



## Studies on Bioprocessing Technique Advanced in Beneficiation of an Egyptian Phosphate Ore by Froth Flotation

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### Abstract

In recent times, considerable research endeavours have been directed towards reducing the magnesium content in phosphate rock concentrate, making it a viable raw material for phosphoric acid production and allied industries. One noteworthy approach in this regard is the utilization of bioprocessing techniques. Nonetheless, this investigation is centered on the utilization of an enzyme obtained from *Aspergillus Niger* fungi cultivated on coffee waste sourced from the National Research Center Microbiology Laboratory. This enzyme is employed as a surface modifier during fatty acid flotation for calcareous phosphate rock. A blend of oleic acid and kerosene serves as the collector. A comprehensive exploration of various factors impacting enzyme activity, such as enzyme dosage, solution pH, temperature, and conditioning time, has been undertaken, aligning with the demands of local, regional, and global markets. Under optimal conditions, the study achieved a concentrate product containing less than 0.8% MgO from the Abu-Tartur feed, originally containing 2.88% MgO, with a remarkable  $P_2O_5$  recovery exceeding 88%.

**Keywords:** Phosphate, Flotation, *Aspergillus Niger* fungi, Oleic acid, Enzyme, Magnesium.

### Introduction

Phosphate ores serve as the primary phosphorus source for various products, including elemental phosphorus, phosphoric acid, and fertilizers. Given the diminishing reserves of phosphate-rich siliceous

ores, there is a significant focus on the enrichment and processing of low-grade dolomitic phosphate ores. Impurities found in phosphate ores, particularly magnesium, can pose substantial challenges to the

phosphoric acid industry, as noted by Yehia et al. [1].

A phosphate rock with a 30%  $P_2O_5$  content is considered commercially viable as long as its magnesium content remains below 1%. Various beneficiation methods have been devised to decrease the magnesium content in phosphate ores:

Blazy and Jdid's work provides an extensive examination of wet magnetic separation [2].

The flotation of dolomite and carbonates from apatite has been investigated in several studies, including those by Anonymous [3], Blazy et al. [4], Blazy et al. [5], Houot et al. [6], Ratobylskaya et al. [7], and Abdel Khalek [8].

The process of heavy media separation (HMS) applied to dolomite, followed by milling the sink product from HMS, and subsequently conducting flotation to separate phosphate minerals from dolomite has been discussed by Lawver et al. [9] and Snow [10].

The flash calcination of phosphate has been explored by Blazy and Jdid [11]. Benson and Martin [1] investigated a process involving leaching using a leaching solution based on carbon dioxide and the subsequent elimination of  $Mg^{2+}$  through ion exchange resin separation.

The elimination of magnesium from diluted phosphoric acid using resin-based separation techniques has been examined in studies conducted by

Rushton et al. [12] and Anonymous [13].

Froth flotation, was an effective technique for processing small-sized particles (10-150  $\mu m$ ), has been introduced and explored in several studies, including those by Rao (2004) [14], Nunes et al. (2012) [15], Veloso et al. (2020) [16], and X. Zhang et al. (2021) [17]. This method differentiates between minerals based on variations in their physicochemical surface characteristics, segregating hydrophobic particles from hydrophilic ones following treatment with specific reagents, as elucidated by Wills and Napier-Munn (2006) [18].

Recent findings suggest that physical separation techniques, with flotation have been particularly effective, can successfully remove magnesium from phosphates, provided that the primary mineral carrier, dolomite, is well crystallized, as discussed by Blazy and Jdid [19]. Many studies have explored alternative processing methods and reagents in pursuit of more efficient approaches. Nevertheless, the high demand for reagents and limitations in recovery rates may not always make these strategies cost-effective. Reagents derived from biological sources are of special interest due to their unique interactions with minerals, as highlighted by Boice [20], El Mahdy et al. [21], R. Yaoyang et al. [22], and Namita et al. [23]. While bioprocessing techniques for ore

leaching are widely recognized, the exploration of biological methods for mineral beneficiation has been relatively limited, as noted by Smith et al. [24]. However, there has been a recent upsurge in interest in utilizing microorganisms as agents for flocculating mineral fines and as collectors in flotation processes, as discussed by Smith and Misra [25] and Misra et al. [26]. This study is specifically focused on employing an enzyme as a surface modifier during the fatty acid flotation of calcareous phosphate rock. It delves into an examination of various factors affecting enzyme activity, including enzyme dosage, solution pH, temperature, and conditioning time with the enzyme.

### **Chemical Nature of Enzyme:**

An enzyme is defined as a protein possessing catalytic properties attributed to its specific activation capability, as described by Furia [27]. Enzymes encompass reactive groups like free amino, carboxyl, hydroxyl, sulfhydroxyl, and imidazole and often incorporate non-protein prosthetic groups. The lengthy peptide chains within native protein molecules are recognized for their precise folding and arrangement, ensuring that in enzymes, the binding sites are appropriately situated to form the essential active centers for substrate binding and catalytic functions, as elucidated by Yaoyang et al. [22]. Both proteins and enzymes undergo

denaturation and lose their activity when exposed to heat, as highlighted by Fiechter [28], or when subjected to harsh chemical conditions, as mentioned by Reed [29]. Enzyme denaturation leads to the unfolding and disordering of the enzyme's structure.

## **Experimental**

### **Materials**

In this research, a sample from the Abu-Tartur phosphate deposit located in the Western Desert of Egypt was employed. The petrographical and mineral analysis of this sample revealed the presence of three distinct types of components:

- Phosphate-bearing minerals, varying in size from 2,000  $\mu\text{m}$  to 100  $\mu\text{m}$ .
- The endogangue, found within the phosphate elements, primarily composed of pyrite.
- The exogangue, predominantly comprising a clay matrix consisting of montmorillonite, illite, kaolinite, ankeritic dolomite, and detritic quartz grains, as reported by Cohen and Hammuod [30] and Zatout and Hussein [31].

For this study, the enzyme used was obtained from *Aspergillus Niger* fungi cultivated on coffee waste. Analytical grade substances such as oleic acid, NaOH, and HCl were also employed.

Top of Form

### **Preparation of Enzyme:**

### ***Fungal Culture:***

A strain of *Aspergillus Niger*, denoted as F-909, was obtained from coffee waste collected locally. This culture has been consistently cultivated on a potato dextrose agar (PDA) medium.

### ***Obtaining Fungal Spores:***

The fungal culture was subjected to sub-culturing on PDA and then allowed to incubate for seven days at a temperature of 30°C. Subsequently, the sub-culture was gently scraped into a conical flask filled with 25 ml of sterilized tap water. The resulting spore suspension was employed to inoculate the experimental flasks at a concentration of 10% v/w.

### ***Setting up the Experimental Flask for Enzyme Production:***

In our investigation, we employed a conical flask with a two-litre capacity. Within this flask, we placed a medium consisting of 100 grams of material, comprising 50 grams of rice bran and 50 grams of wheat bran. To achieve proper moisture content, we added 120 milliliters of tap water to the medium. Subsequently, the flasks were subjected to autoclaving at a temperature of 121°C for 30 minutes. After cooling, these sterilized flasks were inoculated with fungal spore suspensions, constituting 10% of the flask's total volume, and then incubated at 35°C for a period of 72 hours.

### ***Enzyme Extraction Procedure:***

For the enzyme extraction process, we utilized 900 milliliters of tap water, which was pH-adjusted to 4.8 using citric acid. The flasks were subjected to agitation for one hour, followed by filtration through glass wool. Subsequently, the filtrate underwent centrifugation at 5,000 revolutions per minute (rpm) for a duration of ten minutes, resulting in the separation of a supernatant containing the desired enzyme.

### ***Partial purification of the enzyme:***

To partially purify the enzyme, the supernatant underwent a series of steps. Firstly, it was clarified by the addition of 0.5% calcium acetate and 2% lead acetate, resulting in a final pH of 5.0. Subsequently, powdered ammonium sulfate was gradually introduced into the clarified extract while constantly stirring until it reached 65% saturation. This mixture was left to stand overnight. Following this, centrifugation was performed at 4,000 rpm for 30 minutes at a temperature of 40°C, leading to the formation of a precipitate. This precipitate was then reconstituted in a 0.1 M citrate buffer at pH 5.

### ***Drying the Moldy Substrate:***

To the dry moldy substrate, a procedure was followed. At the conclusion of the fermentation period, a five-percent ethanol solution was introduced into the fermentation

flasks containing the moldy substrate. The moldy substrate was then allowed to air dry at a temperature of 30°C for a duration of 3 hours. Once dried, these substrates were packed into polyethylene bags and stored in a refrigerator until needed.

***Preparation of the flotation feed:***

The untreated phosphate ore sample, sourced from the Abu-Tartur region in the Western Desert of Egypt, underwent a series of processing steps. Initially, it was subjected to crushing using a 5x6 Denver Jaw crusher, followed by further grinding in a Wedag roller mill. The crushed sample was then finely ground until it reached a particle size of less than

0.25mm, utilizing a laboratory Wedag rod mill in a closed circuit configuration, employing a 0.25mm sieve. Due to the exceptionally fine nature of the (-0.074mm) fraction, which could adversely affect the flotation process, it was separated and excluded from further processing using a 0.074mm sieve. Furthermore, magnetic separation was performed on the sample with a size range of (-0.25 + 0.074) mm using the Dings cross belt separator, and the outcomes of this separation process are presented in Table (1). The non-magnetic fraction derived from this separation was employed as the flotation feed in this particular study.

**Table (1):-** The Results of The Magnetic Separation For Size (- 0.25 + 0.074) mm.

<b>Product</b>	<b>Wt.%</b>	<b>P<sub>2</sub>O<sub>5</sub> %</b>	<b>MgO %</b>	<b>Fe<sub>2</sub>O<sub>3</sub> %</b>	<b>SiO<sub>2</sub> %</b>
<b>Magnetic fraction</b>	20	10.94	3.20	12.38	14.73
<b>Non Magnetic fraction</b>	80	25.25	2.80	6.88	15.88
<b>Feed</b>	100	22.38	2.88	7.98	15.65

**RESULTS AND DISCUSSION**

***Granulometric analysis of sample:***

The size and chemical compositions of the secondary crushed ore, as outlined in Table (2), reveal that phosphorous-bearing minerals are primarily concentrated in the finer fractions. In contrast, the coarse fractions are characterized by the

prevalence of iron minerals, silicates, and magnesium-bearing minerals. This observation suggests that selective grinding has taken place, driven by variations in the grindability of phosphate and the accompanying minerals.

**Table (2):-** Typical Cumulative Size and Chemical Distribution of the Secondary Crushed Ore (Sieve Analysis)

Size, mm	Wt. %	Wt.% retained	Wt. % passed	P <sub>2</sub> O <sub>5</sub> %	MgO %	Fe <sub>2</sub> O <sub>3</sub> %	SiO <sub>2</sub> %
+11.2	10.92	0	100	11.58	5.35	7.52	26.60
-11.2+8	4.95	15.88	88.67	12.91	3.22	13.47	35.48
-8+4	4.28	20.16	83.72	13.74	3.22	13.41	38.16
-4+2	16.13	36.29	79.44	18.82	2.76	11.89	27.74
-2+1	13.24	49.53	63.31	20.89	1.76	8.29	11.84
-1+0.84	3.74	53.27	50.07	25.15	1.03	11.95	6.82
-0.84+0.5	11.22	64.45	46.33	26.23	1.59	11.87	5.42
-0.5+0.32	7.96	72.45	35.11	27.46	1.13	10.58	4.16
-0.32+0.211	12.11	84.56	27.15	27.08	1.43	10.85	5.00
-0.211+0.125	8.76	93.32	15.04	23.63	1.76	10.38	7.92
-.125+0.105	1.18	94.50	6.28	20.31	3.78	7.15	8.76
-.105+0.074	1.41	95.91	5.10	19.98	4.35	7.38	8.26
-0.074+0.044	3.69	100	0	17.73	4.25	11.41	11.2

<b>Calc. Head assay Original sample</b>				20.88	2.46	10.49	15.47
				22.14	2.88	7.98	15.32

**Characterization of Abu- Tartur phosphorites:**

*Geological outlines of Abu Tartur phosphorites:*

The Abu-Tartur plateau is situated in the Western Desert, approximately 600 kilometers southwest of Cairo. Its southern boundary overlooks the Nubia plain, while it gently slopes northward, forming the predominant terrain of the Western Desert. The plateau's elevations vary between 540 meters and 570 meters above sea level. In the northern and western regions of this area, the plateau's surface is overlaid by limestone from the Eocene Garra Formation, which constitutes the higher step and

constitutes the primary limestone plateau. The phosphate-bearing Duwi Formation comprises coarse-grained phosphorites and phosphatic sandstone, interspersed with black shale and dolostone. It rests unconformably on the Qusseir Formation, with an undulating erosional boundary covered by poorly-sorted pebbly phosphatic sandstone. The lower surfaces of the phosphatic layers typically exhibit substantial bioturbation, characterized by branched and Y-shaped burrows measuring 2 to 5 centimeters in diameter. The Qusseir Formation, on the other hand, consists of varicolored shales, intermingled with layers of



sandstone and siltstone, spanning approximately 75 meters in thickness. Conformably above the Duwi Formation lies the Dakhla Formation, which comprises roughly 150 meters of gray, laminated shales rich in foraminifera, punctuated by marl and chalk beds.

### ***Sample Varieties:***

The samples categorized into groups based on their lithological and mineralogical attributes. These groups include phosphorites and phosphatic specimens, dolostone, and black shales. The subsequent sections provide a comprehensive overview of each of these sample types.

### **Mineralogy:**

#### ***Phosphorites:***

The X-ray diffraction (XRD) analysis of bulk phosphorite samples, as depicted in Figure (1), identified the presence of six mineral phases: francolite, ankerite, quartz, gypsum, anhydrite, and some smectite. Subsequent XRD analysis of individual phosphatic grains revealed that both phosphatic mudclasts and phosphatic bioclasts consist predominantly of francolite. Notably, the X-ray diffraction patterns of both types of grains exhibit relatively broad and indistinct francolite peaks, indicating the low crystallinity of francolite in these samples. Moreover, the peak positions of francolite within the Duwi formation display minor

shifts from the typical francolite, suggesting alterations in the cell parameters due to isomorphous substitutions.

#### ***Dolostone:***

The X-ray diffraction findings reveal that dolostones primarily consist of dolomite, with minor traces of smectite, pyrite, and quartz. Figure (2) provides evidence that XRD analysis effectively identifies the solid solution between ankerite (ferroan dolomite) and standard dolomite. The ratio between d-spaces, specifically 2.89Å and 2.19Å, exhibited an increase from 3.5 for non-ferroan dolomite to 17 for ferroan dolomite. In this particular study, the dolomite present is exclusively of the ferroan variety, with a 2.89Å/2.19Å ratio approximately equal to 19. Upon analyzing the XRD data, it was observed that the calcium content ranges from 55% to 57%, averaging around 54%. Consequently, the examined dolomite is non-stoichiometric for calcium, and its structural formula can be expressed as  $\text{Ca}_{0.56} \text{Mg}_{0.44} \text{CO}_3$ .

#### ***Black Shales:***

The X-ray diffraction (XRD) examination of black shale samples, as shown in Figure (3), revealed the presence of four mineral phases: smectite, ankerite, quartz, and minor amounts of pyrite.



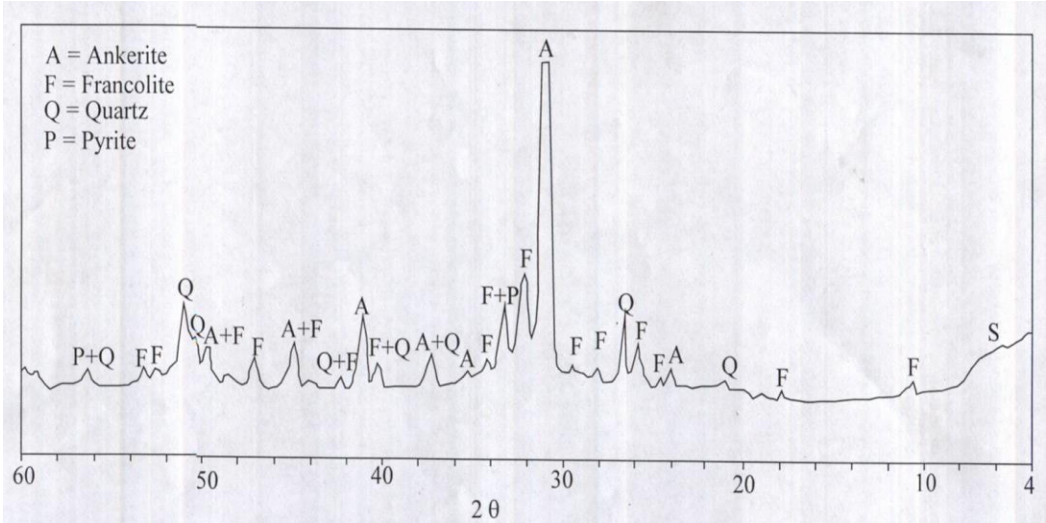


Figure (1):- XRD of phospho

rite sample.

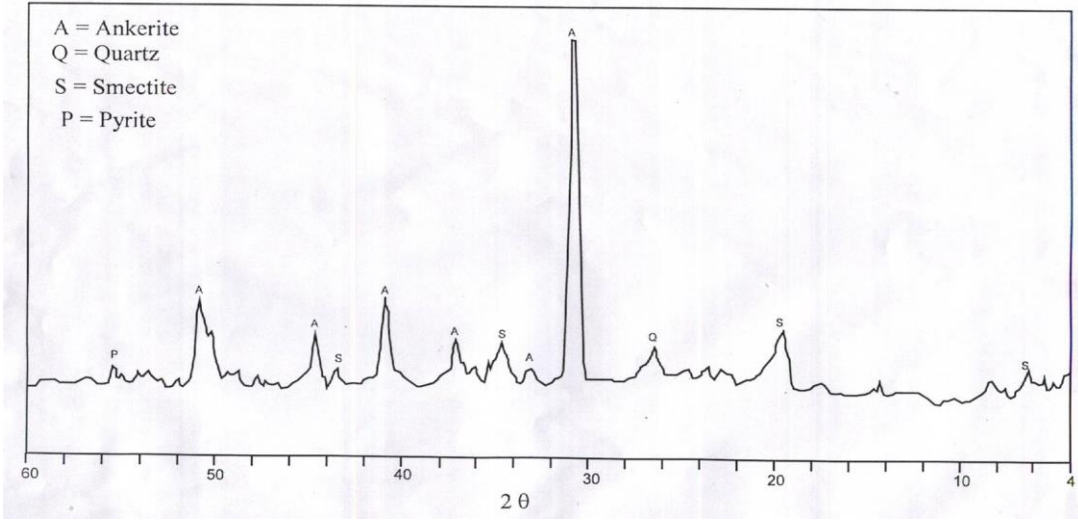


Figure (2):- XRD of Dolostone Sample.

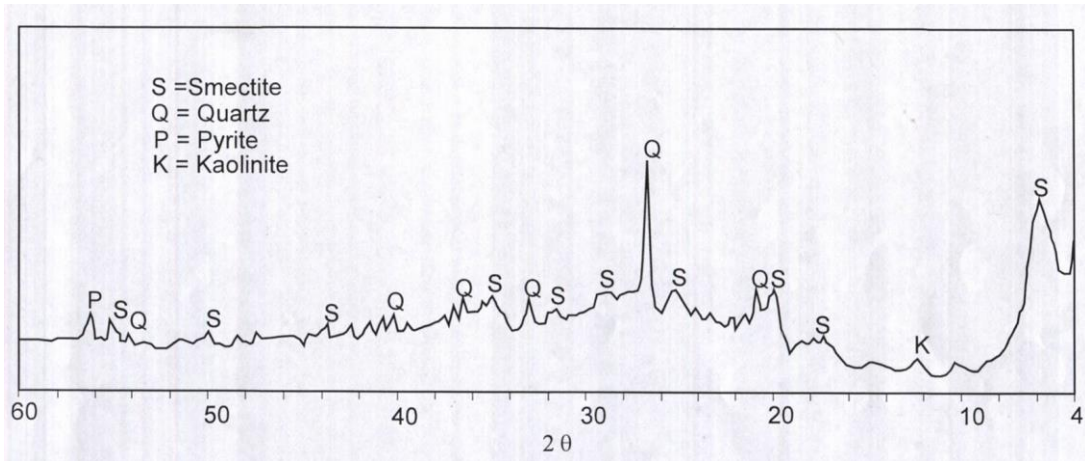


Figure (3):- XRD of Black shale sample.

***Flotation of the phosphate ore utilizing oleic acid as a collector:***

Oleic acid stands as the most extensively employed collector in phosphate flotation, with well-documented solution chemistry characteristics [32]. The flotation process for the finely ground ore sample (-0.25 +0.047mm) involved using an oleic acid/kerosene combination as the collector. In contrast, the utilization of oleate as a collector offers limited selectivity, and it seldom yields a clear phosphate concentrate unless depressants are introduced. The flotation experiments were conducted using a conventional Denver D-12 sub-aeration flotation machine equipped with a one-liter capacity cell. The pulp was conditioned with the collector for 5 minutes at a speed of 2000 rpm, maintaining a solid content of approximately 50% by weight. The actual flotation procedure was executed at a speed of 1500 rpm. Subsequently, the flotation products,

encompassing both the froth and the sink, were gathered, dried, weighed, and subjected to analysis

***Effect of Collector Dose on Flotation:***

In Figure (4), the flotation process was conducted under the following conditions: utilizing an oleic acid/kerosene mixture in a 1:1 ratio, maintaining a pH of 7, a conditioning period of 5 minutes, and performing the process at room temperature. Observations indicate that as the collector dosage increases, there is a corresponding rise in the flotation percentage, and the flotation recovery significantly escalates, nearing complete flotation. For instance, a dose of 4 kg/t is necessary to achieve the flotation of approximately 96.7% by weight of the sample. However, when a higher collector dosage (5 kg/t) is applied, there is a noticeable reduction in the flotation yield. In situations involving low collector dosages, the oleate molecules tend to orient themselves horizontally on the

mineral surface, resulting in suboptimal flotation performance. As the collector dosage is increased, the oleate molecules progressively shift to

an oblique orientation and eventually reach a vertical orientation at higher concentrations.

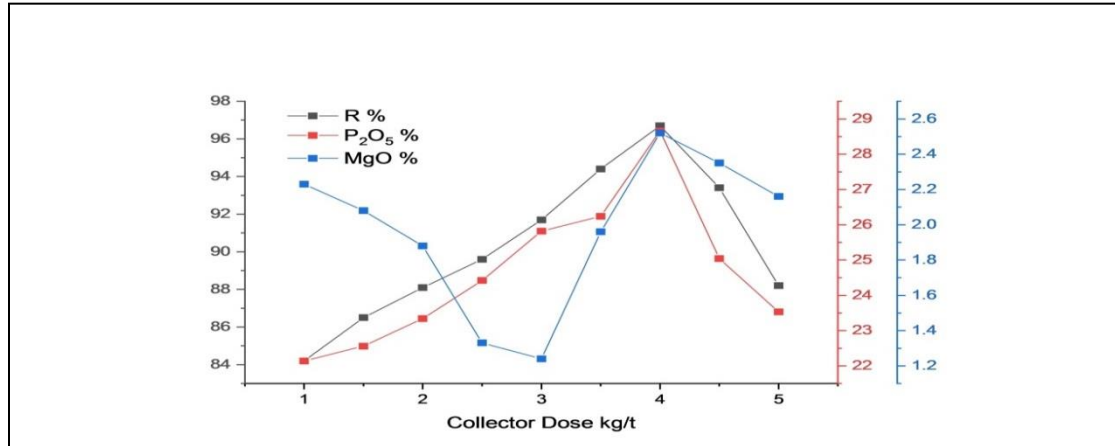


Figure (4):- Effect of collector dose on phosphate flotation.

**Flotation of the phosphate ore using an enzyme as a surface modifier:**

**Bench scale flotation:**

Bench-scale experiments for phosphate flotation were carried out using a Denver D12 flotation cell. A sized phosphate sample with dimensions of 0.25 x 0.074mm was initially treated with a collector (a 1:1 mixture of oleic acid and kerosene) for a duration of five minutes, maintaining the pH at 7.0.

Following the collector conditioning, the enzyme was introduced, and the pulp underwent further conditioning under varying pH levels, temperatures, and durations. Notably, phosphate minerals are directed towards the sink during this process since the enzyme serves as a depressant for phosphate.

**Effect of enzyme dosage:**

P<sub>2</sub>O<sub>5</sub> recovery and MgO content within the phosphate concentrate (sink fraction) were examined as a function of enzyme dosage, utilizing two concentrations of oleic acid/kerosene collectors (0.50 and 1.0 kg/t). The enzyme addition took place at pH 7.0, under ambient conditions (30°C), with a duration of 10 minutes. The results depicted in Figures (5&6) clearly demonstrate that, at a low collector concentration (0.5 kg/t), the enzyme acts as a potent depressant for phosphate-containing minerals when the enzyme dose surpasses 0.45 kg/t. The incorporation of the enzyme led to an enhancement in the P<sub>2</sub>O<sub>5</sub> grade of the concentrate and a reduction in its MgO content. Specifically, the P<sub>2</sub>O<sub>5</sub> grade in the concentrate increased from 22% to 28.04%, while

the MgO content decreased from 2.88% to 1.44%, while achieving a 91.1% recovery of P<sub>2</sub>O<sub>5</sub>. Simultaneously, the grade of MgO in the floated fraction increased from 2.88% to 5.36%, and P<sub>2</sub>O<sub>5</sub> decreased from 22.14% to 9.82%. Conversely, when employing a higher collector concentration (1.0 kg/t) with an enzyme dose of 0.45 kg/t, the P<sub>2</sub>O<sub>5</sub> grade in the concentrate still increased from 22% to 28.17%, and the MgO content decreased from 2.88% to 1.48%, while maintaining a 90.7% recovery of P<sub>2</sub>O<sub>5</sub>. However, no significant improvement in the flotation behavior was observed.

Hence, the subsequent flotation experiments will utilize the lower collector concentration (0.5 kg/t) to mitigate the presence of organic matter in the flotation system. These findings underscore the enzyme's effectiveness as a depressant for phosphate-containing minerals, while carbonates remained unaffected. Nevertheless, the obtained concentrate still contains more than 1% MgO, rendering it unsuitable for the phosphoric acid industry. Subsequent sections will delve into factors influencing enzyme activity, aiming to reduce the MgO content in the phosphate concentrate.

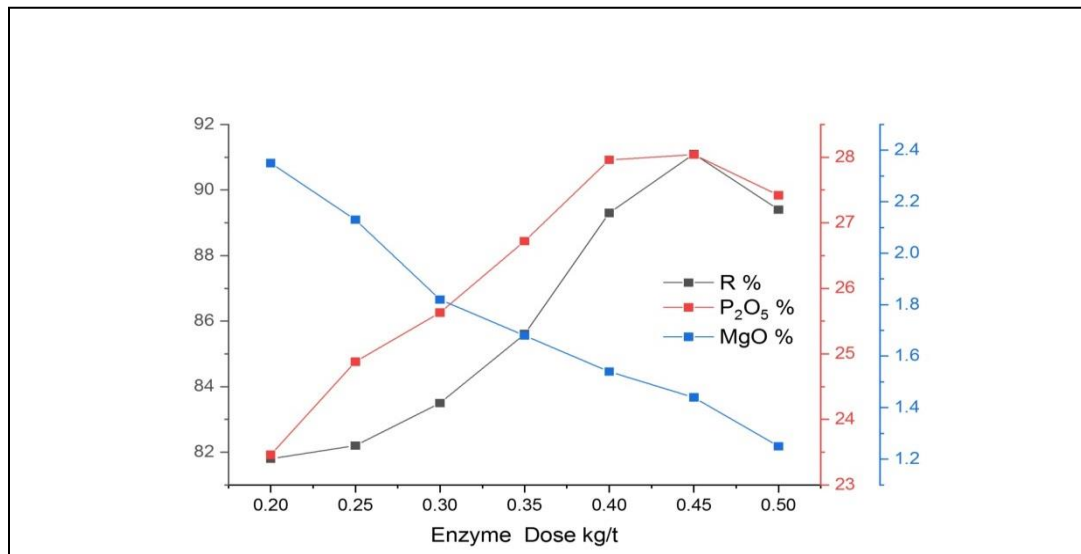


Figure (5):- Effect of enzyme dose on phosphate flotation using 0.5 kg/t collector.

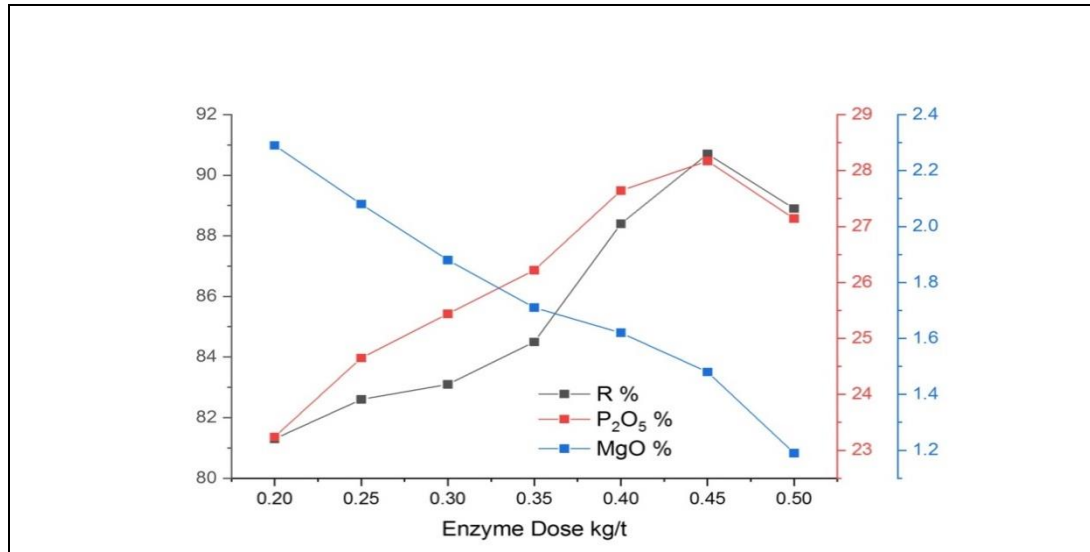


Figure (6):- Effect of enzyme dose on phosphate flotation using 1.0 kg/t collector.

### *Effect of Solution pH:*

The pH level within the system exerts a significant influence on enzyme activity, a phenomenon well-documented by Peterson [33] and Champe and Harvey [34]. The concentration of H<sup>+</sup> ions plays a pivotal role in affecting reaction velocity through various mechanisms. Firstly, the catalytic process typically necessitates specific chemical groups of the enzyme and substrate to be in either an ionized or unionized state to facilitate interaction. Secondly, extremes in pH can induce enzyme denaturation because the structural integrity of the catalytically active protein molecule hinges upon the ionic characteristics of the amino acid side chains.

Furthermore, each enzyme possesses a distinctive pH range where its

activity is most pronounced. For some enzymes, these optima are relatively precise, while for others, they encompass broader pH ranges. The impact of pH on enzyme activity is elucidated in Figure (7), with the utilization of a minimal enzyme dose of 0.3 kg/t and an oleic acid/kerosene collector (0.50 kg/t). Notably, the enzyme exhibits limited activity at pH 6.5, with activity showing a rapid increase beyond this pH point.

It is evident that the most effective separation is achieved at pH 8.5, where phosphate recovery exceeds 90%, accompanied by a MgO content of 1.29% and P<sub>2</sub>O<sub>5</sub> reaching 29.53%. Conversely, the tailing product contains more than 5.37% MgO. Consequently, pH 8.5 has been selected as the optimal pH for conditioning with the enzyme.



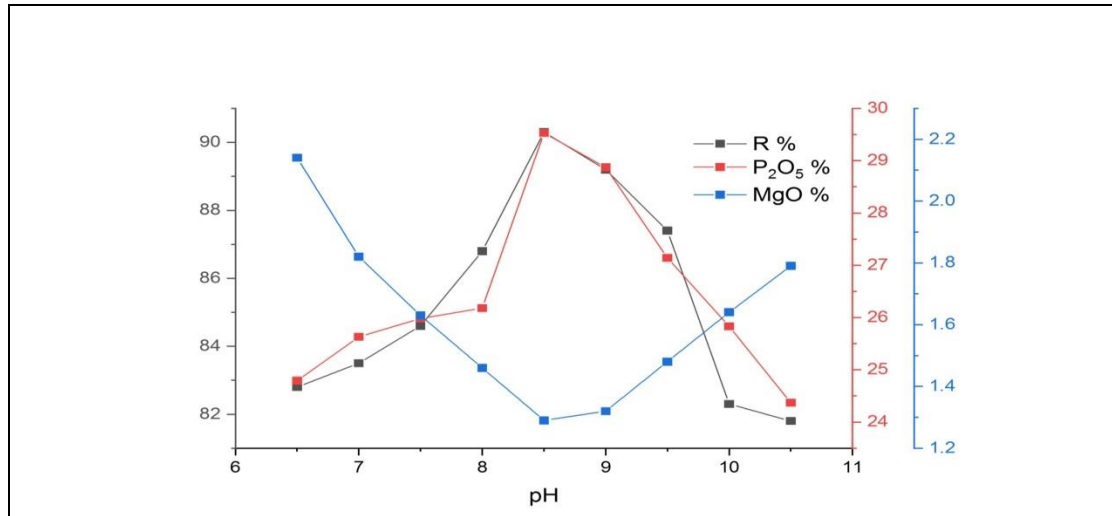


Figure (7):- Effect of pH on phosphate flotation.

**Effect of Temperature:**

Enzyme activity is profoundly influenced by temperature, primarily due to the proteinaceous nature of enzymes. At the higher end of the temperature spectrum, thermal denaturation of enzyme proteins becomes evident. Heat can affect enzymes in two distinct ways. Firstly, it can lead to inactivation as elevated temperatures induce denaturation of the enzyme proteins, resulting in the loss of their catalytic properties. The specific temperatures at which this inactivation occurs vary considerably depending on the particular enzyme. For instance, glucomylase remains effective at 60°C, while bacterial amylases require temperatures of 80°C or even higher for optimal activity. Secondly, temperature affects enzymatic reactions by influencing their rate. Similar to most chemical reactions, enzyme-catalyzed transformations experience an

accelerated rate as the temperature rises. However, in the case of enzyme reactions, increasing the temperature can lead to rapid thermal inactivation of the enzyme, counteracting the increased reaction rate resulting from the higher temperature.

Figure (8) presents the outcomes of heating the pulp on enzyme activity. In this series of experiments, the conditioning pH was set at 8.5, and a lower enzyme dosage of 0.3 kg/t was employed. At temperatures of 30°C and 40°C, the enzyme has a limited impact on the flotation separation. The highest enzyme activity was observed at a temperature of 50°C. Under these conditions, a concentrate featuring 0.94% MgO, a phosphate recovery of 89.6%, and P<sub>2</sub>O<sub>5</sub> content of 29.76% was attained. However, further temperature elevation results in a decline in flotation recovery using the enzyme protein, primarily

due to temperature-induced denaturation of the enzyme.

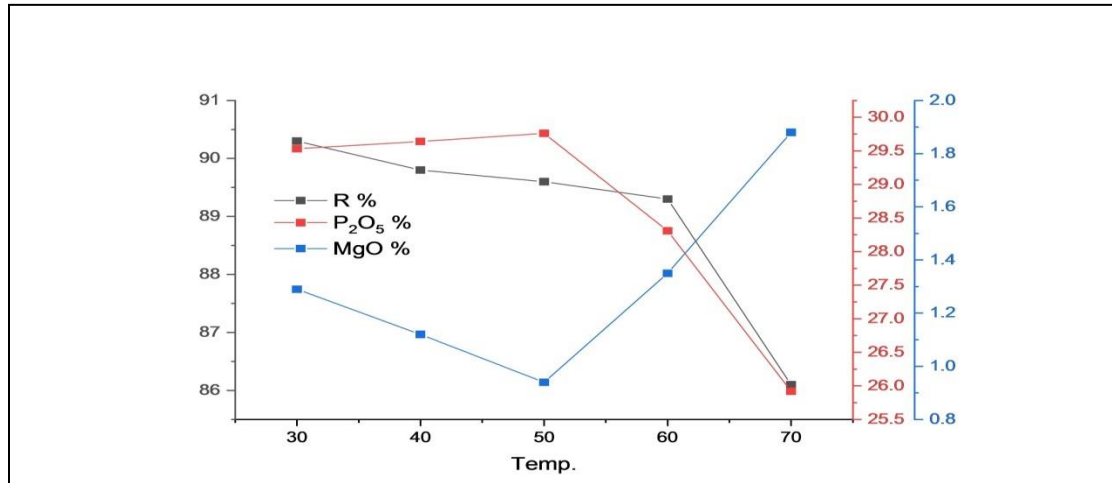


Figure (8):- Effect of temperature on phosphate flotation.

***Effect of Enzyme Conditioning Time with Enzyme:***

In many practical applications of enzymes, the reaction conforms to zero-order kinetics, as indicated by Reed [21]. In such cases, the quantity of product (p) generated is directly proportional to time (t), expressed as  $dp / dt = k_0$ . Consequently, time emerges as a crucial factor in practical enzyme applications, necessitating adequate time for enzyme reactions to progress towards completion.

Figure (9) illustrates the impact of conditioning time with the enzyme on the flotation behavior of the dolomitic phosphate sample under

predetermined conditions, which include a conditioning pH of 8.5 and a temperature of 50°C. It becomes apparent that time plays a pivotal role even when employing a lower enzyme dosage of 0.3 kg/t. Enzyme activation initiates at the 5-minute mark, reaching its optimal performance between 20 to 25 minutes of conditioning time. During this period, a phosphate concentrate featuring a P<sub>2</sub>O<sub>5</sub> content exceeding 30%, a phosphate recovery rate surpassing 88%, and MgO content registering at 0.74% and 0.78%, respectively, were achieved.



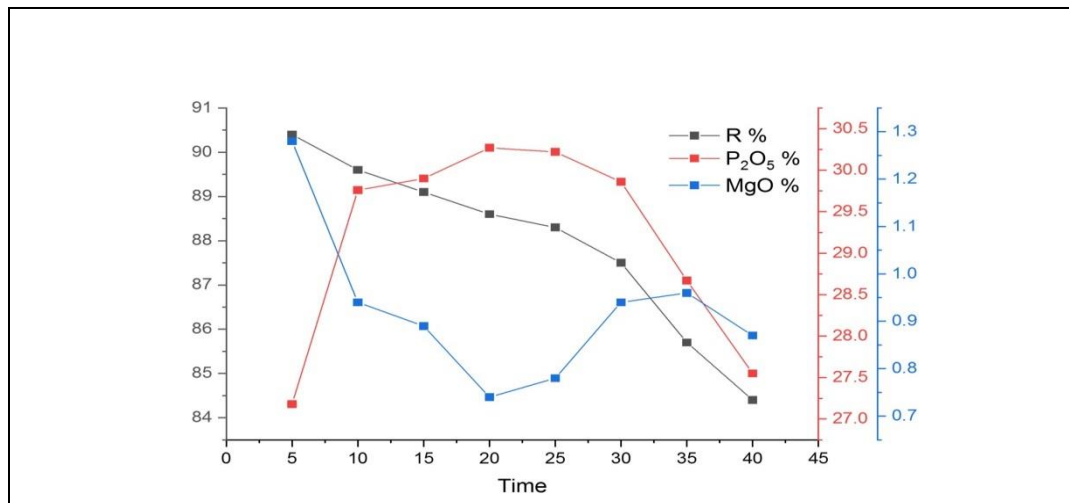


Figure (9):- Effect of enzyme conditioning time on phosphate flotation.

**Possible Mechanism:**

While enzyme molecules are predominantly adorned with hydrophilic functional groups, it is acknowledged that hydrophobic pockets exist on their surfaces, as

noted by Shaltiel [35]. These pockets are amenable to engagement with suitably sized hydrocarbon chains attached to an inert matrix, thus facilitating the formation of hydrophobic bonds.

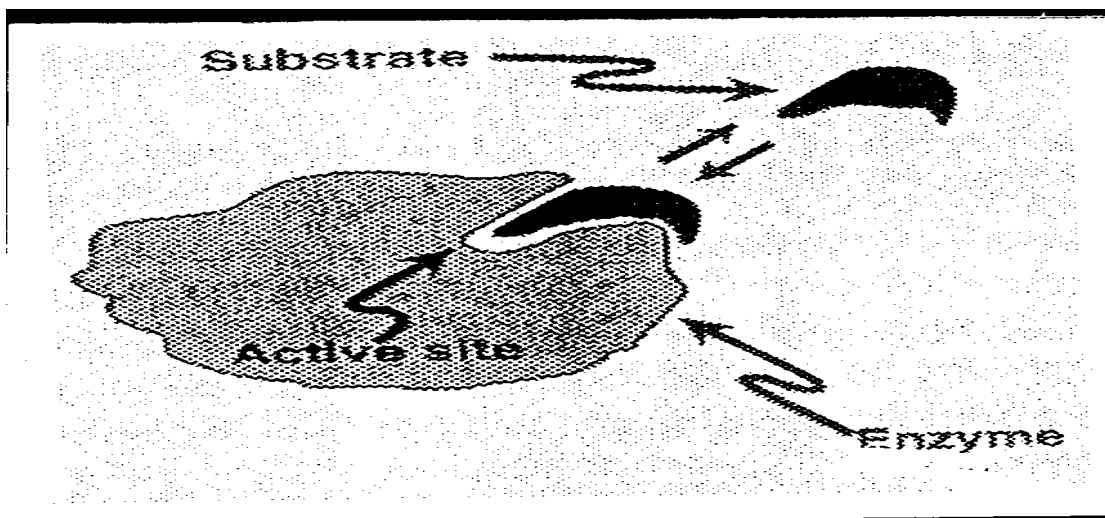


Figure (10):- Illustration depicting an enzyme possessing a single active site that binds to a substrate molecule, as described by Copeland [19].

Furthermore, it has been documented that forces operating within the enzyme's active site, encompassing interactions like hydrogen bonding, electrostatic forces, hydrophobic interactions, and van der Waals forces, play a role in aligning the substrate and enzyme reactive groups in the correct orientation for the reaction to occur. Consequently, it is postulated that a hydrophobic bond forms between the hydrocarbon chain of oleic acid (which is adsorbed onto the mineral surface) and a hydrophobic pocket located on the enzyme's surface, as illustrated in Figure (8). This interaction transforms the surface into a hydrophilic one due to the presence of hydrophilic groups on the enzyme surface. This transformation occurs specifically on the surfaces of phosphate minerals and not on dolomite surfaces. Consequently, the enzyme accommodates the oleate hydrocarbon chains differently on the phosphate surface compared to the dolomite surface, resulting in distinct conformations.

## **CONCLUSIONS**

This research showcases the prospective application of enzymes as surface modifiers to enhance the separation of dolomite and phosphate through fatty acid flotation. It was observed that the enzyme serves as an effective depressant for magnesium in phosphate minerals. Various factors influencing enzyme activity,

including enzyme dosage, solution pH, temperature, and conditioning duration, were investigated. Under optimal conditions utilizing a 0.3 kg/t enzyme dosage, it was achievable to obtain a phosphate product with a 0.74% MgO content, a P<sub>2</sub>O<sub>5</sub> grade of 30%, and a phosphate recovery rate of approximately 88.6%.

## **REFERENCES**

- [1] Yehia, A., Yassin, K., Amar, M. (2019). Upgrading of Phosphate Fines by fatty acids flotation using amylase enzyme as a surface modifier. *Min. Metal. Explr.* 36, 949-955.
- [2] P. Blazy, and E.A. Jdid. (1997). Removal of ferriferous dolomite by magnetic separation from the Egyptian Abu Tartur phosphate ore. *Int. J. Miner. Process.*, 49, 49-58.
- [3] Anonymous. (1986). Warren Spring Laboratory examines two phosphate rock beneficiation processes. *Phosphorous and Potassium*, 142, 35-37.
- [4] P. Blazy, R. Houot, R. Joussemet, and J. Tracez. (1981). Procédé d'enrichissement des minerais à gangues carbonatées et/ou silicates par des réactifs amphotères. *French Pat.* 81/00052.
- [5] P. Blazy, E.A. Jdid, and Acoca A. (1999). Combined use of flotation and separation on resin for magnesium removal from Djanatass phosphate (Kazakhstan). *Journal of Mining and Metallurgy*.
- [6] R. Houot, R. Joussemet, J. Tracez, and R. Brouard. (1985). Selective

flotation of phosphatic ores having a siliceous and /or carbonated gangue. *Int. J. Miner. Process*, 14, 245-264.

[7] L.D. Ratobylskaya, V.I. Klassen, N.N. Boiko, M.I. Bskakova, and Smirnov. (1975). Development and industrial introduction of new concentration process for phosphorites of complex mineral composition. 11th IMPC Simenar on Beneficiation of Lean Phosphate with Carbonate Gangue, Cagliari, 17-39.

[8] Abdel-khalek. (2001). Separation of dolomite from phosphate minerals by flotation with a new amphoteric surfactant as a collector, *Transaction of the Institution of Mining and Metallurgy, Section C, Vol. 110*, May-August, 89-93.

[9] J.E. Lawver,, W.O. McClintock,,and R.E. Snow. (1978). Beneficiation of phosphate rock. A state of the art. Review . *Miner. Sci. Eng.* 10, 278-294.

[10] R.E. Snow. (1979). Beneficiation of phosphate ore. International Mineral and Chemical Corp. of Northbrook. IL, U.S.Pat.No4, 144,969 (3.20.1979).

[11] P. Blazy, and E.A. Jdid. (1997) .Calcination of calcareous sedimentary Akashat Phosphate (Iraq) using a rotary kiln and a flash furnace. *C.R. Acad. Sci. Paris. Earth and Planetary Sciences*, 325, 761-764.

[12] W.E. Rushton, and W.R. Erickson. (1982). Nouveau procede d'elimination de MgO dans l'acide phosphorique, 32th Annual

Sympsium of fertilizer industry, Round Table, Atlanta, 5.

[13] Yehia, A., Abd El-Halim, S., Sharada, H., Fadel, M., Amar, M. (2021). Application of a fungal cellulase as a green depressant of hematite in the reverse anionic flotation of a high-phosphorus iron ore, *Minerals Engineering*.

[14] Rao, S. R. (2004). Surface chemistry of froth flotation, second edition, ed., Kluwer Academic /plenum publisher, New York, P. 33.

[15] Nunes, A.P.L., Pinto, C.L.L, Valadao, G.E.S., Viana, P.R.M. (2012). FLOATABILITY STUDIES OF WAVELLITE and preliminary results on phos[phorous removal from Brazilian iron ore by froth flotation. *Miner. Eng.* 39, 206-212.

[16] Veloso, C. H., Filippov, L.O., Filippova, I.V., Ouvrard, S., Araujo, A.C. (2020). Adsorption of polymers onto iron oxides: equilibrium isotherm. *J.Mater.Res.Technol.* 9, (1), 779-788.

[17] Zhang X., Gu, X., Han, Y. Parra-Alvarez,N. , Claremboux ,V., Kawatra,S.K. (2021). Flotation of iron ores : a review , *miner. Process. Extract. Metal. Rev.* 42, 184-212.

[18] Wills, B. A., Napier-Munn, T. (2006). MINERAL PROCESSING TECHNOLOGY, seventh ed. Elsevier Science &Technology Books, Amsterdam, pp. 267-352.

[19] P. Blazy, E.A. Jdid. (2000). Removal of magnesium from phosphates and phosphoric acid. Proceedings of the XXI International

Mineral Processing Congress, B10-1-B10-8.

[20] Boice, C., M. (2000). Selective adsorption and surface modification of apatite and dolomite by micro-organisms for the advancement of the phosphate flotation process, M.Sc. Thesis, University of Florida, Gainesville, Florida, USA.

[21] El-mahdy, A., M., El-Mofty, S. E., Abdel-khalek, N., A. and Abdel-khalek, M. A. (2003). The Role of Amphoteric Collector in Improving Flotation of Dolomitic Phosphates of Sedimentary Origin.

[22] R. Yaoyang, H. Ongsheng and C. Ruan, (2019). Review on Beneficiation Techniques and Reagents Used for Phosphate Ores Xingfa School of Mining Engineering, Wuhan Institute of Technology, Wuhan 430074, China, 9 (4), 253.

[23] Namita, Deo and K.A. Natarajan. (1997). Interaction of bacillus polymyxa with some oxide minerals with reference to mineral beneficiation and environmental control. Minerals Engineering, 10, 1339-1354.

[24] R.W. Smith, M. Misra, and J. Dubel. (1991). Mineral bioprocessing and the future, Minerals Engineering, 4, 1127-1141.

[25] R.W. Smith, M. Misra. (1993). Mineral bioprocessing, an overview, Mineral Bioprocessing, Edited by R.W. Smith, M. Misra, TMS, Warrendale, PA., 3-26.

[26] M. Misra, S. Chen, R.W. Smith, and A.M Raichur. (1993). Mycobacterium phlei as a flotation collector for hematite,

Minerals and Metallurgical Processing, 170-175.

[27] T.E. Furia. (1972). Handbook of food additives, 2nd Edition, 1, 32-35.

[28] A. Fiechter . (1992). Advances in bio-chemical engineering/biotechnology.

[29] G. Reed. (1966). Enzymes in food processing, Academic Press, New York, 428-432.

[30] E. Cohen, and N. S. Hammoud. (1972). Low temperature roasting in upgrading the nonoxidized phosphate of Abu Tartur Plateau (Western Desert, Egypt). In: D.W. Fuerstenau (Editor), Development in Mineral Processing. Thirteenth International Mineral Processing Congress, Warsaw, 1381-1388.

[31] A.A. Zatout, and M. Hussein. (1980). Investigation of Egypt's Abu Tartur phosphate deposit. Phosphorous and Potassium.

[32] Z. Lafhaj, L.O. Filippov, I. V. Filippova. (2017). Improvement of calcium mineral separation contrast using anionic reagents: electrokinetics properties and flotation, J. Phys.: Conf. Ser., 879 012012.

[33] M.S. Peterson, and A.H. Johnson. (1978). Encyclopedia of food science, 3, 427-432.

[34] P.C. Champe, and R.A. Harvey (1994). Biochemistry 2nd Edition. Lippincott J.B., Company, Philadelphia.

[35] S. Shaltiel. (1975). Hydrophobic chromatography, use in the resolution, purification and probing of proteins, Proceeding of the Tenth FEBS Meeting, 117-12 Bottom of Form