Egyptian Knowledge Bank
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International Journal of
Materials Technology and Innovation
Volume 4, Issue 1 (2024), pages 80-96

IJMTI
Online ISSN 2682-4299

New Challenges in Upgrading of Difficult-to-Treat Ores: A review

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Received ……4 December 2023
Accepted …..10 May 2024
Published ….10 May 2024

Abstract

A significant challenge for mineral processing is to design new economic process options for the beneficiation of difficult-to-treat ores. Ore beneficiation industry in the last periods over many solutions to beneficiate these difficult-to-treat ores to be suitable for industrial applications. Most techniques of mineral beneficiation were reviewed. These include; the design of new devices, the development of new flotation machines, and the design and testing of new flotation reagents. In this article, the challenging areas of current research efforts have been highlighted. Some important difficult-to-treat such as phosphate rocks, iron ores, coal, and kaolin ore have great difficulties in their beneficiation. New treatment methods such as bio-processing, high gradient magnetic separators, and different types of falcons that help to beneficiate these difficult-to-treat ores have been discussed.

Keywords: Challenges, Difficult-to-treat Ores, Phosphate Ores, Iron Ores, Flotation

1. Introduction

Maximum utilization of natural resources for different industrial applications is becoming a key issue in all countries for sustainable development. High demands are made for raw materials. Specifications of raw materials for certain industrial applications are sometimes, very stringent in terms of particle size, chemical analysis, color, brightness, and viscosity. However, suitable beneficiation methods for difficult-to-treat ores are needed to satisfy the market specifications. Improving the technical specification of such natural resources will not only result in rationalization of such resources but also, in improving the quality of the end products and enhancing their competitiveness in the world market.

as a result of a complex mineralogy due to formation conditions and the effect of the weather during the formation of ores, the gangue minerals were found in finely disseminated form and became difficult to treat, in this case, the conventional processing techniques are not suitable for treating this kind of ores for example separation of titanium from kaolin ores, phosphorus from iron ores and manganese from iron ores. In another type, the difficulty is related to the similarity in the physio-chemical properties such as separating dolomite from phosphate.

Beneficiation of these ores became difficult to treat and required new alternative beneficiation methods to beneficiate them to be ready for industrial applications.

In the future, beneficiation of difficult-to-treat ores will be looking for high-performance processing technologies. Innovations on technological processes for ore utilization should be conducted to produce high-grade concentrates with higher added value.

Most ores can be easily treated by conventional methods in case of high liberation size, and difference in the surface properties. The successful beneficiation difficult to treat ore requires attention to the following matters.

- Beneficiation of finely disseminated particles.
- Separation of minerals with similar physico-chemical properties.

1.1 Beneficiation of finely disseminated particles

When the impurities are finely disseminated in the

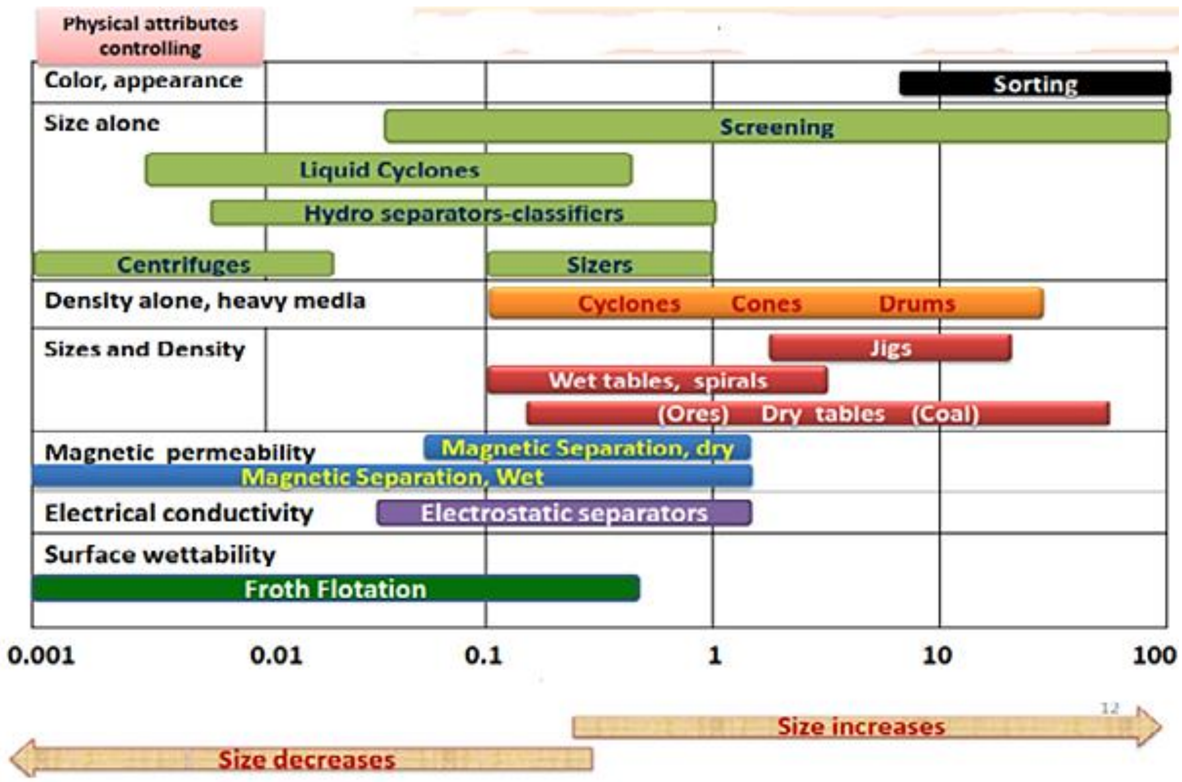

Fig. 1 Effect of particle size distribution on applying conventional mineral processing techniques

crystal structure of the ores they should be finely ground to reach the liberation size, however, at the same time, problems of fine particles appear. Figure 1 shows that with lowering particle size, the most mineral processing techniques are unsuitable. Flotation, one of the most important beneficiation techniques, is now practiced successfully below 10 µm but not less than 1 µm, [1]. However, the flotation problem of fines was solved using advanced cells such as column flotation and new collectors and depressants [2]

1.2 Problems of Fine Particles Flotation

Figure 2 shows that flotation has an ideal range for application, but its yield is low. Accordingly, operators carefully avoid over-grinding of the flotation feed., [3]. Fines are particles with diameters < 100 µm size, very fine those < 20 µm, and ultra-fines the ones < 5 µm. But particles length of 1 µm are colloids. various problems affect their separation such as excess flotation reagent addition, high froth stability, less adhesion, higher dissolution, speed of oxidation, and low selectivity. generally, slimes float slower than intermediate particles size Fig. 3 [4,5].

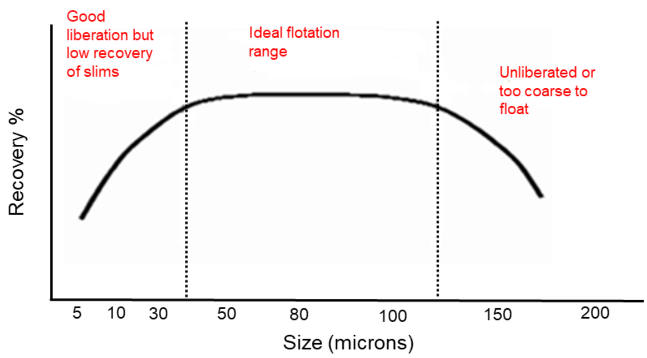

Fig. 2 Flotation size-recovery curve [4]

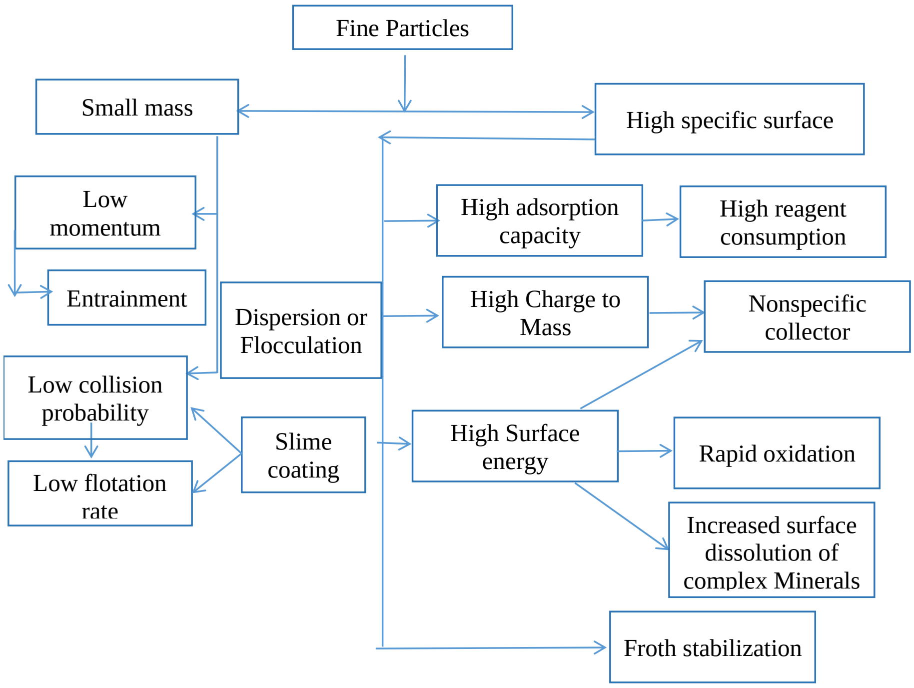

Fig.3. Fine particle separation problems.

1.3. Column Flotation Technology Application in Beneficiation of Difficult-to-treat Fine Particles

In general flotation of fines requires a long time. So, a large tank capacity is preferred. Column flotation achieves this in one single stage after conditioning with the reagent. Compared with other methods that require many stages, the process is very simple and short. Figure 4 shows that the particles are carried out in layers attached to the bubbles. Also, a significant quantity of reagent is consumed on the surface of small particles. The main disadvantages of the conventional flotation process operation are its cost, low recovery, and reagent consumption [6].

Advantages of column flotation:

- Best separation conditions
- Producing high-grade concentrates
- High-efficiency separation
- Natural adaptability to the computer control

In the case of Saudi Arab phosphate ores using column flotation, a concentrate containing 35%, P_2O_5, with 95% recovery and CaO/P_2O_5 equal to 1.53 was obtained from a feed containing 25% P_2O_5 and CaO/P_2O_5 2.1 [7].

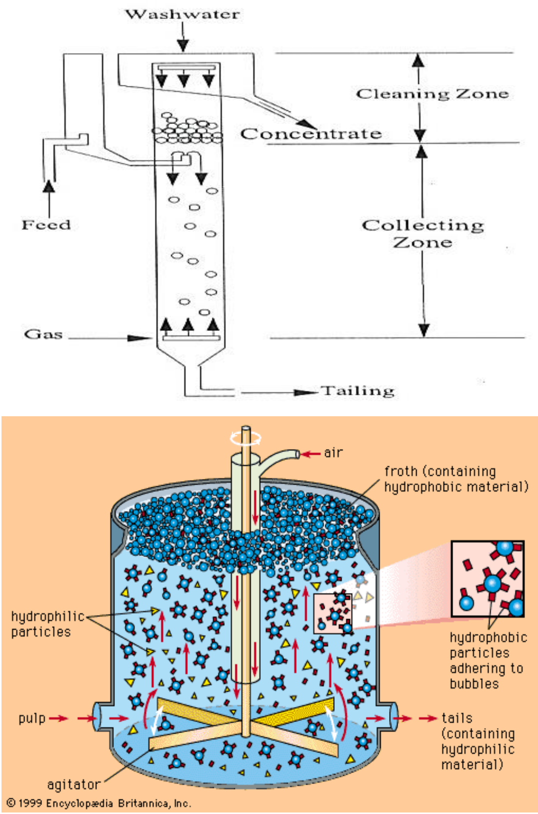

Fig. 4. Column and Denver Flotation cells.[6]

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1.4. Separation of minerals with similar physicochemical properties

As a result of the similarity in surface properties of some ores, various flotation techniques were used. Also, interactions of dissolved ions from other minerals in the pulp. In the present time, beneficiation of poor ores become very important due to depletion of rich ores using flotation techniques. There are many examples such as salt-type minerals separation dolomite from apatite, oxide minerals such as separation of iron oxide from manganese and separation phosphorus from iron oxide. This similarity is related to the mineralogy formation and can be detected from physicochemical measurements such as zeta potential and adhesion measurements.

Recently, bio-processing has become a very important branch in the mineral beneficiation sector as a result of low operating costs and being environmentally friendly [8, 9].

2. Examples of Difficult-to-Treat Ores

2.1. Beneficiation

The best grade should be more than or equal to 30% P_2O_5. Generally, the crude ores are low grade and need beneficiation to be applied in different industrial applications. the beneficiation techniques depend on the mineralizable formation of the ores. Some can be upgraded using crushing and screening others use attrition scrubbing, flotation, magnetic separation etc. according to these mineralogical compositions. [10].

The sedimentary phosphate rocks having carbonate-apatite is a great challenge because surface properties are similar [11]. Flotation of these types the dissolved species have a great effect on interfacial properties between valuable and gangue impurities. New techniques and reagents are developed for producing high-grade phosphate concentrate, suitable for many industrial applications [12, 13].

2.1.1.1. Amphoteric Collectors Application

Using an amphoteric collector with two types of bacteria. were used. The collector-bacteria interaction selectivity increased and a phosphate concentrates of 0.7% MgO and 31.77% P_2O_5 with 68% recovery at pH 11, using 3.0 kg/t collector dose and 4×107 cells bacteria [10]. Other authors improve selectivity through bio-flotation process, a concentrate contains 0.78% MgO, 30.15% P_2O_5 with a recovery of 92.31% from a feed containing 2.45% MgO and 27% P_2O_5. [11].

2.1.1.2. Application of Bacteria

Adsorption of bacteria on the mineral surface changes its electrical surface properties making one of them more hydrophobic and the other hydrophilic.For example; two types of bacteria were examined for the flotation of Florida phosphates. It was shown that two types adsorbed on the dolomite surface more than apatite and make as a depressing agent for dolomite. During anionic flotation of the phosphate [14]. Another author tests two types of bacteria in the processing of carbonaceous ores using statistical designs for optimizing the main operating parameters. The results showed that selective separation of apatite a concentrate containing 0.7% magnesium oxide and 31% P_2O_5 with distribution 93% at pH 5.5, 108 cells numbers and a collector dosage 2 kg/ t [15,16,17,18].

2.1.1.3. Enzymes Application

Enzymes are group of biological macromolecules composed of proteins with high molecular weight and contains hydrophilic and hydrophobic pockets on their surfaces, Fig.5. the interaction with hydrocarbon chains, implanted on an inert matrix, forming hydrophobic bonds However; hydrogen bonds or ionic interaction with oleic acid occurred on the mineral surface, Fig.6 & Fig.7. This. [19,20,21].

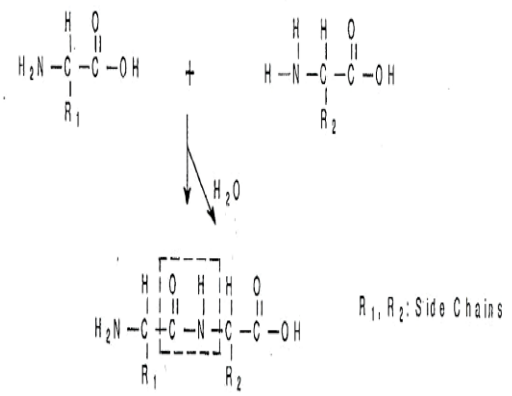

Fig.5. Shape of two amino acids [21].

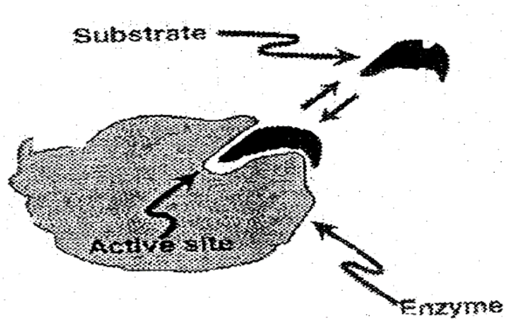

Fig.6 An enzyme binds to a substrate molecule [21]

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In a study and at best working conditions, a phospho-concentrate containing less than 0.60% magnesium oxide and 29.5% phosphorus pentoxide with recovery of 94% [21]. Also, Cellulase was used during the flotation of calcareous phosphate ores. At the optimum conditions, a concentrate containing 0.89% magnesium oxide with P_2O_5 recovery of 75% was obtained from the origin containing 2.2% magnesium oxide,[22]. Besides, the amylase was used in the flotation of phosphate fines. At the optimum condition, phosphor-concentrate contains 29.22% phosphorus pentoxide, and 0.57% magnesium oxide, from feed sample contains 18.27 phosphorus pentoxide, 1.78% magnesium oxide [23].

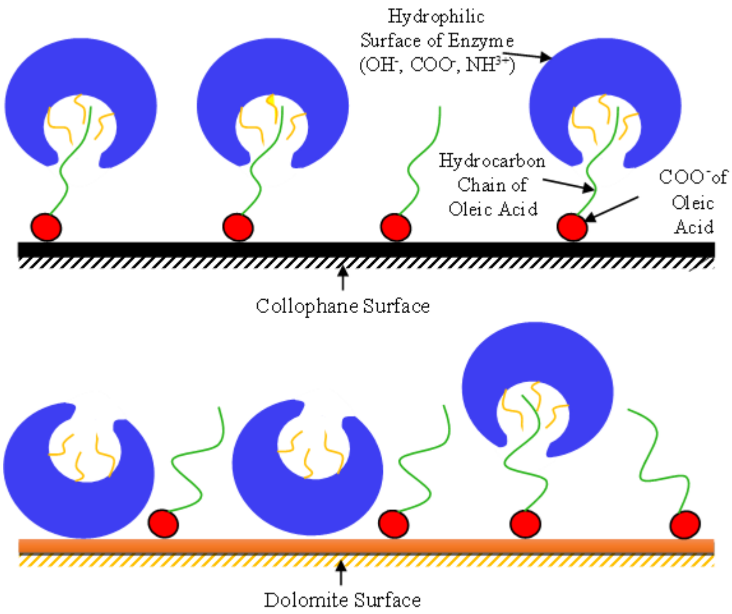


Fig.7 Oleic acid and enzyme on the mineral surface [21]

2.2. Beneficiation of Difficult-to-Treat Iron Ore

Iron ore is used, almost in the production of crude steel. Many new developments are underway in iron ore processing and steel manufacture. As a result of lowering high-grade ores, it is important to treat poor ores. This will require removing impurities to be suitable for industrial specifications. So, improving the system of processing is required to overcome this challenge and improve low grade ores. This system has to be more efficient than the existing one to ensure the same rate of production and continue to meet export demands.

Simple processing methods of some iron ores as crushing, screening, and washing are required, and more efficient beneficiation techniques to enhance quality for efficient blast furnace operations also are required. The Egyptian iron ores in general contain various.

difficulty in separation related to similarity in surface properties and fine dissemination, resulted from geological settings, which cause great problems during magnification Fig 8, 9. [24, 25, 26, 27].

Such as aluminum, phosphorus, Manganese, silica, and this poses major beneficiation problems especially in the fines processing range.Presence of phosphorus and manganese are great challenge in the iron ores. The difficulty in separation related to similarity in surface properties and fine dissemination, resulted from geological settings, which cause great problems during magnification Fig 8, 9. [24, 25, 26, 27].

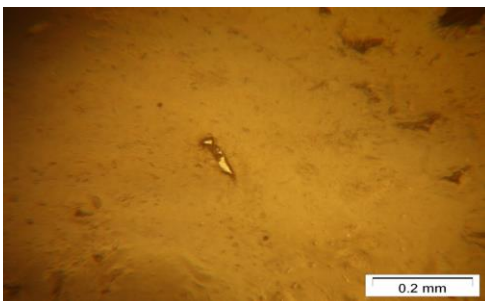


Fig.8. Apatite present as fine disseminated grains within the hematite matrix [24]

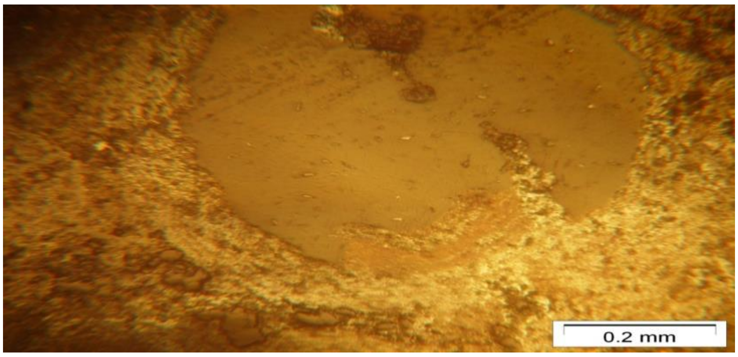


Fig.9. Chamosite present in the Ooid of hematite including fine dissminated apatite [24]

2.2.1. New Trends to beneficiate Difficult-to-Treat Iron Ore

2.2.1.1. High-intensity Magnetic Separation Application

It was used for the beneficiation of many iron ores for example an ore contains 51.6% iron, 8.76% silicon oxide, and 3.06% barium oxide after magnetic separation a concentrate contains 61% Fe(t) 90.3% recovery, at particle size 0.125 mm [28, 29]. In another study using gravity and high-intensity magnetic separation, a concentrate containing 50-70% Fe(t) with 60% recovery by both methods was obtained [30].

Beneficiation of Wadi Haifa iron ore. by gravity followed by magnetic separation a concentrate has 64% Fe (t) with recovery 70%, was obtained. [31]

2.2.1.2. Application of Microwave followed by Magnetic Separation

In the case of Aswan region iron ores, a significant reduction in grinding energy consumption was achieved [33]. Figure 10 shows the results of hematite fines after treatment with microwave and conventional heating, indicating that the microwave heating rate was higher, some phase changes were observed, and saving 15% to 50% over traditional operations. [34,35].

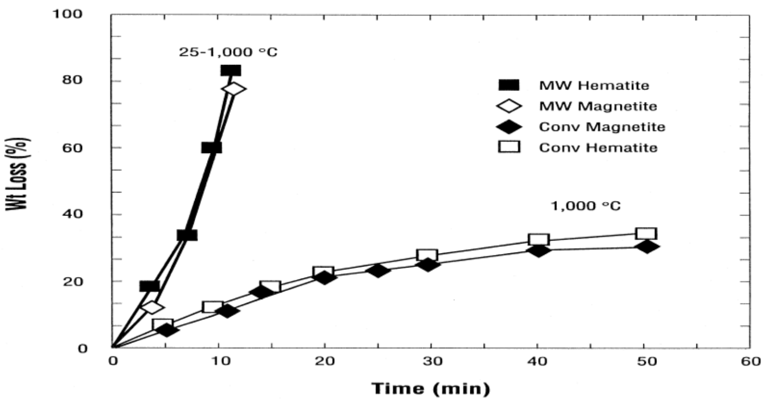


Fig.10. Comparison between microwave and traditional methods reduction[34].

Studying the dephosphorization of oolitic hematite ores by microwave indicates that it is a promising technique for the pre-reduction process in improving recovery, and could be followed by the smelting process [36]. In another study involving reduction roasting by microwave followed by magnetic separation, it was found that an iron concentrate having 63–65% total iron with recovery 85-90% in the same time reduction roasting and magnetic separation of the same sample could not be upgraded to > 61% Fet. the effect of microwave in Fig.11,12,13, [36].

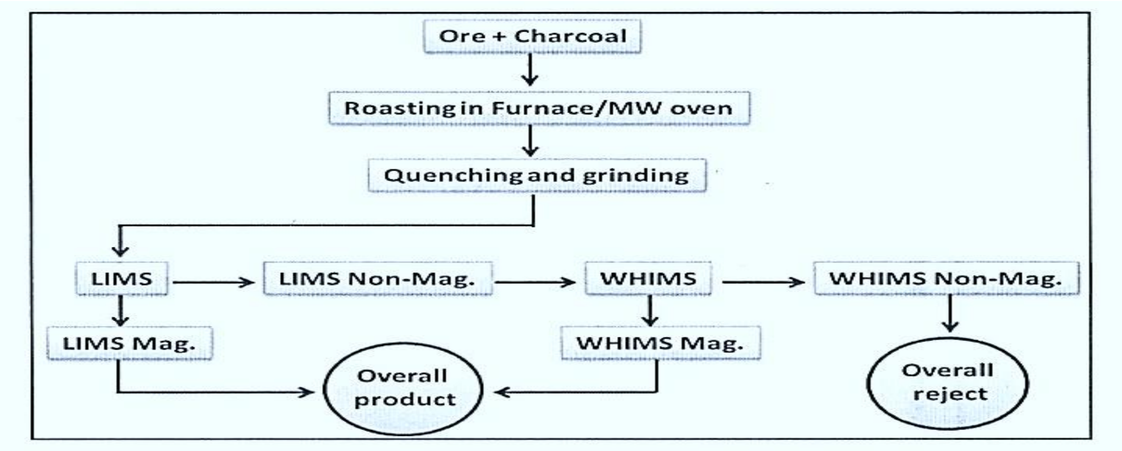


Fig. 11. India iron ore mines flow sheet [36]

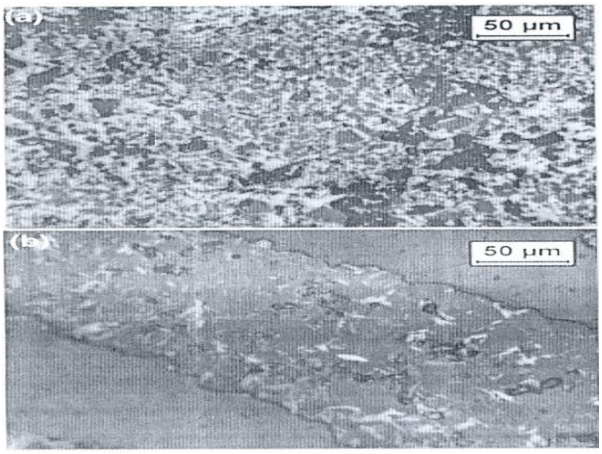
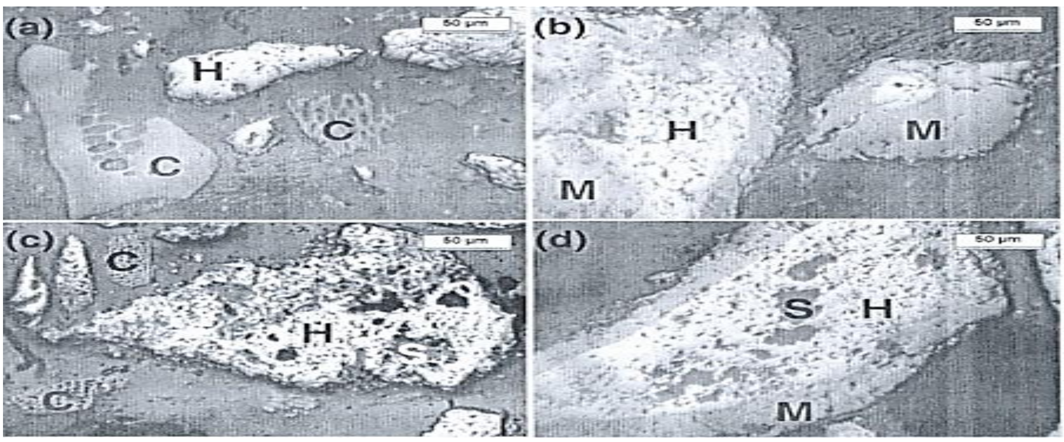


Fig. 12. SEM of the sample before microwave treatment[36].



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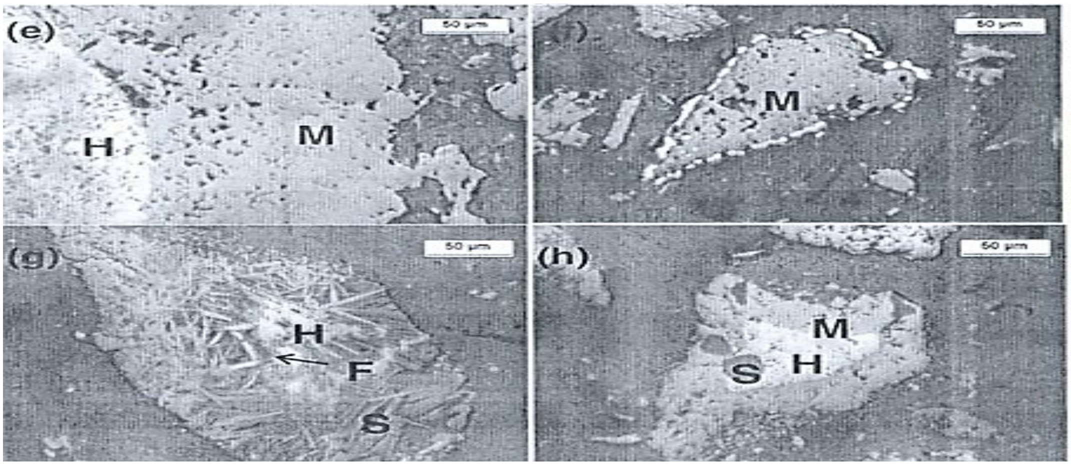

Fig.13. SEM of the sample after microwave treatment[36].

3.1.3. Application of Bio-beneficiation for Upgrading Difficult-to-treat Iron Ores

Adsorption of bacteria isolated on the surface of iron ores, as flotation collectors for for iron beneficiation [37, 38]. Separating phosphorus in the bio-flotation of Aswan iron ore indicated that a concentrate containing 0.28% P_2O_5%, 95.6% Fe_2O_3 with recovery of 77.8% [39].

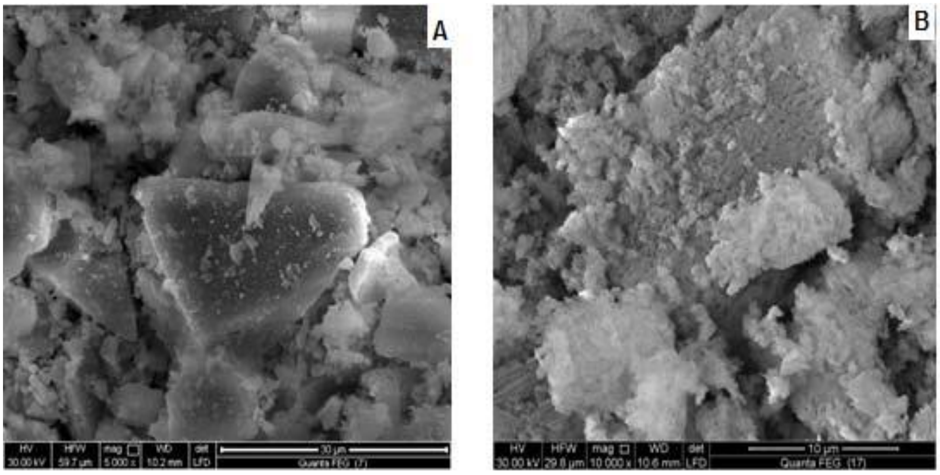

Fig.14 SEM of Iron oxide before and after treatment with Brevundimonas diminuta [39].

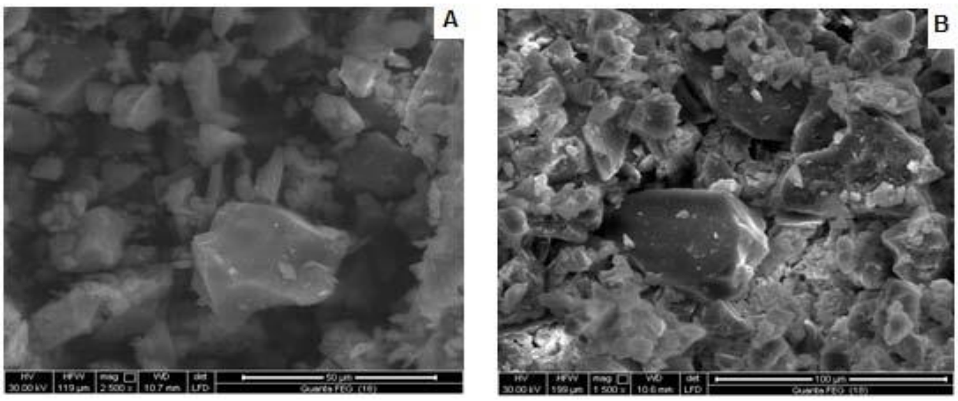

Fig.15 SEM of silica before and after treatment with Brevundimonas diminuta [39].

Adsorption of Paenibacillus polymyxa bacteria on mineral surfaces brought significant surface chemical changes according to bacteria chemical composition with high selectivity in separation such as silica and alumina from iron oxide, [40]. bio- flotation of El-Gedida locality the results indicated that a concentrate containing 3.7% MnO_2, 71.30% Fe_2O_3 with a recovery 72.46% [42].

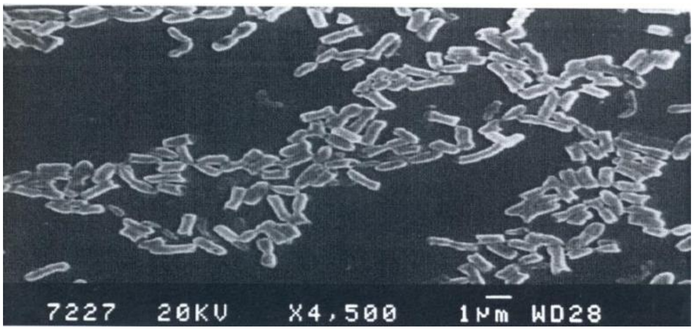

Fig.16. SEM of Paenibacillus polymyxa[41]

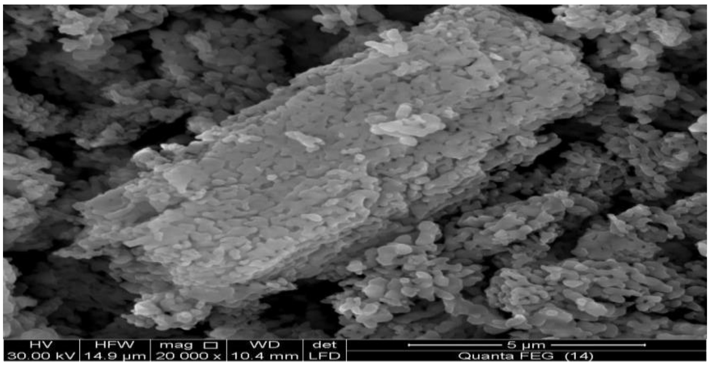

Fig.17.SEM of pure iron after treated with Paenibacillus polymyxa[41]

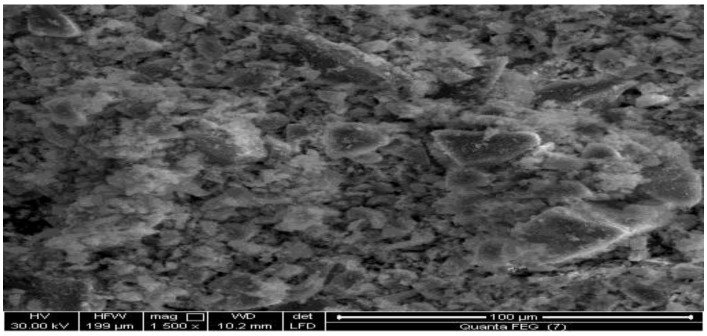

Fig.18 .SEM of pure quartz after treated with Paenibacillus polymyxa[41]

At the same time, bio-flocculation uses the same type of bacterial strain for the same region. A concentrate containing 2.54% MnO_2 0.25% SiO_2 and 74.40% Fe_2O_3 with a hematite recovery of 75% from a feed containing 8.79% MnO_2, and 67.90% Fe_2O_3 was obtained [42]. The bio-flotation of Aswan iron ore using Bacillus cereus isolated showed that phosphors were lowered from 1.5 to 0.4 % [43]. Using selective bio-flotation technique to separate a binary mixture containing 90% iron oxide and 10% apatite by weight a concentrate containing 96.4% iron oxide and 0.61% apatite with recovery 87.8% and applying on the national iron ore a concentrate with 95.6 % iron oxide and 0.28% apatite with recovery 77.8% from a feed

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contains 82.4% iron oxide and 1.7% apatite using Bacillus psychrourans as a bio-collector [44]. Another hydrophobic bacterium, Rhodococcus opacus (R. opacus), has been utilized as a flotation collector in the separation of hematite from a hematite–quartz suspension. Related to the Mycobacteria, the bacterial cells adhered to both quartz and hematite, but had little adhesion to quartz compared with hematite [35]

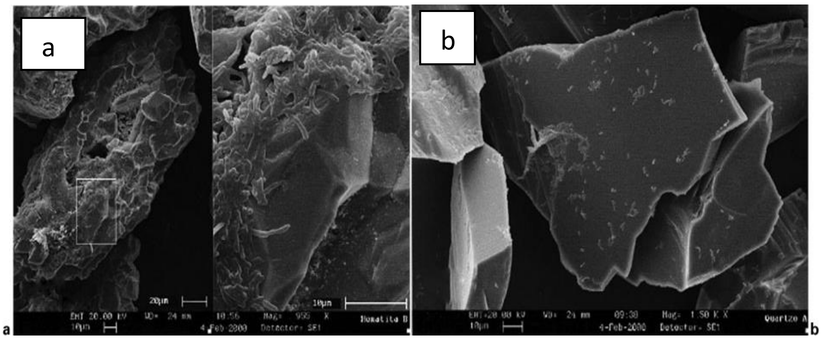

Fig.19. SEM of (a) hematite & (b) quartz particles floated with R. opacus cells in bio-flotation [45]

2.3. Beneficiation of Difficult-to-Treat Coal Ore

Coal is the basic source of energy. The relatively high sulfur content in coal made it unsuitable either for the use of environmentally safe fuel or for export (the international acceptable limit is < 1% total sulfur). The calorific value of El-Maghara coal is about 7367 k cal/kg, which is of a promising value compared to the international standards. Petrography investigation of the coal sample showed that most of the inorganic sulfur was found as pyrite mineral (1.6% pyritic sulfur) and was found below 50 µm and sometimes below 5 µm in size so great efforts were made to overcome the sulfur problem in El-Maghara coal region [46].

2.3.1. New Trends to beneficiate Difficult-to-Treat Coal ore

2.3.1.1. Application of Falcon Concentrator to Treat High Sulfur Coal

The Falcon was successfully used to remove a large portion of the total sulfur and ash from coal with coal recovery larger than 90% at particle size as low as 10 µm. They concluded that the separation process performance depends on solids percent in the feed [47, 48, 49, 50]. Applying the SB-40 Falcon Concentrator, to El-Maghara coal a clean coal product assayed 1.73% total sulfur and 0.47% inorganic (pyritic) sulfur was obtained with a separation efficiency 70.91% [51]. There are many studies on the El-Magar Coal [50, 51, 52, 53]. separation of pyrite particles below 20 µm using semi-continuous SB-40 Falcon Concentrator [44].

Fig.20 Falcon Concentrator

2.3.1.2. Application of Wet High Gradient Magnetic Separator to Upgrade High Sulfur Coal

Also, in El-Maghara when applied high gradient magnetic separation (WHGMS) using the “Boxmag Rapid” separator, a clean coal product assayed 1.94% total sulfur and 0.58% pyritic sulfur was obtained with a separation efficiency 38.75%, at the optimum conditions, 10 l/h feeding rate, 5% pulp density, 2200 Gauss, and 0.35% canister loading capacity with steel wool of approximate filament diameters between 50-20µm. [54].

Fig. 21 Wet high magnetic Separator “Box-mag Rapid”.

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2.3.1.4 Application of Bio-processing for Upgrading Difficult-to-Treat Coal Ore

Using two types of bacteria to separate ash and pyritic sulfur of El-Mghara coal. The results were confirmed by zeta potential measurements Fig. 22 and 23. [55, 56, 57]. The chemotropic bacterium Thiobacillus ferrooxidans is used as a pyrite-selective biological surfactant in the removal of pyritic sulfur from coal. The adherence of bacteria made pyrite surface more hydrophilic, which facilitates separation by increasing the tendency of pyrite to depress while coal is floated. The results showed a reduction in pyritic sulfur content from 3% to 1.2% with 80% recovery [58].

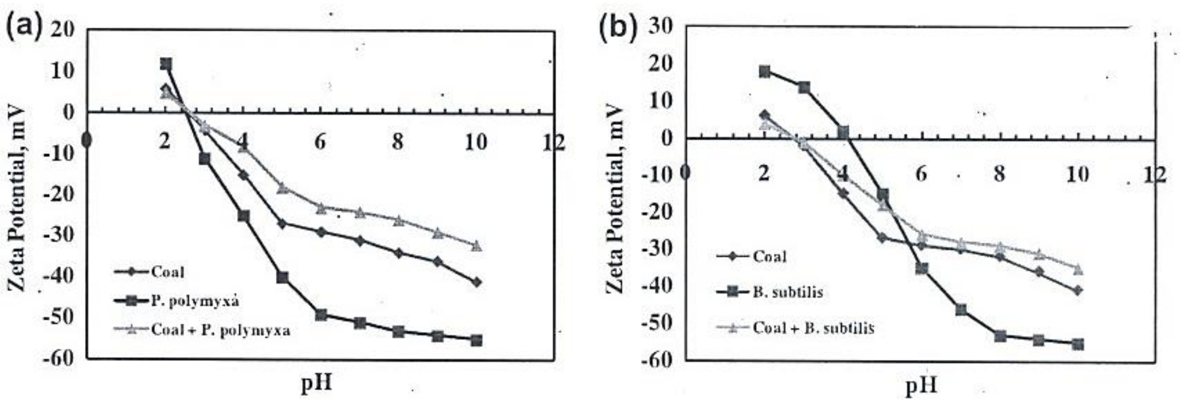

Fig.22. Surface charge of coal with P. polymaxa and B. subtilis [55].

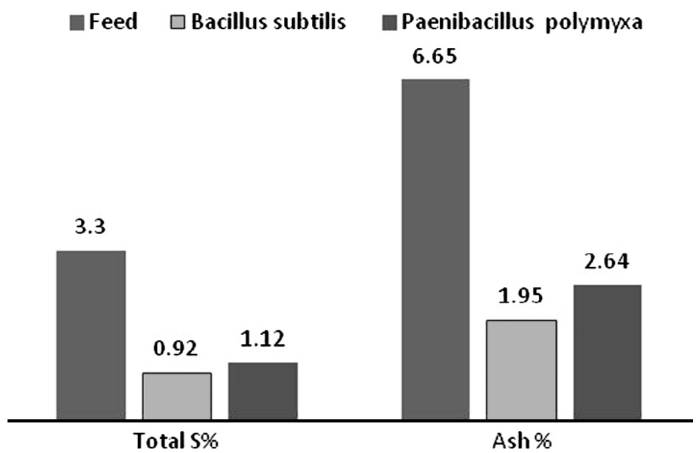

Fig.23. Effect of B. subtilis and P. polymyxa on ash and sulfur separation[55]

2.4 Beneficiation of Difficult-to-treat Kaolin Ore

Kaolin is a very important industrial mineral because it has many industrial applications. Some crude kaolin, contains colored impurities that have a bad effect on its applications and it was found that finely disseminated below 2 µm. Conventional methods such as purification and bleaching fail to remove these impurities.

2.4.1. New Trends to beneficiate Difficult-to-Treat Kaolin Ore

2.4.1.1. Application of Magnetic Separation& Flotation

Syrian kaolin was beneficiated and iron oxide content decreased from 5.40% to 0.85% with increasing the optical properties and can be used in the paper industry [59].

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2.4.1.2. Application of High Gradient Magnetic Filter to Improve Kaolin Quality

Removing the impurities by magnetic filtration from kaolin increase brightness and in the same time decrease reagents consumption, Fig..24 [60, 61, 62, 63, 64].

The beneficiation of Egyptian Kaolin and the results indicated that optical properties were raised and the product can be used in different industries. The selective flocculation process is very important in kaolin purification, [65, 66].

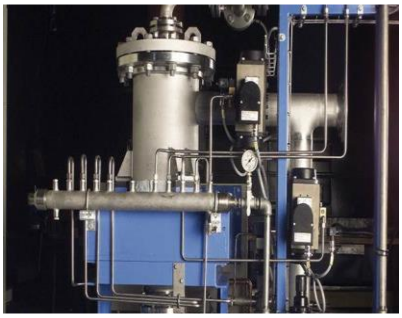

Fig. 24 High Gradient Magnetic Filter

The flocculation process to occur should be:

- Addition of dispersing agent, such as sodium silicates.
- Addition of flocculating agents, such as polymers.
- Conditioning at low shear for growth, of floc.

Selective flocculation of Brasilin kaolin for removing colored impurities. The obtained results indicated that it is possible to diminish TiO_2 content and increase kaolin brightness (Iso) from 82 to 88%, [67, 68].

2.4.1.4. Application of Carrier Flotation to Improve Kaolin Quality

It can be achieved via the enhanced aggregation between fine (carried) and coarse (carrier) particles under intense agitation and followed by froth flotation. Fig.25. Fine particles to be then floated, [69,70].

Beneficiation of Egyptian kaolin by this technique was investigated Fig.25.[59] and the recovery reached to 57.95%, [71].

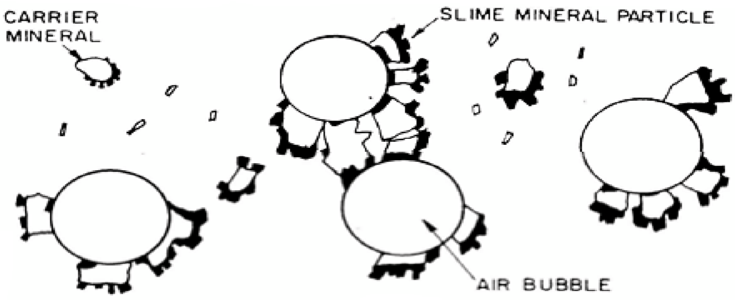

Fig. 25. Schematic representation of the ultra-flotation or carrier flotation process[70]

2.4.1.3 Application of Bio-processing to Improve Kaolin Quality

Using bio-flocculation methods in beneficiation of the Egyptian kaolin ores using Micrococcus luteus produces a concentrate contains 0.2% TiO_2 from original sample contains 3.1% with recovery 75%.[71].

A successful adsorption of the S. Galinarum onto kaolin surface caused an aggregation for mineral particles leading to a change in their size distribution which indicates more selectivity towards kaolin. From surface charge study of S. Galinarum it varied from +5 to -35 mv over the range of pH 1-12, i.e this bacterial isolate hydrophobic in nature has iso-electric point at pH 1.8. Conditioning of kaolin with this bacterial isolate leads to a displacement to 2.5 and the hydrophobic effect appeared at pH range 4.5-11. These results indicated a higher bacterial affinity to kaolin mineral surface, [72].

Another study using Cells of B. subtilis could be efficiently grown and adapted in the presence of both hematite and kaolinite Fig 26., polysaccharides exhibited higher adsorption density on hematite, while proteins adsorbed onto kaolinite surface. the interaction rendered hematite more hydrophilic and kaolinite hydrophobic. [73]

IJMTI vol. 4 , issue 1 (2024) 80-96 https://doi.org/10.21608/ijmti.2024.253140.1099

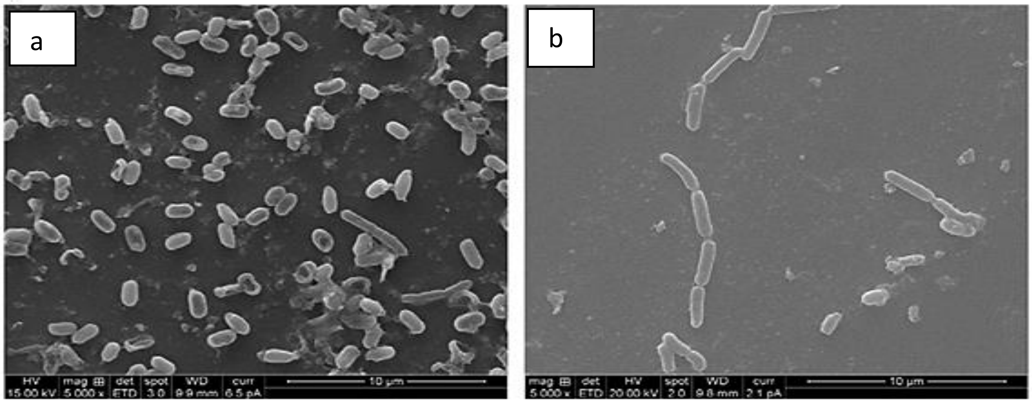

Fig.26 SEM of Bacillus attached onto (a) hematite& (b) kaolin.

5. Conclusions

- Beneficiation of difficult-to-treat ores is very important subject, especially with decreasing the high-grade ores.
- Similarity in surface properties and fine disseminated impurities the most challenging in ores beneficiation.
- The New trends in mineral beneficiation technologies offer reasonable results with some difficult-to- treat ores and cannot do with others.
- The Scientists do their efforts to find the best alternative new methods and/or modifying the current as well.
- Currently,bio-beneficiation technologies are the best methods in treating difficult-to-treat minerals because it is an economically viable, and an environmentally benign process but are still on laboratory scale.
- Separation of particles is the main challenge to the present and the future industry of minerals due to the depletion of the high-grade ores.
- Most of today's ores are complex ores with very low liberation sizes that have to undergo fine grinding processes.
- Flotation is considered as the most effective technique regarding the handling of fine particle separation using methods such as the flotation column, Air- Sparged Hydrocyclone.
- Bio-beneficiation is a large step in the development of fine particles separation but, however, there is still a room for more enhancements.
- Studying the Mechanisms of the bio-processing on the level of molecular biology through DNA of the microorganism's bacteria or fungi may lead to a revolution in bio- beneficiation (by help of genetic engineering).

The development of a dry process will become of great importance, due to the global (and local) shortage of fresh water resources.

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