.7
Er	3.8
Tm	0.5
Yb	1.6
Lu	0.3
Y	202
U	71
ΣREEs = 305 ppm	

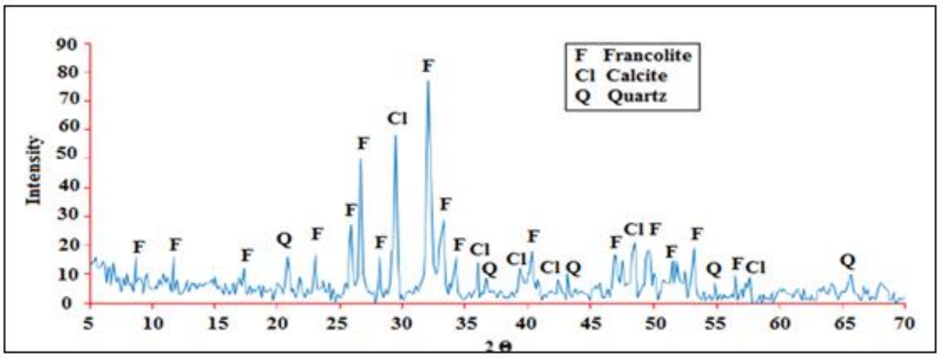


Fig (1): XRD pattern of East Sebaiya phosphate sample

3.2. Wet size analysis of sedimentary phosphate ore.

From the sieving results of the apatite ore shown in Table (5), The effect of particle size on the phosphate flotation is studied using phosphate ore of different particle sizes (≤1000, 500, 500-300, 300-150, 150-100, 100-75, 75-49 µm). But the particle sizes of less than 75 µm could have a detrimental effect on the flotation operation, particularly in reagents consumption due to increasing of the surface area of that size. Therefore, the removal of this size fraction from the ore would be beneficial to reduce production costs. On the other hand, the recovery of apatite decreasing as the particle sizes increased to reach a minimum P_2O_5 recovery% at a particle size of ≤1000 µm. This behavior can be explained due to the difference in hardness between apatite and calcite as a main constituent, leading the powder to contain coarse apatite particles and fine calcite particles during crushing of ore [23]. Anyway, it is suggested to prepare the ore feed to the flotation cell in a way having100 -75 µm particle size range of the high apatite content and somewhat moderate surface area.

Table (5): P_2O_5 recovery of different size fractions of 500g sedimentary phosphate ore.

Fraction size., µm	P_2O_5 Recovery., %
≤1000	14.26
500	15.90
500-300	17.20
300-150	17.53
150-100	19.42
100-75	21.66
75-49	22.00

3.3. Zeta potential measurements.

A Zeta potential analyzer measured the change in zeta potentials between pH 2 to 12 of pure apatite, silica and clay minerals. The isoelectric point for apatite was at pH 4.7. The phosphate flotation feed was conditioned in an alkaline medium where the phosphate particles were negatively charged. Table (6) and Fig (3) shows the change in surface charge corresponding to the pH. At a pH value started from 2 quartz and clay minerals exhibited zeta potentials that were more negative than apatite. This means that the repulsive electrostatic force between clay minerals and quartz is much stronger than that of clay minerals and apatite. Clay minerals attach to a quartz surface more preferentially than apatite surface. Removing clay particles from apatite can significantly improve the flotation selectivity.

Table (6): Zeta potential of apatite, quartz and clay dispersions as a function of pH.

Component	Apatite								
Zeta potential, mV	30	5	-10	-15	-18	-20	-20	-24	-26
pH	2.2	4.7	5.4	6	6.4	9	9.2	11.2	12
Component	Quartz								
Zeta potential, mV	-10	-18	-39	-46	-48	-50		-52	
pH	2.2	3	7.2	7.8	8.9	11.4		11.8	
Component	Other gangue minerals								
Zeta potential, mV	-20	-24	-28	-35	-38	-40		-42	
pH	2	3.2	7.6	9.7	10.2	11		11.2	

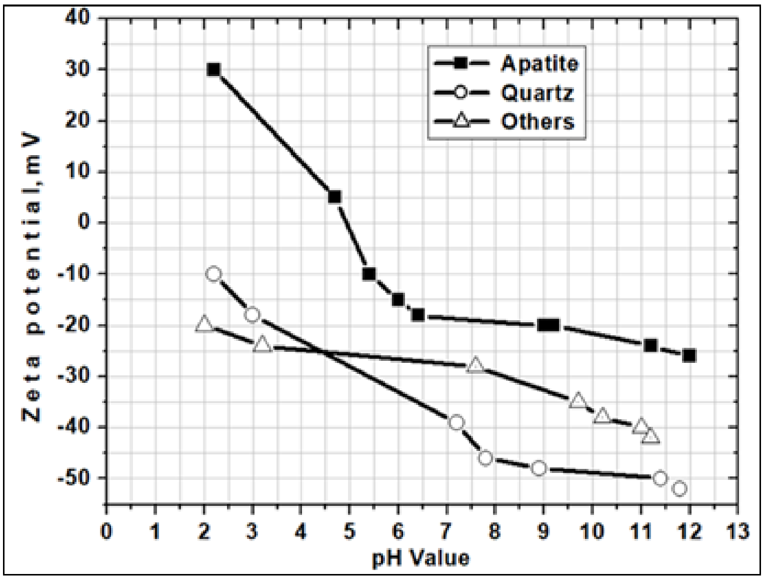


Fig (3): Zeta potential of apatite, quartz and clay dispersions as a function of pH

To examine the precedence of addition order of collector and depressor on the charge of apatite particles, another set of experiments was performed at pH9 where the collector was added, followed by depressor and vice versa as shown in Table (7) and Fig (4). From the zeta potential values, it is noted that, the interaction of sesame oil soap (collector) with apatite was much stronger when added first before gelatinized corn starch (depressor) (-12 mV zeta potential value was recorded) as compared to the case when depressor was added before collector where the zeta potential shifted towards more negative value= -25 mV). These results are consistent with the observed low recovery, % of phosphate and low content of apatite, % minerals when the depressor was added before the collector in the preliminary flotation tests, where the observed was ~25% P_2O_5 and 53% recovery. For this reason, the collector was added before the depressor in all flotation experiments.

Table (7): Zeta potential of apatite before and after mixing with the collector and depressor at pH 9

Investigated medium	Apatite	Apatite +Collector	Apatite+ Collector+ Depressor	Apatite + Depressor	Apatite+ Depressor +Collector
Zeta potential value (mV)	-17	-2	-12	-23	-25

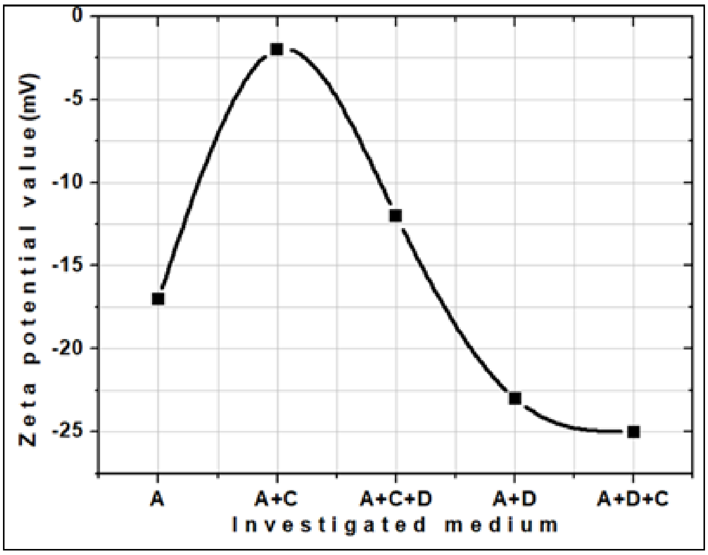


Fig (4): Zeta potential of apatite before and after mixing with collector and depressor at pH9
A is apatite, C is Collector and D is depressor

4. Flotation Experiments

4.1. Effect of sesame oil soap dosage as a collector

Sesame oil has an advantage of containing a relatively high level of unsaturated compounds, especially polyunsaturated fatty acids (linoleic acid, linolenic acid and oleic acid). It has a wide diversity of structures with different fatty acids attached at the hydroxyl groups, depending on the fatty acid composition of a particular vegetable oil. In the basic solution the polyunsaturated fatty acid collector first undergoes saponification (Equation 2), where the fatty acid (RCOOH) is reacted with a base (OH^-) to produce carboxylate ions ($RCOO^-$) and water (H_2O). The carboxylate ions then react with calcium on the francolite surface and render the francolite surface hydrophobic via chemisorption (Equation 3) [24, 25]. Chemisorption is the most prevalent adsorption mechanism for this system.

$$RCOOH(aq) + OH^- \rightarrow RCOO^-(aq) + H_2O \quad (2)$$

$$Ca^{+2}(aq) + 2RCOO^-(aq) \rightarrow Ca(RCOO)_2(S) \quad (3)$$

The effect of sesame oil soap dosage on flotation performance of phosphate ore was evaluated and the results are given in Fig (5). In these experiments, 2g/ kg corn starch was used as a depressor for carbonate and silica at 25 °C, 100-75 µm particle size, 1:3 S/L mass ratio, pulp pH 8, 2.0 cm/s air superficial velocity and 2 minutes' flotation time. Both the recovery and grade of P_2O_5 increases by increasing the collector dosage till reaching the critical value of sesame oil 1.5 g/kg where a concentrate of 26.14 % of P_2O_5 was obtained. Further addition of sesame oil soap increases of recovery at the expense of the grade P_2O_5 25.0 % and 24.11 % respectively as tabulated in Table (8).

Table (8): Effect of sesame oil soap dosage /g as a collector on the content;% and recovery; % of apatite (100-75 µm particle size, 2 g/kg corn starch depressor, 1:3 S/L ratio, pulp pH 8, 2 minutes flotation time, air superficial velocity 2.0 cm/s, 2000 RPM) at 25 °C.

Collector/g	Weight., g	P_2O_5. %	Recovery. %
0.5	404	23.5	40.40
0.75	422	23.8	42.22
1.0	546	24.2	54.6
1.5	612	26.14	61.2
1.75	624	25.0	62.4
2.0	668	24.11	66.8

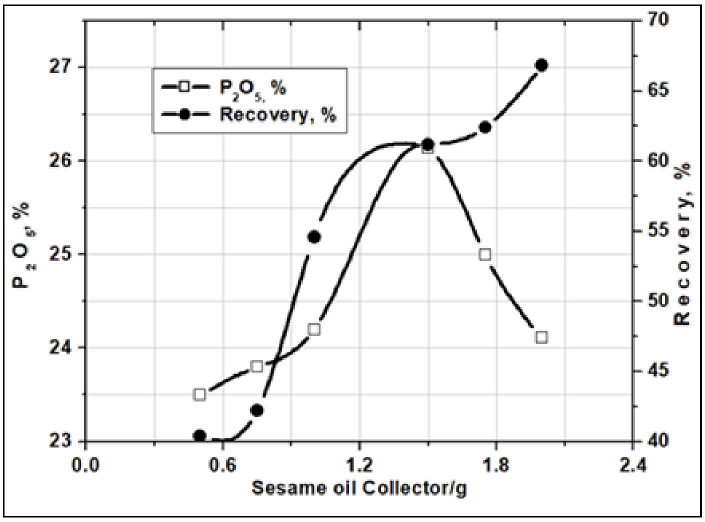


Fig (5): Effect of sesame oil soap dosage /g as a collector on the content;% and recovery; % of apatite (100-75 µm particle size, 2 g/kg corn starch depressor , 1:3 S/L ratio, pulp pH 8, 2 minutes flotation time and air superficial velocity 2.0 cm/s and 2000 RPM) at 25 °C.

It is obvious that there are no significant changes in the values of P_2O_5 % obtained at 0.5 and 0.75 g/ kg collector quantity were 23.5% and 23.8 % respectively. This can be attributed to the insufficient quantity of the collector that is needed for the flotation of apatite whereas, when the collector quantity increases to 1.5 g / kg, the P_2O_5 % of concentrate reaches a maximum value of 26.14% P_2O_5 with a recovery of 61.2 %, it is clear that the optimum dosage of sesame oil is 1.5 g / kg. The unsaturation of sesame oil is proven by the high (*iodine index 123*) which is extremely important in the characterization of lipid oils, either triglycerides, or free fatty acids. This index is a measure of the number of C=C bonds present in the aliphatic hydrocarbon chain of the constituent fatty acids. Therefore, it can give a good estimate of the lipid composition, in terms of the individual fatty acids, whether they are saturated (palmitic and stearic acids), cis-mono-unsaturated (oleic acid), cis-di-unsaturated (linoleic acid) or cis-tri-unsaturated (linolenic acid). Moreover, since the rest of the soap is formed by long saturated chains, which associated with a large amount of unsaturated, produce very compact adsorbed films, the final result would be highly hydrophobic interfaces, which would lead to very high buoyancy [26]. Therefore, this dose is used in the subsequent tests at which the apatite become more hydrophobic, easy to float and separated from other gangues. It's also noted that at pH 8, it is noted that sesame oil soap shows a distinct dual functionality as a collector and frother, causes excessive foaming in phosphate flotation, the found results agree with DuRietz, Rosano and others **[**27, 28**]** , where they found that long-chain fatty acids used for commercial flotation applications go through a molecular complex (RCOOH-$RCOO^{-}$) present in 1:1 proportion in this pH range of these surfactants have distinct dual functionality as a collector and frother.

From the above mentioned, we conclude that sesame oil as a surfactant vegetable oil decrease the surface tension of the liquid surface, making possible the formation of an intense and stable froth phase and increasing the number of bubbles with a more appropriate bubble size (smaller bubble), required to hold and transport the bubble-particle aggregates.

4.2. Effect of gelatinized corn starch dosage as a depressor

Depressors play a vital role in phosphate flotation in preventing the flotation of unwanted minerals in direct flotation or of phosphate minerals in reverse flotation. Starch and starch derivatives have as reagents widely used in mineral processing, mainly in flotation where they are used as depressors.

Starch is a natural polymer derived from the condensation of a - D (+) glucose units, through 1: α-4 (Amylose) and l: α-6 bonds (Amylopectin) that have different molecular weights vary in a wide range as well as the ratio between the larger and nonlinear amylopectin macromolecules and the smaller and linear amylose species. The So-called non modified corn starches employed in the mineral industry, of a high molecular weight above 300,000 Dalton are highly hydrophilic, due to the presence of several OH–groups in the monomer unit D-glucose, and are also able to extend in solution and "bridge" together mineral particles, acting as a flocculant **[**29**]**.

Therefore, the effect of the gelatinized cornstarch addition on clay mineral (silicate and carbonate) depression and its effect on P_2O_5 content and recovery of the concentrate studied thereupon. The tests were conducted at the conditions of 1.5 g / kg saponified sesame oil soap, 1:3 S/L mass ratio, pulp pH 8, 2.0 cm/s air superficial velocity and 2 minutes' flotation time at 25 °C using different quantities (2, 4, 5, 6, 8, 9 g/ kg) of the depressor after gelatinized with 1N sodium hydroxide solutions (depressor: NaOH ratio= 4:1 w/w) added to depressor suspensions in water (10% w/w), under magnetic stirring for 20 min.

Table (9): Effect of gelatinized corn starch as a depressor /g on the content; % and recovery; % of apatite (1.5 g/kg sesame oil soap collector, 1:3 S/L ratio, pulp pH 8, 2 minutes flotation time and air superficial velocity 2.0 cm/s, 2000RPM) at 25 °C.

Depressor/g	Weight., g	P_2O_5. %	Recovery. %
2	566	26.14	56.6
4	596	26.87	59.6
5	650	27.41	65.0
6	723	28.37	72.3
7	751	30	75.1
9	784	30.5	78.4

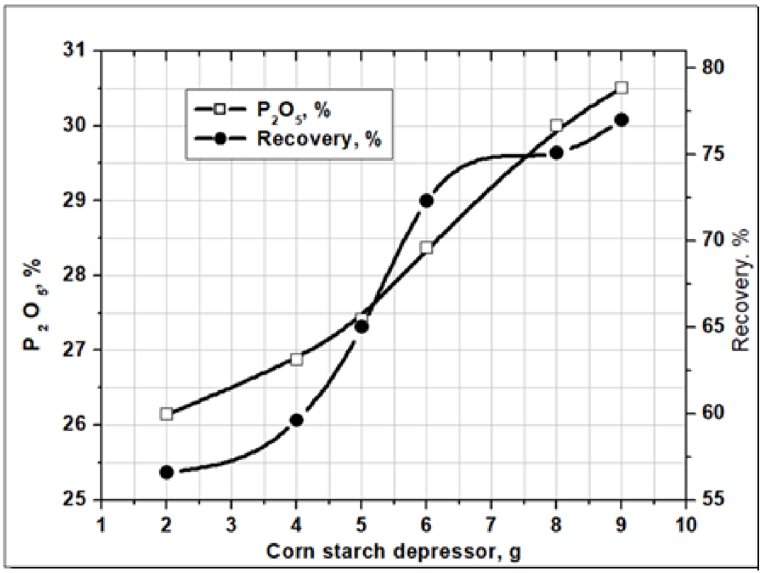


Fig. (6): Effect of gelatinized corn starch as a depressor /g on the content; % and recovery; % of apatite (100-75 µm particle size, 1.5 g/kg sesame oil soap collector, 1:3 S/L ratio, pulp pH 8, 2 minutes flotation time, air superficial velocity 2.0 cm/s, 2000 RPM) at 25 °C.

The results obtained are shown in Table (9) and Fig (6), which clearly shown that the content of P_2O_5 increases from 23.48% in feed to 26.14% in the concentrate at a depressor quantity of 2 g/ kg and increases slightly up to 27.41% with a recovery of 65% at a depressor quantity of 5 g/ kg, it reaches a higher value in these experiments 28.37% P_2O_5 with recovery of 72.3% at a depressor quantity of 6 g/ kg. Whereas, at high corn starch consumption, the corn starch may precipitate and form a coating layer on the calcite particles and reduces the release of Ca-ions to the solution [30]. This result in forming a less amount of the collector 1.5g/ kg becomes more efficient. Therefore, any reduction in producing such ionic species by adding a large dosage of gelatinized corn starch will improve the separation selectivity unless exceeds about 6 g/ kg. Despite using depressor quantities of 7 g/ kg and 9 g/ kg give a valuable apatite content of high P_2O_5 percent's, 30.2% and 30.5%, respectively, with a recovery of 75.1% and 78.4%, respectively, the gelatinized corn starch is more efficient as a depressor for silica and calcite at a 6g/ kg dosage to avoid consuming larger quantities of depressor and keep the economic feasibility of the experiments.

The selectivity of corn starch as a depressor is indispensable ingredient in the flotation reagent scheme targeting selective separation of different minerals in sedimentary phosphate rock, especially when added after the saponified sesame oil collector, where it enhance the adsorption of collector and inherently hydrophobic minerals and rock-forming gangue minerals, a drastic increasing in P_2O_5 content and recovery of apatite was obtained during the experimental work, the fact being attributed to that, In the starch polymer only three hydroxyl groups of the cyclic glucose units are free and may rotate to one side of the molecule ring, making that side more hydrophilic. The opposite side is consequently slightly hydrophobic due to the exposed –CH groups. In fact, in aqueous solutions amylose polymer forms a helical structure with six glucose monomers per turn. The interior of the helix is hydrophobic, whereas the outer shell is hydrophilic [31].

4.3. Effect of pH value of the pulp.

The pH of the pulp is considered as one of the important factors that has a high effect on phosphate flotation to establish the correct sequence of pH adjustment procedures. The solution pH determines the extent of ionization and hydrolysis of collector; this helps or hinders the adsorption of the collector at the various ionized solid/liquid interfaces, contributing to greater or lesser selectivity of flotation [29]. Therefore, the effect of pH on flotation performance of East Sebaiya phosphate ore was next studied. Several experiments were studied by varying the pH values from 8 to 10 as shown in Fig (7). while the other flotation conditions were fixed at 100-75 µm particle size, 1.5 g/kg sesame oil collector, 6g /kg corn starch depressor and 1:3 S/L ratio, 2 min flotation time, 2 cm/s air superficial velocity, 2000 RPM) at 25 °C.

Table (10) and Fig (7) demonstrate the effect of pH of pulp in the presence of 1.5 g/ kg of sesame oil soap collector and 6g/ kg corn starch as a depressor while using sodium hydroxide as pH regulator. It can be seen that the flotation efficiency, increased with increasing pH values starting from pH 8. It is observed that the using of sesame oil soap as a collector showed a better results working and high recovery in pH ranges of 9, 9.5 and 10 where it gives a high closer value of grade 29.5%, 30.46% and 31.12% respectively with a recovery of 78.8 %, 81.5 % and 84.6% respectively. The found results agree with other works using oils extracted from fruits. Results of micro flotation tests performed by Costa [32], shows that Amazon fruit oils showed apatite recoveries near 100% at concentrations of 2.5 mg /L (for buriti, inaja ´and andiroba ´ oils) and 5 mg /L (for passion fruit and Brazil nut oils). Therefore, the results for sesame oil as a collector (composed by 41.32% linoleic acid, 39.92% oleic acid and 8.55% palmitic acid) approach these results, reaching recoveries about 84.6% at optimum dosages of collector; also, it is clearly observed a formation of micelles during the flotation process. This phenomenon of micelles formation was attributed to the chain length ranges of lipid constituents from 6 to 18 carbon atoms and the main properties have a tendency to hydrolysis or dissociation (ruled by the pH of the solution), lowering of the surface tension at the air liquid interface and trend to micelles formation in the case of long chain homologues, [29]. Generally, under basic condition a strong adsorption of H_2O (electro static interaction) would be formed, this due to the presence of functional groups such as [-OH], [-COOH], [C=O] in the structural formula of most poly saturated and unsaturated fatty acids of sesame oil and corn starch. This interaction of water molecules with such functional groups producing a stable wet film on the calcite and silica surface, makes its surface becomes more hydrophilic [33].

Table (10): Effect of pH of the pulp on the content % and recovery % of apatite (1.5 g/kg sesame oil collector, 6g /kg corn starch depressor and 1:3 S/L ratio, 2 min flotation time, 2 cm/s air superficial velocity, 2000 RPM) at 25 °C .

pH value	Weight., g	P_2O_5. %	Recovery. %
8.0	723	28.37	72.3
8.5	762	28.76	76.2
9.0	788	29.5	78.8
9.5	815	30.46	81.5
10	846	31.12	84.6

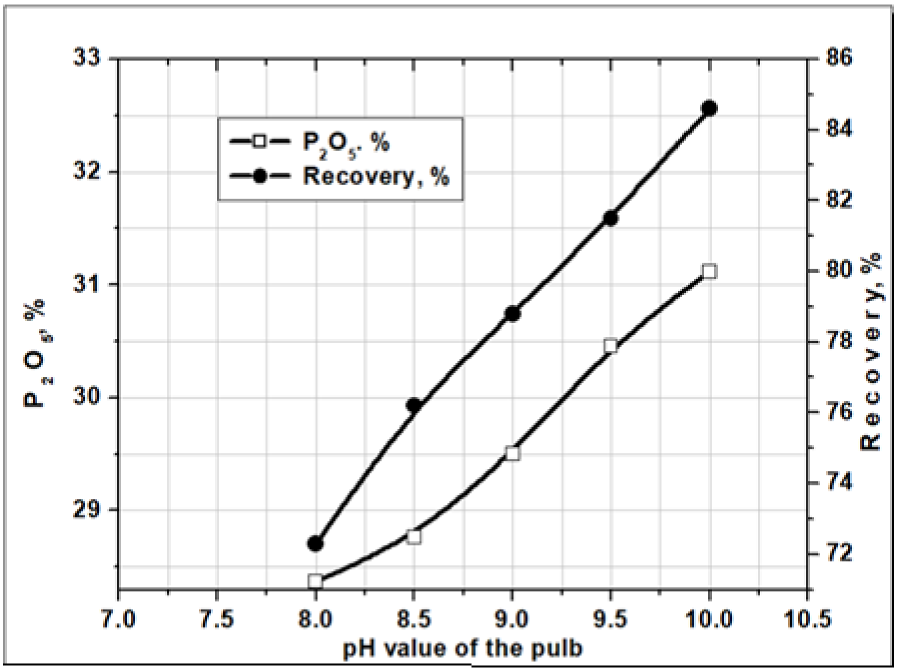


Fig (7): Effect of pH of the pulp on the content % and recovery % of apatite (100-75 µm particle size, 1.5 g/kg sesame oil collector, 6g /kg corn starch depressor and 1:3 S/L ratio, 2 min flotation time, 2 cm/s air superficial velocity, 2000 RPM) at 25 °C.

4.4. Effect of air superficial velocity on apatite flotation

The effect of air superficial velocity on the separation of apatite from calcite and silicates using flotation process was studied with advantage of differences in their surface properties. The experimental runs were carried out by decreasing the involved air superficial velocity of "Denver, D-12" flotation machine from 2.0 cm/s to 1.6 cm/s at pH 10 of the pulp, this velocity range was selected because of its influence on the hydraulics of "Denver" flotation cell and the bubble diameters. While the other flotation conditions were fixed at (100-75 µm particle size, 1.5 g/kg sesame oil collector, 6g/kg corn starch depressor, pH pulp 10 and 1:3 S/L ratio, 2 min flotation time, 2000 RPM and 25 °C.

As shown in Table (11) and Fig (8), the decreasing of air superficial velocity of 2 cm/s to 1.6cm/s increased the apatite hydrophobicity and so on, the grade and recovery increased. Generally, under basic condition a strong adsorption of H_2O (electro static interaction) would be formed, this may attribute to the presence of functional groups such as [-OH], [-COOH], [C=O] in the structural formula of most poly saturated and unsaturated fatty acids of sesame oil. This interaction of water molecules with such functional groups producing a stable wet film on the apatite surface, makes its surface becomes more hydrophobic.

It is worth pointing out that, the recovery., % increase with decreasing of air superficial velocity from 2 cm/s to 1.6cm/s, and small bubbles produced which have a high surface area, increasing the apatite - small bubbles collision probability and so improving the rate of apatite particle-bubbles adhesion. The found results agree with Yoon [34].

It can be also observed that the recovery is directly increased as the air superficial velocity decreased from 2 cm/s to 1.6 cm/s where the highest P_2O_5., % content and recovery., % obtained 31.93% and 89.4% respectively. These results may associate with an increased apatite hydrophobicity obtained at basic condition (pH 10 of the pulp), producing a high adhesion rate of particle-bubbles and so on, the recovery increased. These results may be attributed to the stability of apatite surface charge in the basic condition. The air flow rate is a significant factor in ore flotation indicating that a high air flow rate generates higher bubbles sizes which change the flow regime, deteriorate the flotation process and vice versa. So that the air superficial velocity markedly enhanced flotation selectivity, producing high adhesion rate of particle-bubbles and so on, the grade, recovery and separation efficiency increased. So, in all cases, flotation grade and recovery were improved significantly involving suitable accurate air superficial velocity (1.6 cm/s) during the flotation process.

Table (11): Effect of air superficial velocity on the content; % and recovery % of apatite (1.5 g/kg sesame oil collector, 6g/kg corn starch depressor, pH pulp 10 and 1:3 solid/Liquid ratio and 2 minutes flotation time and 2000 RPM) at 25 °C.

Air superficial velocity., Cm/S	Weight., g	P_2O_5. %	Recovery. %
2	846	31.12	84.6
1.8	860	31.54	86
1.6	894	31.93	89.4

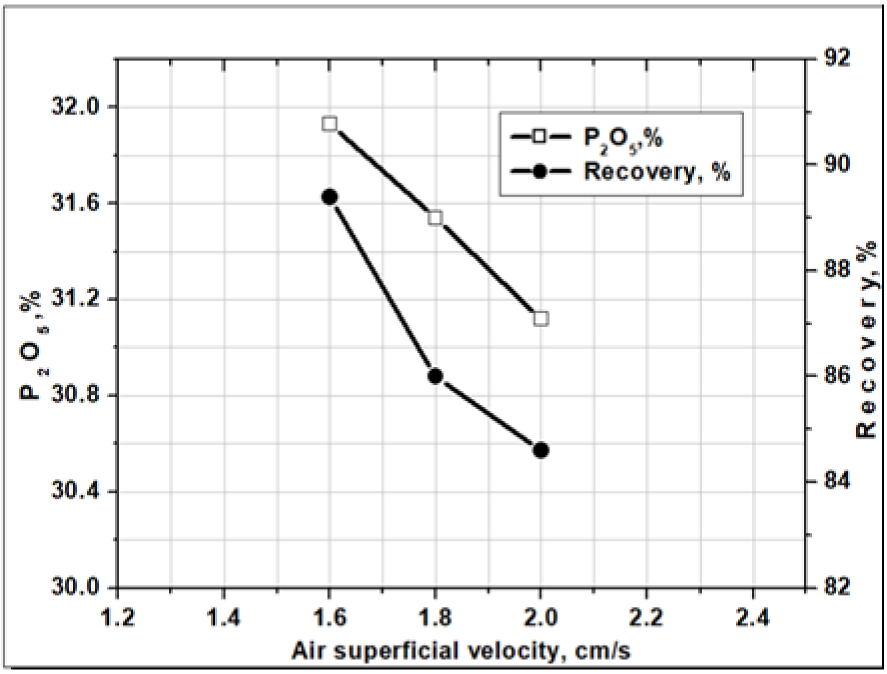


Fig (8): Effect of air superficial velocity on the content; % and recovery % of apatite (100-75 µm particle size, 1.5 g/kg sesame oil collector, 6g/kg corn starch depressor, pH pulp 10 and 1:3 S/L ratio, 2 min flotation time, 2000 RPM) at 25 °C.

4.5. Effect of pulp temperature on apatite flotation.

The effect of reaction temperature on the floatation process was investigated for the temperatures of, 25, 30, 37, 40, 45 and 50 °C while the other flotation conditions were fixed at 100-75 µm particle size, 1.5 g/kg sesame oil collector, 6g/kg corn starch depressor, pH pulp 10 and 1:3 S/L ratio, 2 min flotation time, 2000 RPM with 1.6 cm/s air superficial velocity.

As can be seen in Table (12) and Fig (9), in which the experimental results are shown, P_2O_5% content and the recovery % using 1.5 g/ kg sesame oil soap dosage and a pulp temperature of 25 was much higher compared with other higher temperatures. It was evident that the sesame oil soap had a more satisfactory collecting performance at 25°C., 31.93 % P_2O_5 with 89.4 % recovery, this was attributed to a higher index of hydrogen deficiency (IHD) of the sesame oil, i.e. The higher unsaturation degree (iodine value 123). The sesame oil rich in linoleic, linolenic and oleic acids, which are polyunsaturated acids containing a multiple double bond, presented the best performance as collectors for apatite at 25°C. The sharply decreasing in the recovery and the concentration of apatite was explained in the previous literature **[**35**]**, by the fact that increasing the temperature would reduce the viscosity of water and enhance the elutriation of the gangues back to the pulp, and thus caused the decrease of the flotation rate with the extend of temperature.

Elutriation: is a process for separating lighter particles from heavier ones using a vertically directed stream of gas or liquid or is the separation of larger particles from smaller ones, using an upward flow of air against particles which are falling.

Table (12): Effect of the pulp temperature on the content; % and recovery % of apatite (100-75 µm particle size, 1.5 g/kg sesame oil collector, 6g/kg corn starch depressor, pH pulp 10 and 1:3 S/L ratio, 2 min flotation time, 2000 RPM) with 1.6 cm/s air superficial velocity.

Pulp temperature, °C	Weight., g	P_2O_5. %	Recovery. %
25	894	31.93	89.4
30	894	31.93	89.4
37	878	30.09	87.8
40	813	28.73	81.3
45	670	26.5	67
50	620	26.13	62

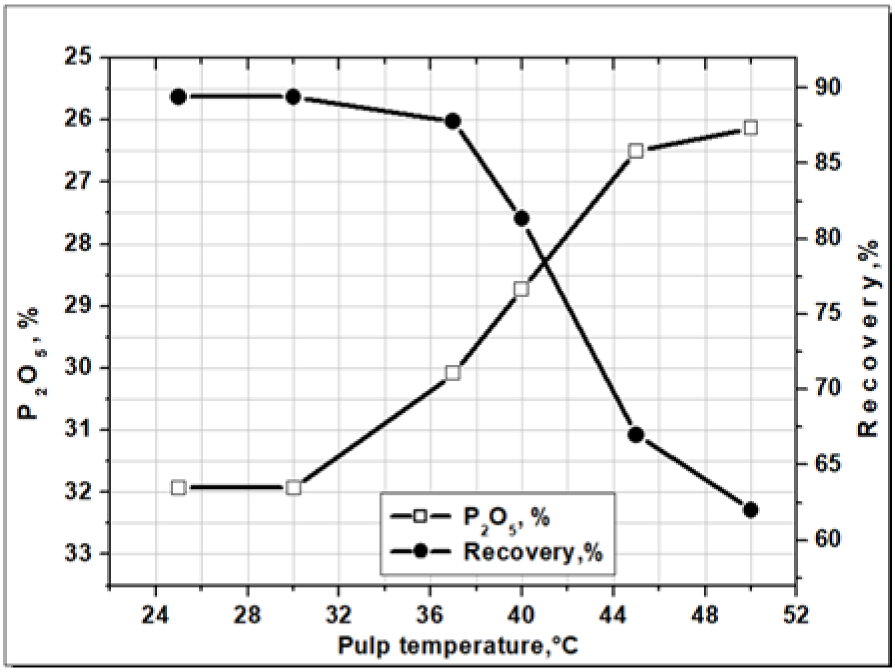


Fig. (9): Effect of the pulp temperature on the content; % and recovery % of apatite (100-75 µm particle size, 1.5 g/kg sesame oil collector, 6g/kg corn starch depressor, pH pulp 10 and 1:3 S/L ratio, 2 min flotation time, 2000 RPM) with 1.6 cm/s air superficial velocity.

4.6. Effect of time on the flotation kinetics of phosphate ore at room temperature

Flotation time is one of the most important factors affecting the upgrading of the phosphate ore. In order to study the effect of contact time upon the flotation efficiency, several experiments were studied at different interval times of 0.5, 1, 1.5, 2, 2.5, 3 ,4 ,5 ,6 ,8 minutes, while the other flotation conditions were fixed at 100-75 µm particle size, 1.5 g/kg sesame oil collector, 6g/kg corn starch depressor, pH pulp 10 and 1:3 S/L ratio, 2000 RPM and 1.6 cm/s air superficial velocity at 25°C.

From the obtained results in Table (13) and Fig (10). It was indicated that P_2O_5., % and the recovery., % gradually increased with increasing the contact time till reaching the maximum value of 32.77% and 94.7% respectively at 3 min and remains constant thereafter. Hence, the flotation equilibrium suitable time considered to complete the all parameters of flotation work has been taken at 3 min.

Table (13): Effect of flotation time on the content; % and recovery % of apatite (1.5 g/kg sesame oil collector and 6 g/kg corn starch depressor in 10 pH pulp, 1:3 solid/Liquid ratio, 1.6 cm/s air superficial velocity and 2000 RPM) at 25°C.

Time., min	Weight., g	P_2O_5. %	Recovery. %
0.5	438	27.35	43.8
1	514	28	51.4
1.5	733	28.90	73.3
2	900	31.81	90
2.5	926	32.5	92.6
3	947	32.77	94.7
4	931	32.01	93.1
5	931	32.01	93.1
6	931	32.01	93.1

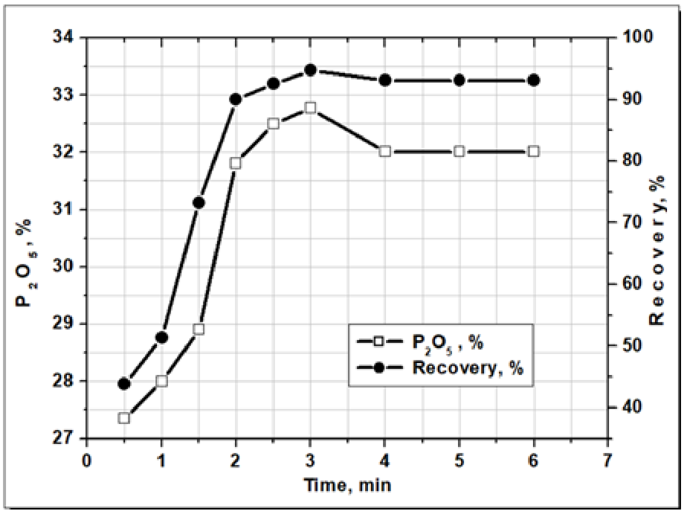


Fig (10): Effect of flotation time on the content; % and recovery % of apatite (100-75 µm particle size, 1.5 g/kg sesame oil collector, 6g/kg corn starch depressor, pH pulp 10 and 1:3 S/L ratio, 2000 RPM and 1.6 cm/s air superficial velocity) at 25°C.

Despite there is no significant change in P_2O_5 grade of the phosphate concentrate through the interval time from 3 to 6 min, it was selected 3 min as an optimum value according to the observed during the experimental work, which showed that this time was enough to float sufficient quantity of impurities. Where it gives acceptable of both apatite content 32.77 % and recovery, 94.7%, also the froth of concentrate reached a maximum quantity at 3 min as compared with other intervals time and would be scrapped. On the other hand, in 5 and upon minutes the apatite content % and recovery had slightly decreased to 32.01% and 93.1% respectively and remain constant.

Comparing these results, with that of Table (3) of phosphate raw material, it can be seen, in addition to high P_2O_5 grade, decrease sharply in silica content and the weight ratio of CaO/P_2O_5 to an acceptable level of industrial requirements (P_2O_5 ≥30%, MgO <1%, CaO/P_2O_5 ratio <1.6%) as represented in Table (14). On the other hand, SEM analysis of raw ore and the flotation products were performed to identify the morphological change and mineral phase transformation occurring in the flotation process. As seen from Fig (11), there were a lot of obvious impurities which appears on the surface of the raw ore, Fig (11a). The majority of these impurities were successfully removed after the direct flotation, as the surface of the final concentrate became relatively smooth, Fig(11b). This result confirms the success of the direct flotation process using sesame oil as a collector with corn starch as a depressor at room temperature in alkaline medium to upgrade the phosphate rock from the East Sebaiya locality, while the main gangue minerals, quartz and dolomite, were effectively rejected into the tailing products through the flotation process. These tailings were subjected to a cleaning stage, i.e. Physical treatment (washing and desliming) without adding further reagents to remove fine clay mineral as much as possible.

A final concentrate with 11.37 % P_2O_5, recovery of about 42 % and L.O.I. of about 22.42 % with low content of radioelement were obtained after such physical cleaning, Table (15).

Table (14): The chemical compositions of the phosphate concentrate after floatation.

Component	Content
P_2O_5	32.77 %
CaO	41. 15 %
SiO_2	7.93 %
Al_2O_3	0.5 %
Fe_2O_3	1.45 %
K_2O	1.61 %
Na_2O	0.2 %
MgO	0.33 %
SO_4^{--}	2.3 %
Cl	<0.01%
F	2.78 %
L.O.I	8.98 %
U	93 ppm
ΣREEs	348 ppm

Table (15): Chemical composition of the tailing product after flotation

Component	Content
P_2O_5	11.37 %
CaO	42.1 %
MgO	0.5 %
SiO_2	9.24 %
K_2O	0.8 %
Na_2O	0.47 %
Al_2O_3	0.85 %
Fe_2O_3	1.06 %
Cl	0.29 %
F	1.23 %
Organic	6.25 %
Others	3.42 %
L.O.I	22.42 %
U	6 ppm
Th	0.06 ppm
Ra	1 ppm

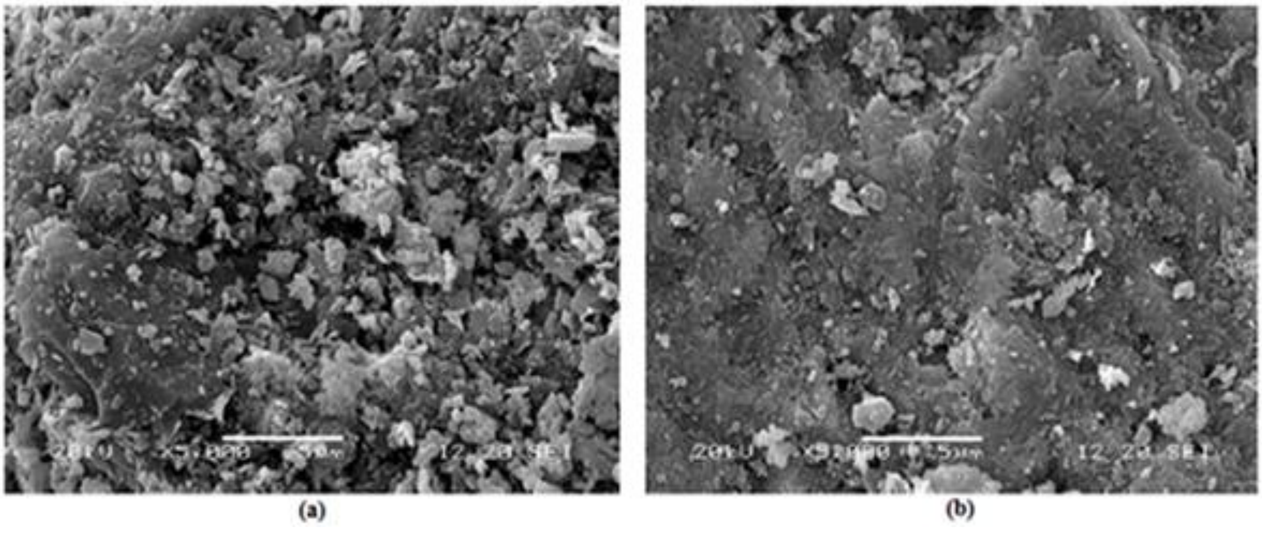


Fig (11): SEM of phosphate samples, (a) raw ore; (b) final concentration

5. Flowsheet of Froth Flotation Results.

According to the optimum conditions of the above flotation processes, an experimental circuit was consisted of direct froth flotation for the removal of silicates and carbonate was carried out. The flowsheet and optimal parameters of the flotation were shown in Fig (12). As shown, phosphates concentrate with a high grade 34.2% P_2O_5 and recovery of 94.7% was obtained through the flotation experiments. It revealed that the separation of silicates and carbonates from the sedimentary phosphate minerals can be successfully achieved by a direct froth flotation process after a series of parameters have been optimized.

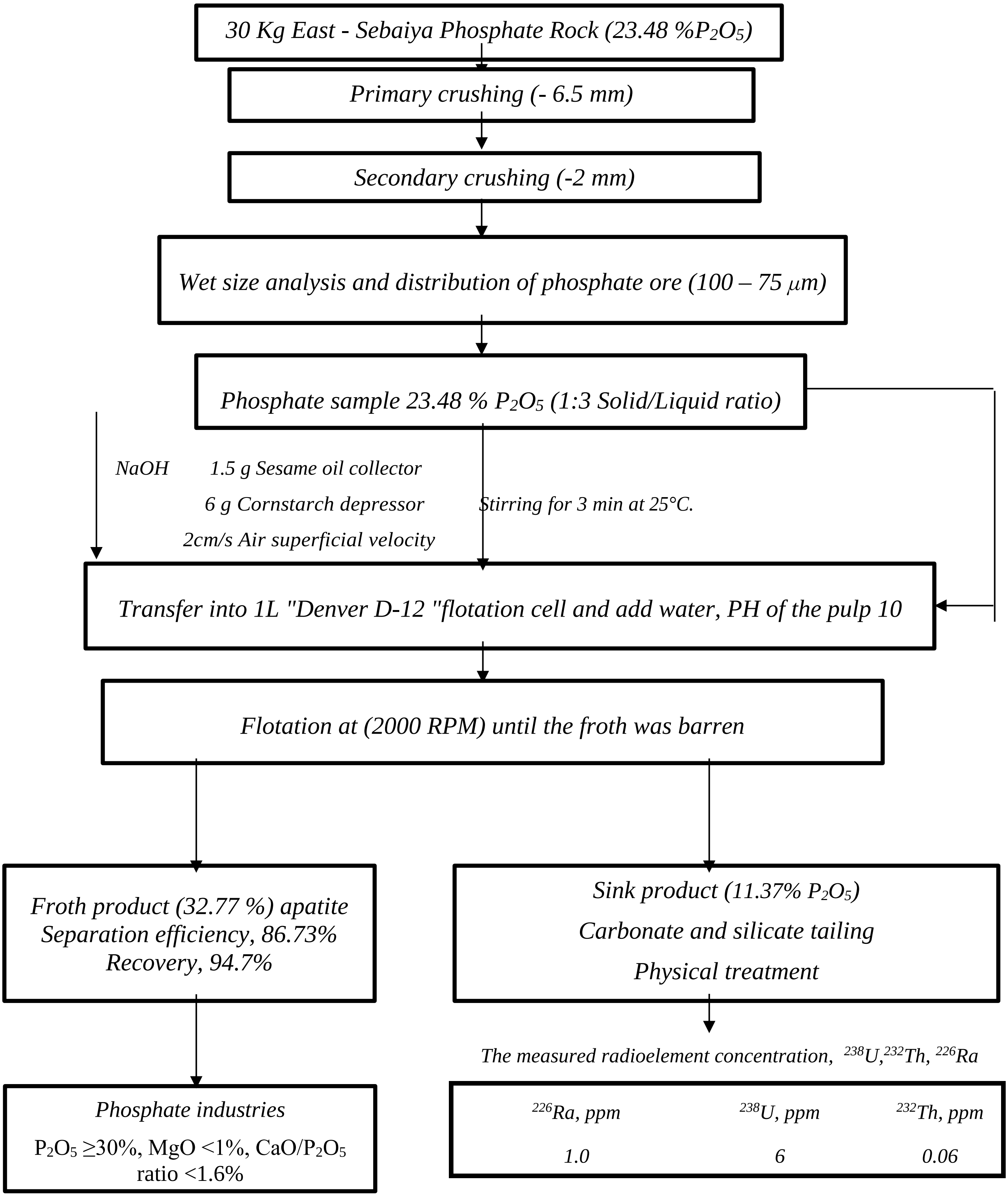


Fig (12): Flotation experiment circuit for the removal of silicate and carbonate.

6. Conclusion

Based on the test results of this work, the following conclusions can be drawn:

The direct floatation tests using saponified sesame oil indicate that this oil can be used satisfactorily as collector apatite flotation. Sesame oil showed better results working in pH 10 in the presence of cornstarch as a depressor of quartz and carbonate gangues which showed substantial recovery of apatite. The grade and recovery of concentrates are significantly affected by changing the studied parameters. On applying the optimum conditions (i.e., 1.5

g/kg saponified sesame oil and 6g/kg gelatinized corn starch, pH 10 using NaOH, 1:3 S/L mass ratio with 1.6 cm/s air superficial velocity. At 3 minutes' intervals flotation time, a final concentrate with 32.77 % P_2O_5, 41.15 % CaO and 7.93 % SiO_2 with a recovery about 94.7 % was obtained.

The sesame oil rich in linoleic, linolenic and oleic acids, which are polyunsaturated acids, presented the best performance as collectors for apatite, with linoleic being the best collector. This result encourages further studies about the application of this oil in the mineral flotation and provides a new source of economic feasibility and friendly environment reagent, contributing to the recovery of the species, encouraging the preservation and commercial production and generating innovation in Egyptian phosphate mining production.

Gelatinized corn starch is more efficient in the depression of quartz and calcite, this behavior is due to complexation involving precipitation of a coating layer on the quartz and calcite particles reduces the release of Ca-ions to the solution, especially when added after the saponified sesame oil collector, where it enhances the adsorption of collector and inherently hydrophobic minerals and rock-forming gangue minerals

The air flow rate is a significant factor in ore flotation indicating that a high air flow rate generates higher bubbles sizes which change the flow regime, deteriorate the flotation process and vice versa. Decreasing of air superficial velocity leads to small bubbles produced, which have a high surface area, increasing the apatite-small bubbles collision probability and so improving the rate of apatite particle - bubbles adhesion.

The study looked at the preserved quantity of natural radioactive materials (NORM) uranium, thorium and radium, which would harm the environment in general and soil in particular when used in the manufacture of phosphate fertilizers, the study ended with the distribution of these radionuclides between different products and phosphate wastes after flotation. Fortunately, it is distributed in low proportions with the phosphate tailing.

All the experiments were conducted at room temperature; the results suggest that sesame oil would be helpful to reduce the production costs of the reagents and energy consumption.

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