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Challenges & New Trends in Beneficiation of phosphate ores -Review Article

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ABSTRACT

The depletion of high grade reserves coupled with increasing market pressure for improved product quality has forced phosphate producers to re-examine their process flow-sheets and evaluate alternate or supplement processing routes. The world is rich in phosphate resources, but most of these resources are of middle and low grade ores, in the same time it is difficult to obtain high grade concentrate with high recovery using traditional separation methods. As a result of increasing complex mineralogy, steadily decreasing ore grades and ever increasing economic and environmental problems, the mineral processing industry over the past decade had to evolve appropriate means to beneficiate low grades phosphate ores deposits. Some of the important emerging trends and the evolutionary changes which have occurred in mineral processing technology are reviewed. New treating methods such as column flotation, nano-bubble flotation technique, application of amphoteric collectors, bio-processing, and application of surface modification using enzymes help to beneficiate low grade phosphate ores.

Introduction

Minerals resources are being depleted at faster rates than ever. These resources are finite; therefore, they must be used sparingly to ensure their availability for future generations. The extraction of valuable minerals from ores results in a wide variety of by-products. Some of these by-products contain residual minerals of commercial value. Many efforts are under way to minimize or reduce the tailings generated during the processing of ores and render the process more efficient and have a positive environmental impact and contributing to sustainable development. Therefore, the recovery of resources from processing wastes has attracted growing attention in recent year [1]. Phosphate rock is a primary source of phosphorous in fertilizers, and a phosphorous chemical product represents a vital non-renewable resource. It is neither substitutable nor recyclable in agricultural applications. While most of the phosphate resources cannot be directly treated as feed stock due to the low grade of P_2O_5 and high content of gangue minerals, as a result of the fact that each ore deposit has its own characteristics, each phosphate locality has its own beneficiation flow sheet to separate its associated gangues to for certain industrial application. The major associated gangue minerals are carbonates (dolomite, calcite, and ankerite), silicate minerals, and clays of ultra-fine particle size [2,3,4,5]. So to reach a good phosphate concentrate, the beneficiation methods and reagents become more extremely critical to achieve selective separation of phosphate minerals based on their chemical composition and texture of the origin sample. The high-grade phosphate ore will go through the wet process and pyrogenic process respectively, to obtain the intermediate products of phosphoric acid and phosphorus, which can be used to produce various phosphate fertilizers and phosphates generally, most of the phosphate ores contain valuable minerals in finely disseminated or in similarity in surface charge properties with the gangue minerals and this makes the recovery of these ores mineral particles exceedingly difficult [6].

1. Types of phosphate rocks

There are five major types of phosphate resources in the world [7, 8]

- Marine phosphate deposits.
- Igneous phosphate deposits.
- Metamorphic deposits.
- Biogenic deposits.
- Phosphate deposits as a result of weathering.

2. Upgrading Techniques for phosphates according to the ore type

1-Siliceous ores:

These ores contain quartz, chalcedony or different forms of silica. Such ores could be upgraded economically by such techniques as flotation or gravity separation methods.

2-Clayey ores:

These ores contain clays, hydrous iron and aluminum silicates or oxides as gangues and could be removed by simple beneficiation techniques such as scrubbing and washing. Dispersing agents should be added.

3-Calcareous ores of sedimentary origin:

These ores contain calcite and/or dolomite as the major impurities with small amounts of silica. It is usually difficult to remove the carbonate minerals efficiently from such ores by conventional techniques as flotation [9, 10] or by physical separation methods. Due to similarity in the physical properties of carbonates and phosphates, separation by physical means is difficult also; the carbonate minerals are finely disseminated into the phosphate particles.

4- Phosphate ores associated with organic matter, which sometimes called "black phosphates" [11].This type of ores is

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generally upgraded by heating up to about 800 °C. the organic material and the residual organic carbon are burned without significantly affecting the qualities of the sedimentary phosphates such as solubility and reactivity

5- Phosphate ores containing more than one type of the gangue minerals: all the sedimentary phosphate types contain mixtures of undesired constituents. These ores require series of upgrading operations depending on the type of gangue minerals.

(6) Igneous and metamorphic phosphate ores: The main gangue materials in these ores are sulfides, magnetite, carbonates (calcite, dolomite, siderite, and ankerite), nephelinesyenite, pyroxenite, foskorite, etc. Beneficiation of these ores may include, after crushing and grinding, washing, desliming, magnetic separation, and flotation depending on the types of gangue minerals present. However, flotation is a common step in all of them [12].

4. Beneficiation of Fine phosphate particles

In general when the gangue minerals are finely disseminated with the valuable minerals, a high degree of grinding is required to reach the liberation size causing fine particles problems. Also, during mining and transport operations fines can be produced. As a result of the losses of mineral and metal values in the fine size range, considerable interest is growing in developing new processes and in improving old processes for the recovery of fine particles. Standard physical separations are made in mineral processing plants utilizing differences in physical properties of desired and gangue minerals. Therefore, it is imperative to first of all discuss about the size limits of standard separation methods.

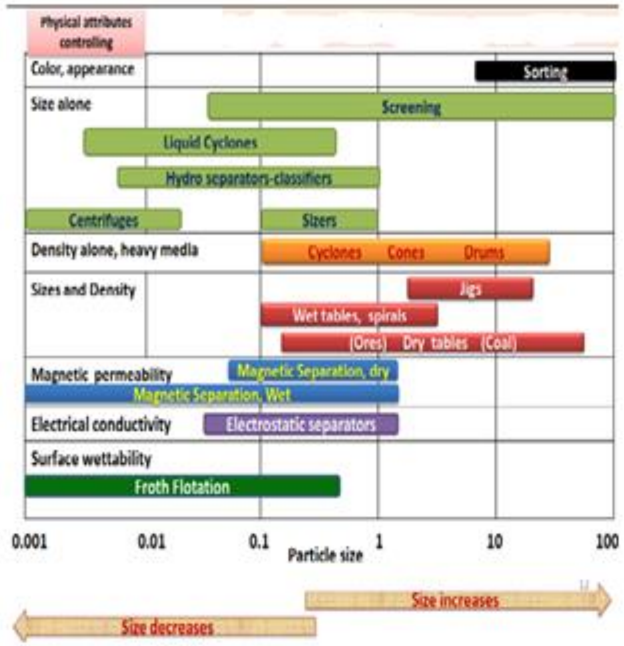

Fig 1. Effective size range of application of conventional mineral processing techniques

Fig.1 shows the general size range applicability of unit concentration processes. It is evident that most mineral processing techniques fail in the ultra-fine size range. One of the most important concentrating techniques, flotation is now practiced successfully below 10 µm but not below 1 µm [13]. However, flotation problem of fines was solved using modified flotation cells such as column flotation.

The conventional view of the flotation size recovery curve is shown in Fig. 2. It shows that flotation is not recommended in fine range. Accordingly, operators carefully avoid over grinding of the feed because of the extremely complicated physico-chemico-mechanical conditions found in the flotation method. There is a general agreement that flotation decreases with a decrease in particle size in the fine particle range [14]. It was proposed that particles with diameters less than 100 µm size, very fines those less than 20 µm, and ultra-fines the ones less than 5 µm. But particles length 1 µm in size, belong to the colloidal size range.

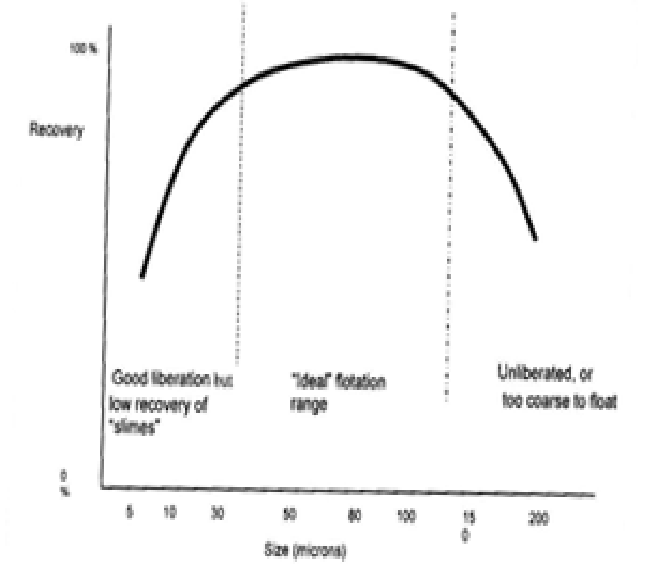

Fig 2. Typical recovery versus size curve.

Due to the small mass and large surface area of fines, various problems affect their separation including; high reagent consumption, excess froth stability, low adhesion probability, higher dissolution, rapid oxidation, and non-specific collector adsorption. Generally, slimes float more slowly than particles of intermediate size, Fig.3. [15, 16]. The marketable phosphate is usually 30% P_2O_5 or higher. The run-of-mine material is mostly of lower grade which needs processing or upgrading. The processing techniques of phosphate ores depend mostly on the type of associated gangue minerals present in the mined rock. In some cases, simple, inexpensive techniques are enough to produce the required grade. For example, crushing and screening is used to get rid of the coarse hard siliceous material, and attrition scrubbing and desliming is used to remove the clayey fine fraction. If silica is the main gangue material, single-stage or double-stage flotation is the conventional mineral processing technique used in this case. If the ore is igneous carbonatitic alkaline or ultra-basic phosphate deposit, crushing, grinding, scrubbing, and flotation associated with other steps such as magnetic and/or gravity separation is proved to be successful in upgrading this type of ores. [17].

The sedimentary phosphate ores having carbonate-apatite as the main phosphate minerals and containing carbonates (calcite and/or dolomite) represent a challenge in the field of phosphate concentration due to similarity in the physico-chemical properties of the ore surfaces constituents, [18]. During flotation of carbonaceous phosphate ores; apatite, calcite and dolomite will dissolve in water producing dissolved species. These dissolved species can have a harmful effect on interfacial properties of both phosphate and carbonate minerals. New flotation systems are being developed to treat these challenging phosphate ores to produce a high-grade phosphate, to improve the phosphate recovery and enrichment efficiency product suitable for fertilizers and other phosphate compounds [19, 20].

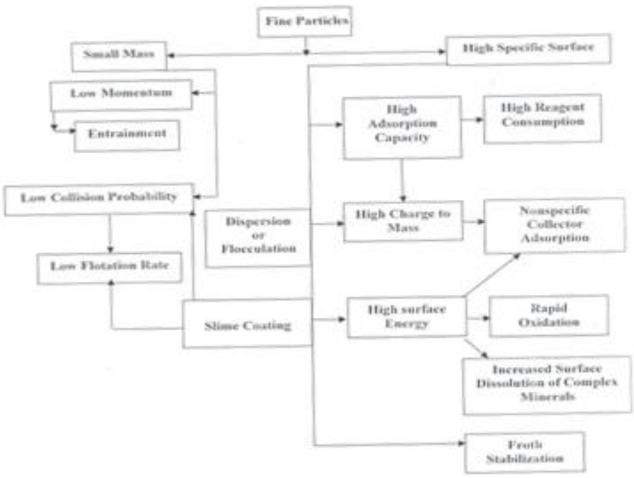

Fig 3. Problems of fine particles separation

5. Effect of Nanobubble on Flotation of Fine and Ultrafine Particles

From Figure 4 the effect of nanobubbles on the surface of the particles make activation for the flotation through promoting the attachment of larger bubbles where the attachment between nanobubbles and conventional size bubbles is more than bubble/solid attachment. i.e. nanobubbles act as a secondary collector for particles, reducing flotation collector dosage, increase particle attachment probability and reducing the detachment probability. This leads to substantially improved flotation recovery of poorly floating fine and ultrafine particles. The potential of cavitation generated picobubbles in improving fine particle froth flotation recovery has been demonstrated by tests on fine silica [21], inserting a cavitation tube with addition of small amount of air in the feed stream (0.15 l/min) showed a significant increase in fine silica recovery from 30% to 52%. The results were better than using a static mixer in the feed stream. A similar conclusion was reached by [22]. The advantage of cavitation generated pico-nano bubbles incorporating with conventional size bubbles in flotation has been explained by two factors that contribute to the increased flotation rate constant: a) the pico-nano bubbles formed in situ on hydrophobic particles may cause flocculation by a bubble-bridging mechanism, resulting in increasing the collision probability with the bubbles; b) particles frosted with pico-nano bubbles may present a surface favorable attachment to flotation sized bubbles [23]. Besides, generating nanobubbles by hydrodynamic cavitation revealed that the energy dissipation levels for cavity formation in a flowing liquid could be much lower than predicted, depending on the content of dissolved gases, presence of free gas nuclei and design of cavitation tubes [24].

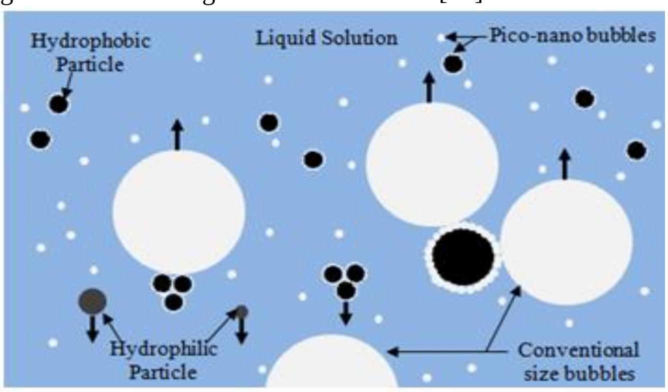

Fig 4. Effect of pico-nano bubbles on coarse, fine and ultrafine particles

6. Application of Column Flotation Technology to Beneficiate low Grade Fine phosphate ores.

Fine phosphate particles flotation is traditionally accomplished with conventional stirred tank flotation machines. Long flotation times are generally required to achieve the desired separation of fine particles. As a result the capacity of a plant is reduced and large floor space is required**.** In conventional flotation and due to the small mass and momentum of fine particles, they may be carried into the froth after getting either entrained in the liquid or mechanically entrapped with particles being floated. The column has proved particularly attractive for cleaning applications and can achieve in a single stage upgrading comparable to several stages of mechanical cells, often with improved recoveries. Because of the efficient cleaning action, flotation columns can upgrade a fine sized concentrates in a single step, where conventional flotation machines would require several sequential stages. Flotation columns offer improved metallurgy, simplified circuits and easier control compared to conventional cells. Fig.4. the fine particles, in conventional flotation cell, are carried into the froth as mechanical carry over in layers of water attached to air bubbles. When such particles are of gangue minerals, the effect is the reduction of the concentrate grade. Also, the large specific surface area of fine particles increases the adsorption capacity of reagents when considered on a mass basis.

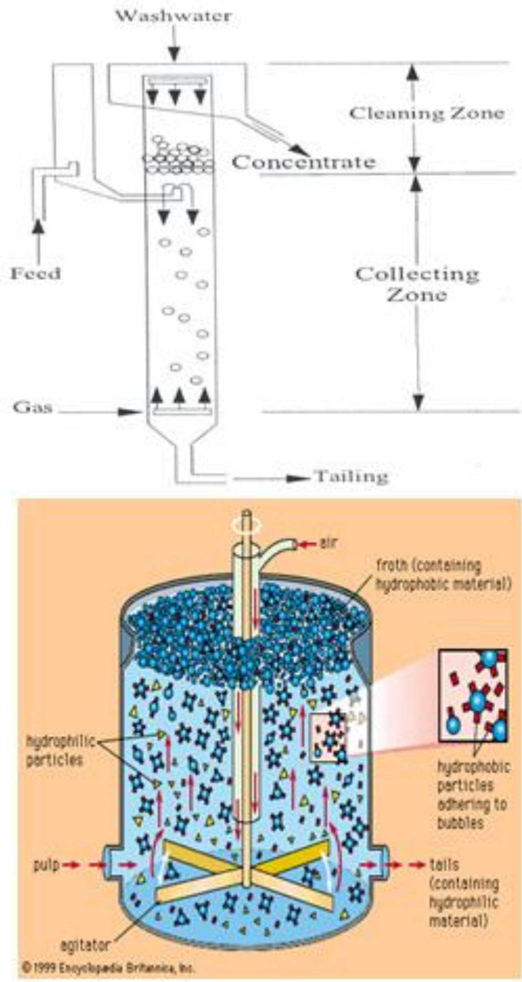

Fig 4. Column flotation cell and Denver Flotation cell

The column holds several distinct advantages over conventional flotation such as the following

- More quiescent separation conditions due to the lack of turbulence caused by mechanical impellers.

- Capability to produce high grade concentrates by employing.

i. Wash water additions to the froth.
ii. Increased froth depth.
iii. Counter current flow of bubbles and pulp.

- Increased energy efficiency.
- Decreased floor space requirement.
- Natural adaptability to the computer control because the control is based on flows into and out of the column.
- Producing small-bubbles can carry fine and ultra-fine particles:. There are different ways to generate small bubbles: using dissolved air flotation, picobubbles, electroflotation, and colloidal gas aphrons [25, 26, 27, 28]. For example, in beneficiation of Saudi phosphate ores by column flotation technology a concentrate with 35%, P_2O_5, 95% recovery and a lower $CaO:P_2O_5$ ratio of 1.53 was obtained from a feed containing 25% P_2O_5 and $CaO:P_2O_5$ 2.1 [29].

7. New Trends to Beneficiate Low Grade Phosphate Ore

7.1. Application of Amphoteric Collectors

Dolomite-phosphate separation was investigated using amphoteric collector (dodecyl-*N*-carboxyethyl-*N*-hyroxyethyl-imidazoline) in presence of bacteria. Two types ofbacteria,Corynebacterium-diphtheriae intermedius (CDI), and Pseudomonas aeruginosa(PA), were used. The collector-bacteria interaction shows improving in the flotation selectivity. Phosphates concentrate of 0.7% magnesium oxide and 31.77% P_2O_5 with a recovery of 68% at the optimum conditions [28]. Besides, the amenability of carbonate separation from Abu-Tartur phosphate ore, through flotation process, using either sodium oleate or a new amphoteric collector for flotation of dolomite was obtained. For oleate-microorganisms system, a concentrate containing 0.78 % magnesium oxide and 30.15 % $P_2O_5$with a recovery of 92.31% was obtained from a feed containing about 2.45 % magnesium oxide and 27 % P_2O_5. For amphoteric-microorganisms system, a concentrate containing 0.69 % magnesium oxide and 30.72 % P_2O_5 with a recovery of 80.15 % was obtained [30].

7.2. Application of Surface Modification using Bacteria.

In this case, the bacteria are used to modify the mineral surface through adsorbing onto particles surfaces make one of them more hydrophobic and the other hydrophilic.

For example; the cell walls of both M.phlei and B.licheniformis JF-2 were tested for flotation of Florida phosphate pebble. It was shown that M. phlei was markedly adsorbed on the dolomite and apatite surfaces. The bacterium demonstrated more affinity towards dolomite than apatite, and that B. licheniformis JF-2has even more affinity than M.phlei for adhesion onto dolomite. Flotation tests revealed that both bacteria act as a depressant of dolomite during phosphate flotation using anionic collectors. Using these bacteria a flotation concentrate with less than 1% magnesium oxide content can be obtained from Florida phosphate pebble flotation [31].

In another study two types of bacteria were tested in beneficiation of carbonaceous phosphate ore. Flotation experiments were carried out using statistical designs for optimizing the main operating parameters. The main parameters used in this study were micro-organism concentration, pH and collector dosage. The optimization process was conducted using rotatable central composite design (RCCD) as a tool for optimization. The design results showed that selective separation of carbonate from phosphate can be obtained using bacteria. An optimum conditions, concentrate containing 0.7% magnesium oxide and 31%P_2O_5 with recovery of 93% can be obtained [32].

In another study bio-beneficiation using bacteria adapted from the phosphate surface for removal undesirable gangue minerals from the desired valuable phosphate minerals. A concentrate with 18.5% P_2O_5 and 33.03% SiO_2has been obtained from a binary mixture having11.65% P_2O_5 and SiO_2 40.98 %. At optimum conditions on natural phosphate ore containing 21.89%, a concentrate with 27.2 % P_2O_5 has been obtained using Bacillus cereus bacteria [33] Also, Using Desulfovibrio desulfuricans bacterial isolate during flotation of another phosphate rock a concentrate contains 98 % P_2O_5 and 2 % SiO_2 with a recovery of 70% could be obtained from a mixture containing 90 % by weight apatite and 10% by weight silica. Applying the same conditions on a natural phosphate rock, a concentrate containing 30 % P_2O_5 and 10 % SiO_2 with 68 % recovery was obtained from a feed containing 20.52 % P_2O_5 and 23.51 % SiO_2 [34].

7.3. Application of Surface Modification using Enzymes

Enzymes are a group of biological macromolecules. All known enzymes are proteins. They are high molecular weight compounds made up principally of chains of amino acids linked together by peptide bonds. Enzyme molecules are coated mostly with hydrophilic functional groups and it is understood that they have hydrophobic pockets on their surfaces, Fig.5. These pockets are available for interaction with appropriately sized hydrocarbon chains, implanted on an inert matrix, forming hydrophobic bonds However; enzyme can form either hydrogen bonds or ionic interaction with oleic acid containing hydrocarbon chain either in solution or on mineral surface, Figs.6 &7. This hypothesis was used in the flotation separation of some minerals commodities.

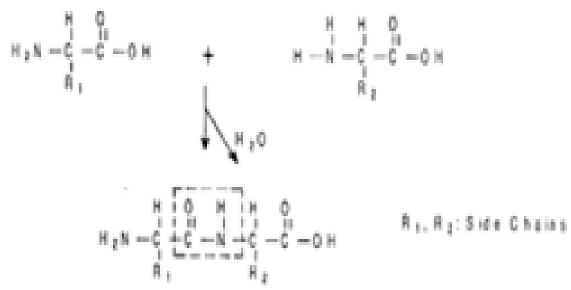

Fig 5. Typical protein structure-two amino acids joined by peptide bond

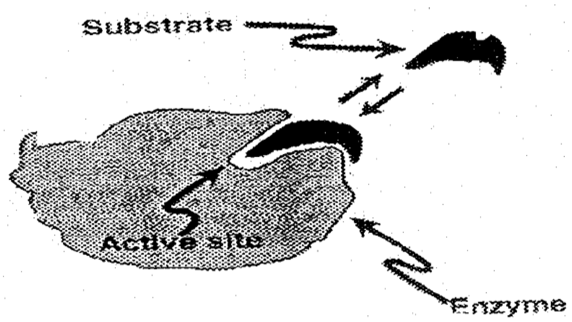

Fig 6. Schematic representation of an enzyme with one active site binding to a substrate molecule

It was found that enzyme functions as a depressant for phosphates during flotation of calcareous phosphate ore, [34]. At optimum conditions of enzyme dosage, solution pH, temperature and conditioning time, and in the presence of 0.03 kg/t enzyme, a concentrate containing less than 0.60% MgO and 29.5% P_2O_5 with P_2O_5 recovery of about 94% was obtained, [34]. Cellulase enzyme was used in the flotation of the calcareous phosphate ore. Under the optimum flotation conditions, 0.04% cellulase and $5x10^{-3}$ M oleic acid, a phosphate concentrate containing 0.89% MgO with P_2O_5 recovery of 75% was obtained from the phosphate ore containing 2.2%MgO,[35] .Besides, the amylase enzyme was used in the flotation of phosphate fines. At the optimum conditions of 0.25% enzyme dose, and 0.05M oleic acid, a phosphor-concentrate contain 29.22% P_2O_5, 0.57% MgO, 11.70% SiO_2 was obtained from a feed sample contains 18.27% P_2O_5, 1.78% MgO, and 17.56% SiO_2 [36,37].

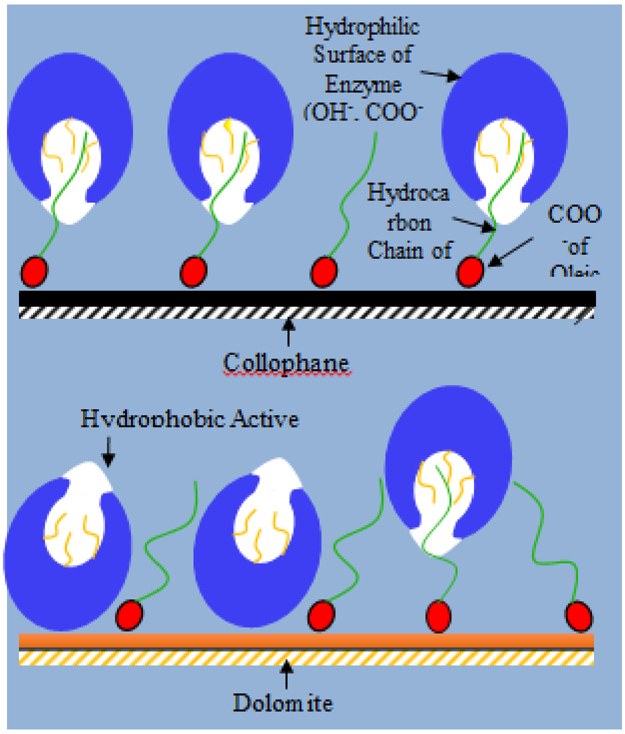

Fig 7. Schematic diagram for the probable mechanism of the interaction of oleic acid and enzyme on the mineral surface [35]

8. Conclusion

- Beneficiation of low grade phosphate ores is very important subject, especially with the rapid decrease of the high grade ores.
- Conventional methods give better results when the liberation between valuable and gangue impurities in relatively coarse particle size
- Similarity of surface properties and fine disseminated gangues are the most challenging obstacles in phosphate ore beneficiation.
- The new trends in mineral beneficiation technologies offer reasonable results in beneficiation of low grade phosphate ores.
- Application of amphoteric collectors was used in dolomite-phosphate separation and get better results.
- The bacteria and enzyme are used to modify the phosphate surface through adsorbing onto particles surfaces make one of them more hydrophobic and the other hydrophilic and considered a best methods for beneficiation of low grade and fines in the same time.
- The drawbacks of bio-beneficiation methods that are in laboratory scale.

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