Physicochemical study and application for pyrolusite separation from high manganese-iron ore in the presence of microorganisms

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Abstract: *Paenibacillus polymyxa* bacteria strain as a surface modifier in a flotation process could remove 64.89% of MnO_2 from high manganese iron ore. A concentrate containing 3.7% MnO_2, 0.5% SiO_2 and 71.30% Fe_2O_3, with a hematite recovery of 72.46% is produced from a feed containing 8.79% MnO_2, 0.49% SiO_2 and 67.90% Fe_2O_3. The bio-flotation results indicated that such type of bacteria is selective for upgrading El-Gedida iron ore from the Western Desert of Egypt. The role of *Paenibacillus polymyxa* on the surface properties of pyrolusite and hematite single minerals was investigated through zeta potential, FTIR and adsorption measurements.

1. Introduction

Egypt has iron ores in different locations such as the East Aswan of the Eastern Desert, Bahariya Oasis of the Western Desert, and in several localities of the Eastern Desert near the Red Sea coast. The iron ore deposits vary in their mineralogical, chemical composition and the nature of associated minerals (Yassin, 2013). These ores contain harmful elements as silica, manganese, barium, carbonates or chlorides (Ahmed et al., 2007). Although manganese is added into steel for reduction and desulfurization, but the presence of manganese in the iron ore causes harm to the reduction process of iron oxides in the blast furnace (Baioumy et al., 2013). Manganese forms strong oxides, which are partially reduced in the blast furnace and goes to the slag. This is why the reduction behavior of manganese in the blast furnace was extensively studied by many researchers, trying to avoid the harmful effect of manganese in the iron making and steel industries (Terayama et al., 1996; Attui et al., 1999; El-Geassy et al., 2008). Because of the high similarity of their surface properties, the iron and manganese are usually associated with their deposits (Urban et al., 1992; Saad et al., 1994; Corona-Esquivel et al., 2000). Removal of manganese mineral from Egyptian iron ores through the conventional methods is difficult. This is due to the complex nature of these ores. Thus, the exploitation of these iron ores is still needed more investigation.

Recently, bio-technology is becoming more attractive in mineral processes due to its lower operating costs. Moreover, it can treat difficult to beneficiate low grade ores. Microorganisms play an important role in developing the bioleaching of manganese from its low-grade ores (Solojenken et al., 1976; Somasundaran et al., 1998; Rao et al., 2010). Since the bacteria adhere to a mineral surface within a few minutes and start altering the surface properties, the microorganisms have numerous applications in the flotation and flocculation processes. Biological processes are attractive since microorganism or microbial fat and secreted metabolites can have specific interactions with minerals. Such interactions of microorganisms and their agents with minerals can be indirect, with biological products acting as surface-active agents, or direct due to microbial adhesion or attachment to particles bringing out surface modification. Both types of interactions can lead to alteration of mineral hydrophobicity, and in some cases cause flocculation or dispersion of mineral suspension (Somasundaran et al., 1998). Some

microorganisms such as *Bacillus cereus* have a hydrophilic character which causes some degree of mineral dispersion, while *Pseudomonas songnenensis* has a hydrophobic character which causes some degree of aggregation. According to Natarajan and Deo, (2001) the microbe was adapted to the particular mineral, i.e. it was grown in the presence of the mineral, this approach of adaptation made the organism secrete different bio-surfactants in the presence of different minerals thereby making the attachment selective.Exopolymers, or metabolites interact with the organism and the minerals in a variety of ways. The metabolites of Bacillus polymyxa, such as the polysaccharides, proteins and organic acids are important in the surface modification of oxide minerals, such as hematite (Deo and Natarajan, 1997).

Mackay School of Mines, USA, showed that M. phlei can function as a collector for hematite. This is due to its high negative charge and hydrophobicity (Van Loosdrecht et al., 1987). In the acidic conditions the bacteria had a positively charged surface, thus giving place to possible electrostatic attraction between the bacterial cells and the quartz particle negatively charged.The mineral surface after bacteria interaction are covered with an adsorbed layer of proteins containing several amino groups, making the mineral relatively more hydrophobic (Deo and Natarajan, 1997).

Many microorganisms can be efficiently used for beneficiation of iron ores through microbially-induced flotation or selective flocculation. When microorganisms were grown in the presence of hematitemineral, bioproteins and exopolysaccharides were generated. Bacteria such as *Paenibacillus polymyxa* can be used for biodegradation of flotation collectors such as amines and oleates and also to strip residual collector reagents from floated concentrates. The selective bacterial adhesion on mineral surface is important for selective surface modification which leads to an efficient separation (Geoghegan et al., 2007). *Paenibacillus polymyxa* could remove the silica and kaolinite from iron ore through flocculation of it in sulfide minerals (Natarajan and Deo, 2001; Vijayalakshmi and Raichur, 2003; Sarvamangala and Natarajan, 2012).

This work aims to study the role of interaction of *Paenibacilluspolymyxa* on the surface properties of hematite and pyrolusite single minerals through the zeta potential and adsorption experiments. Also, the flotation behavior in the presence of *P. polymyxa* for separation of MnO_2 from high manganese iron ores is studied.

2. Materials and methods

2.1. Materials

A representative sample of Bahariya Oasis iron ore, El-Gedida area, Western Desert of Egypt was collected for the experiments. Single minerals of hematite and pyrolusite were delivered from 'Wards' Company, USA. The purity 99% of these samples was confirmed using XRF. The –200 mesh fractions were used in adsorption. HCl and NaOH of analytical grade from Aldrich were used for pH regulation.

2.2. Methods

2.2.1. Characterization

Philips PW 1730 powder X-ray diffractometer with Fe-filtered Co (K-alpha) run at 30 kV and 20 mA was used to examine single minerals. Infrared vibrational spectra were recorded on a Nicolet Magna 750 Fourier-transform spectrometer. For each sample, 28 scans were accumulated over the 400-4000 cm^{-1} spectral range employing the transmittance mode and a resolution of 4 cm^{-1}.

2.2.2. Isolation and growing of bacteria

Bacterial strain was isolated from the iron ore surface through vigorous agitation of iron sample with 0.4% sodium chloride, NaCl, solution for 30 min on a rotary shaker at 30°C, and allowed to be settled. The supernatant obtained was serially diluted with sterile water and spread on the surface of nutrient agar plates which were incubated at 30°C. Selected bacterial isolates was isolated, purified by streaking on nutrient agar plates (Saleh, 2013). The dye tetrazolium violet is used to indicate utilization of substrates (Vilinska and Rao, 2008).

2.2.3. Zeta potential measurements

A laser Zeta Meter "Malvern Instruments Model Zeta Sizer-2000" was used for zeta potential measurements. A 0.01 g of the pure hematite or pyrolusite minerals was mixed with 50 ml double distilled water in the presence of bacteria isolate. The presence of various ions alters the zeta potential of both microorganisms and minerals so,ionic strength was fixed at 2×10^{-2} M using NaCl solution. The suspension was conditioned for 30 min at desired pH. After conditioning, the pH was recorded (Shashikala and Raichur, 2002; Abdel-Khalek and El-Midany, 2013).

2.2.4. Adhesion measurements

Adhesion of the bacterial isolate on the mineral surfaces was determined by dry weight difference before and after conditioning the mineral particles with bacteria. About 0.5 g of the −200 mesh mineral is added to 80 ml of the bacterial suspension with a fixed initial concentration of 2×10^8 cells/ml and then conditioned for 60 min at desired pH. It is allowed to settle for 20 min and then it is dried at 40 - 45°C for 1 hr using dryer with air stirrer. Adhesion studies were performed as a function of difference in weight before and after drying (Saleh, 2013).

2.2.5. Flotation experiments

A bench-scale flotation experiment is conducted using a micro scale flotation. Single minerals, binary mixtures and natural iron ore were conditioned with bacterial isolates, at a desired pH in a horizontal shaker for certain conditioning time. It is then transferred to the micro-flotation column unit. The air pressure was adjusted at 30 cm^3/min. A five-minute flotation was performed till demineralized froth. Both the float and sink fractions were collected, dried, weighed and chemically analyzed (Saleh, 2013).

3. Results and discussion

3.1. Characterization of iron ore

The XRD analysis of the El-Gedida iron ore showed that the iron bearing minerals occur as hematite and goethite, Fig. 1. Pyrolusite mineral (MnO_2) is identified as the main manganese bearing minerals in this sample. It is dominated by a mixture of manganese oxide and hydroxide minerals. So, this iron ore is classified as a high manganese iron ore. Traces of quartz are also identified. The complete chemical analysis of the iron ore sample through the XRF analysis showed that the sample contains 67.9% Fe_2O_3 and 8.79% MnO_2 with minor amount of silica and alumina. Also, TiO_2, CaO, MgO, Na_2O, K_2O, and P_2O_5 are detected. The ignition loss is 19.6%, Table 1.

3.2. Interaction of bacteria with pure minerals

3.2.1. Zeta potential measurement

The zeta potential of *Paenibacillus polymyxa* varies from +5 to −40 mv over the entire range of pH (2 – 8) with an isoelectric point (IEP) corresponding to pH of 2.4. The general structure of bacteria is mainly
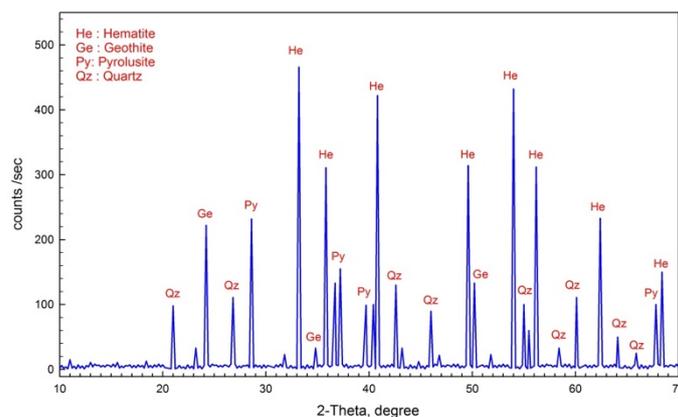

Fig. 1. XRD spectrum of the Bahariya iron ore

Table 1. Chemical analysis of the Bahariya iron ore

Constituent	Mineral
Na_2O	0.54
MnO_2	8.79
MgO	0.81
Al_2O_3	1.49
SiO_2	0.49
P_2O_5	0.07
K_2O	0.07
CaO	0.20
TiO_2	0.04
Fe_2O_3	67.9
L.O.I.	19.6
Total	100

composed of polysaccharides and lipids (protein). Protein contains two important functional groups, a carboxylic acid group (-COOH) and an amino group ($-NH_2$) (Brock et al., 1994). These functional groups are mostly protonated at pH < 2, but become progressively negatively charged with increasing pH due to proton dissociation of carboxyl (pH 2-6), phospholipids (pH 2.4-7.2), phosphodiester (pH 3.2-3.5), hydroxyl (pH 9-10) and amino groups (pH 9-11). Physiological conditions of most bacterial strains are negatively charged, as the number of carboxyl and phosphate groups exceeds the number of amino groups. The IEP is determined by the balance between anionic and cationic acid/base groups at the cell surface. At higher pH it becomes progressively negatively charged due to proton dissociation (Rong et al., 2008). The shift of iso-electric points of minerals can be explained based on this surface interaction (Abdel-Khalek et al., 2017).

The zeta potential of hematite is shifted to the more negative direction as a result of *P. polymyxa* treatment, Fig. 2. The zeta potential tends to go to the positive side at pH range (6-8), which indicates the increasing of hydrophobic character of the mineral surface. The iso-electric point (IEP) of the hematite is shifted from 2.2 to 2.6 which agree the reported IEP (Deo et al., 2001; Shashikala and Raichur, 2002; De Mesquitaa et al., 2003). On the other hand, the zeta potential of pyrolusite is positive up to pH 3.5 and then it is converted to a negative charge. The negativity of the pyrolusite is higher than that of untreated pyrolusite. The isoelectric point (IEP) is shifted from 2.5 to 3.3, Fig. 3. Although, both bacteria and the mineral surfaces have the same charge, the adhesion is based on the surface heterogeneity of the bacteria with a poly-saccharide envelope. It includes also, hydroxyl, hydrophobic and ionic moieties. The flexible fimbriae regulate the surface charge. The dissolving ions from the mineral alter the surface charge of the bacteria to reduce repulsion (Rao et al., 2010). The hydrogen bonding and chemical interaction also play significant roles in bacterial interaction with single minerals (Jiang et al., 2004). Also, the flexible fimbriae can possibly regulate the surface charge characteristics, depending on the
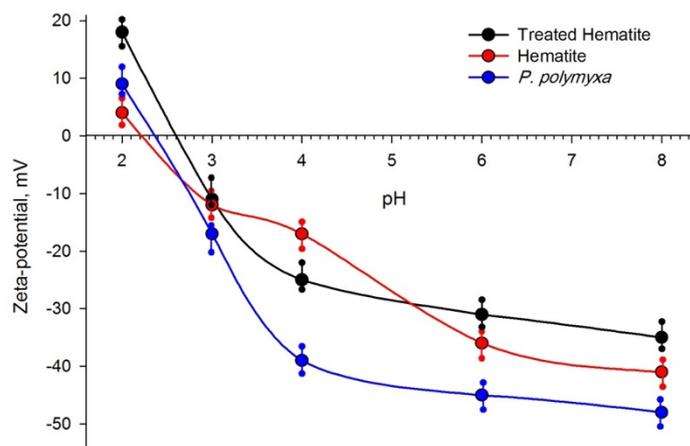
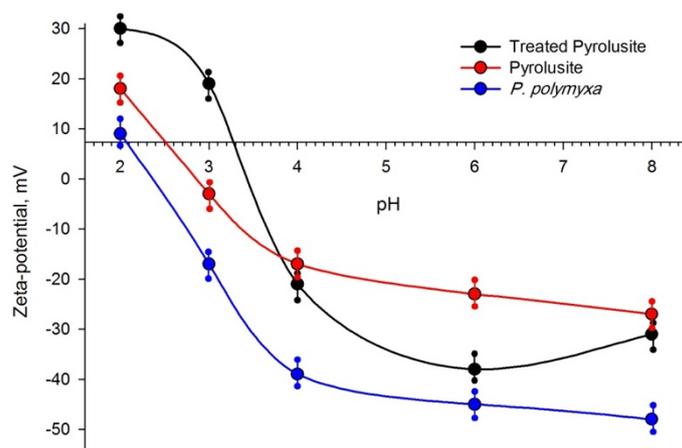Fig. 2. Zeta Potential of pure hematite mineral and after treatment with *P. polymyxa*

Fig. 3. Zeta Potential of pure pyrolusite mineral and after treatment with *P. polymyxa*

environment. The dissolved species from the minerals also alter the surface charge of the bacteria in a direction, which reduces repulsion, and thus favor adhesion (Somasundaran et al., 1998).

Deo and Natarajan, (2001) have mentioned that the effect of bacteria interaction on the surface chemical behavior of hematite was different in that the measured zeta potentials were observed to shift towards more negative values, both with metabolites and bio-polysaccharides. It is reported that the isoelectric point of quartz shifted as a result of bacteria protein and metabolite interaction while the presence of bacterial polysaccharides did not significantly alter the surface chemistry of quartz (Smith and Mishra, 1991).

3.2.2. FTIR measurement

FTIR spectra of hematite before and after treatment with *P. polymyxa* are given in Fig. 4. New peaks have appeared due to the interaction of *P. polymyxa* cells with hematite mineral. While the band at 3450 cm^{-1} is attributed to the presence of carboxylate anion and another peak at 2341 cm^{-1} is that of CH_2 rocking and OH bending modes or the C-OH group of frees polysaccharides. The peak at 2918 cm^{-1} may be due to C-OH stretching vibrations. The peak at 1041 cm^{-1} is of a primary alcoholic group of CH_2OH and another peak at 674 cm^{-1} may be due to CH_2 rocking vibrations, (Deo et al., 2001). The change in FTIR as a result of bacteria interaction proved that the type of adsorption occurred is mainly chemical adsorption which makes hematite surface hydrophobic more than that of pyrolusite (Deo and Natarajan, 1997; Selim, and Rostom, 2018).

As shown in Fig. 5, FTIR spectra of the pyrolusite sample, before *P. polymyxa* treatment, showed the characteristic bands for pyrolusite (absorbance bands of 3445 cm^{-1} assigned to hydroxyl groups,
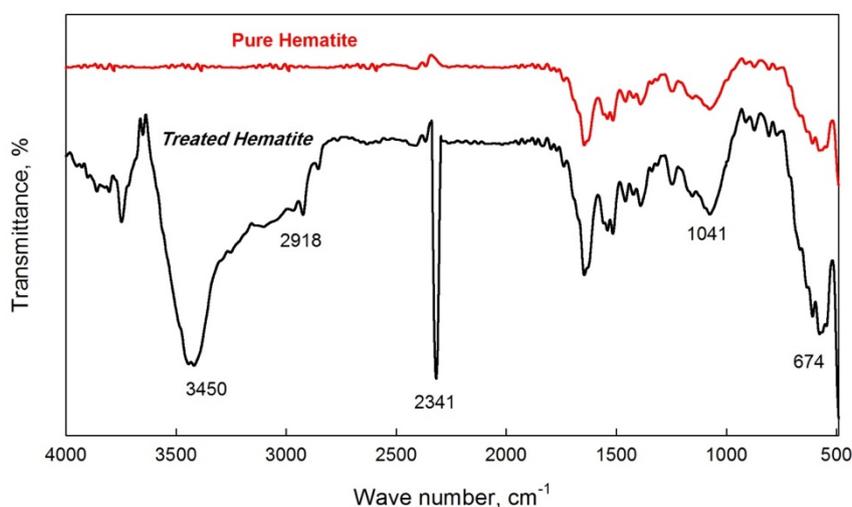

Fig. 4. FTIR spectra of hematite and after treatment with *P. polymyxa*

1091 cm^{-1} assigned to Si-O). The FTIR spectra of pyrolusite, after *P. polymyxa* treatment, showed similar characteristic bands as the untreated one. This indicated that absorbance bands of 3422 cm^{-1} and 1091 cm^{-1} might not associate with functional groups presented on the *P. polymyxa* cell wall which could interact with the sample surfaces. The absorbance band of hydroxyl group was broadened and the wave number 3445 cm^{-1} moves lower, 3422 cm^{-1}, due to the role of hydrogen bonding. The absorbance band of 1091 cm^{-1} was widened, which may be subject to interference from other bands (Yang et al., 2014).
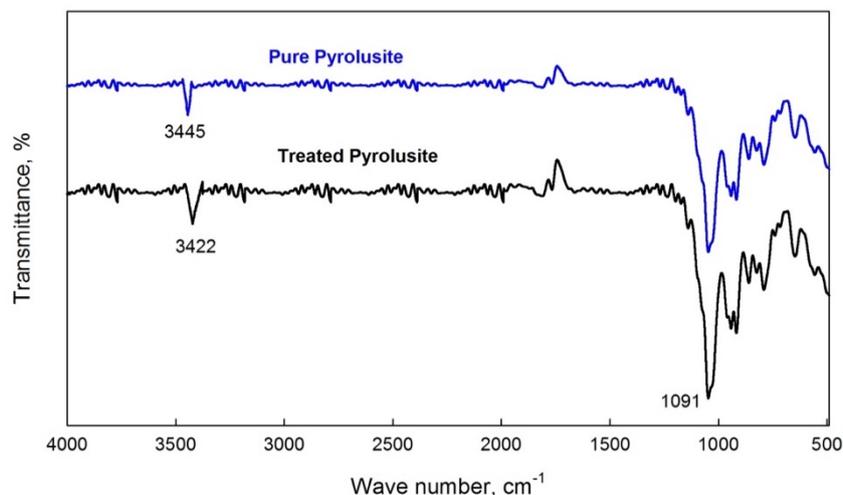

Fig. 5. FTIR spectra of pyrolusite and after treatment with *P. polymyxa*

It is reported that the weak adsorption of polysaccharide on the mineral surface has no significant effect on minerals behavior. The hydrophobic effect where the adsorption of polysaccharides onto mineral surfaces is much higher than that of protein adsorption. The excretion of extracellular polymeric substances composed of macromolecules as polysaccharides, proteins and lipids promotes the development of the biofilms on mineral surfaces. The number of function groups is not the only factor that plays a role in the adsorption of biomolecules on surface of minerals. The total charge and the spacing between them plays a role for design of biomolecules to interact with the mineral surfaces Sparks et al., (2015).

3.2.3. Effect of pH on bacteria adsorption

By conditioning of the single minerals with 5×10^8 cells/ml of bacteria strain, it was found that the adsorption *P. polymyxa* and is pH dependent. As shown in Fig. 6, the adsorption stability is occurring at a pH range from 2 to 6 for hematite and pyrolusite minerals with higher affinity to pyrolusite. It is followed by a gradual decrease from pH 6 to pH 10. According to Dickson and Koohmaraie, (1989) bacterial attachment to any surface is related to surface charges on both cells and substratum. The inter-
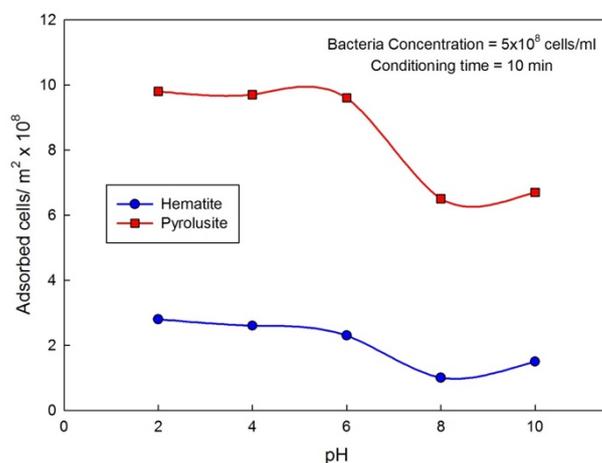

Fig. 6. Effect of pH on adsorption of *P. polymyxa* onto single minerals

facial region of the mineral substrate and biofilm is modified by the presence of microorganisms and their metabolic products. Charge separation can occur by dissociation of ionizable groups, such as –OH, -COOH, -NH and –SO, –H. Thus, with oxide mineral dissociation of surface OH can occur and the surface may become positively or negatively charged depending on the pH.

3.2.4. Effect of bacteria concentration on its adsorption

At the natural pH of 5.5 to 6.5 and according to the results obtained from the effect of pH onto the adsorption of the selected bacterial strain on different minerals, the adsorption density onto hematite and pyrolusite increases with increasing the concentration of *P. polymyxa*. The results show that the adsorption behavior at higher concentration of *P. polymyxa* is much higher in pyrolusite mineral, Fig. 7.

Mechanisms of adsorption of bacteria on mineral surface include the presence of surface appendages, cell surfaces, and exopolymers (Somasundaran et al., 1998). Appendages are mostly protein and may bind to specific molecules available on the mineral surfaces as the cell surface appendage of Thiobacillus ferrooxidans when grown on sulfur of chalcopyrite. Adsorption of bacteria and cell excreted compounds, such as polysaccharides, on pyrite surface increased the wettability of the mineral surface, thus decreasing the floatability of pyrite. Besides electrostatic forces, hydrogen bonding and chemical interaction also play significant roles in bacterial interaction with single minerals (Jiang et al., 2004).

Neutral macromolecule can also be adsorbed on charged or uncharged mineral surfaces. If the surface is charged, then adsorption of a biomolecule can cause a redistribution of the counter ion charge. This would lead to shifts in zeta potentials. Therefore, on any hydrophilic surface, adsorption of exo-polysaccharides (biofilm) can occur by strong hydrogen bonding between amino or carboxyl groups, peptide units or ether as well as other polar groups on biological and mineral surfaces. This will also lead to redistribution of charges in the double layer. The polysaccharides, consisting of several flexible sequences, may adopt different conformations at the mineral-solution interface (Natarajan and Deo, 2000).
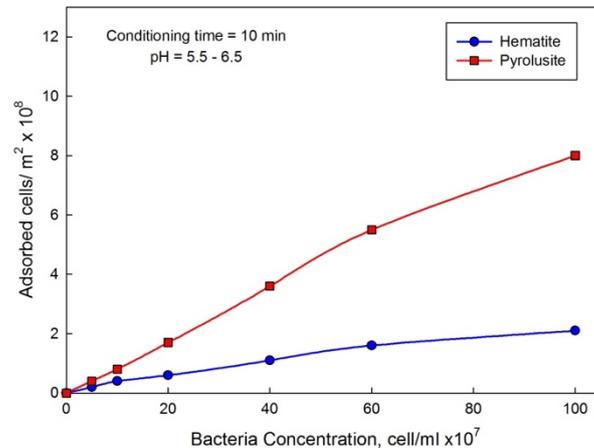

Fig. 7. Effect of *P. polymyxa* concentration on its adsorption onto single minerals

3.3. Bio-Flotation of single minerals

Fig. 8 shows the effect of pH on the floatability of single minerals as a result of conditioning with 5×10^9 cells/ml of *P. polymyxa* for 10 min. The results illustrated that conditioning time has an important effect on the adsorption of *P. polymyxa* onto the surface of minerals. The bacteria contain polysaccharide and protein, which are composed of functional groups such as COOH, OH, and amine beside the hydrocarbon chain. Thus, it is expected that the pH of the medium will represent an important factor in determining the adsorption of bacteria onto mineral surfaces as a result of ionization of these functional groups with changing pH (Yassin, 2013). The highest floatability for hematite is recorded at lower (acidic) pH. This may be as a result of polysaccharide adsorption, which in turn, increases its hydrophobicity. It can be observed that, for each mineral, there is a decrease in floatability with increasing pH. The highest floatability of both hematite and pyrolusite minerals is shown at pH 3.

The effect of concentration of *P. polymyxa* on the floatability of hematite and pyrolusite minerals was performed at the conditioning time of 10 min and pH 3, Fig. 9. The increasing of *P. polymyxa* concentration increases the floatability of hematite, and then it is slightly decreased. It may be due to a build-up of *P. polymyxa* on the mineral surface that affects the hydrophobicity of hematite and pyrolusite mineral. Predominance of bacterial polysaccharides on interacted hematiteand proteins on pyrolusite may be responsible for the surface chemical changes. The bacterial strains could be preadapted to different mineral substrates (Natarajan and Deo, 2001).

Although, *Paenibacillus polymyxa* showed higher adsorption by pyrolusite mineral, its floatability is less than hematite mineral. This may be explained by FTIR results which proved the significant change of hematite surface rather than pyrolusite mineral. It is proved that the adsorption occurred on hematite is mainly chemical adsorption which makes its surface more hydrophobic than that of pyrolusite.

Fig. 10, shows that the increasing of the conditioning time, increases the adsorption till certain time where all active sites on the surface are occupied then desorption may take place. The experiments were performed at pH 3, and 5×10^9 cells/ml of *P. polymyxa*. At the same time, the floatability decreases with increasing the conditioning time. This may be related to that the adsorption of bacteria occurred in a short time, which agrees with other authors (Brock et al., 1994; Deo and Natarajan, 1999; Deo and Natarajan, 2001). These results also showed that a conditioning time of 10 min is the optimum to get the highest yield of hematite.
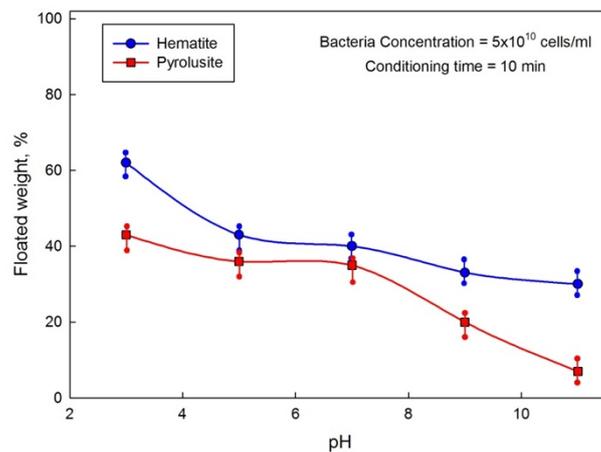

Fig. 8. Flotation of single minerals in the presence of *P. polymyxa* as a function of pH
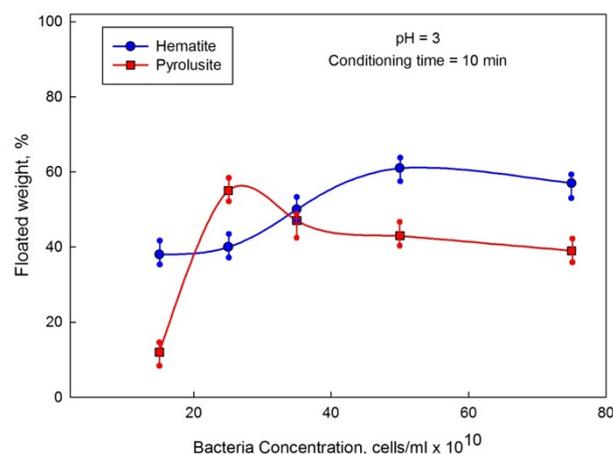

Fig. 9. Flotation of single minerals as a function of *P. polymyxa* concentration

3.4. Application of bio-flotation for binary mixtures and natural iron ore

The bacteria strain is used as a surface modifier to increase the flotation selectively. The binary mixture of 90% pure hematite mineral 10% pyrolusite mineral by weighing is employed as a bio-flotation feed. Fig. 11 shows the effect of *Paenibacillus polymyxa* concentration (cell count) on the pyrolusite decreasing

at pH 3. The results showed that the presence of 5×10^{10} cells/ml of *P. polymyxa* could floated hematite leaving pyrolusite, where the MnO_2 was reduced by 65% in the binary mixture contains 10% pyrolusite mineral. At higher *P. polymyxa* concentrations the removal percent is slightly decreased which may be due to a build-up of *P. polymyxa* on the mineral surfacethat affects the hydrophobicity of hematite and pyrolusite minerals.

Fig. 12 shows the bio-flotation of the natural iron ore containing 8.79% MnO_2, 0.49% SiO_2 and 67.90%
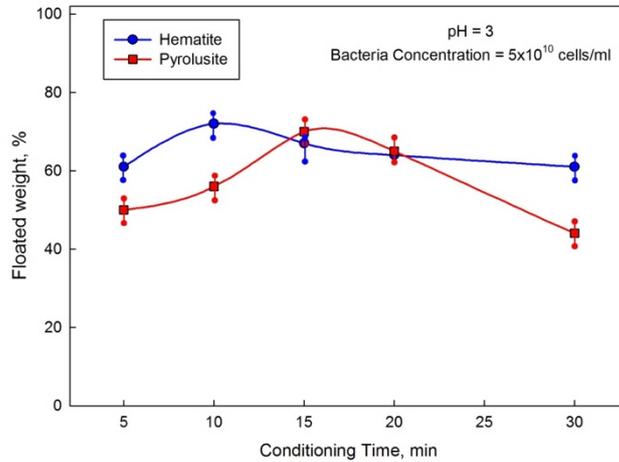

Fig. 10. Flotation of single minerals as a function of conditioning time
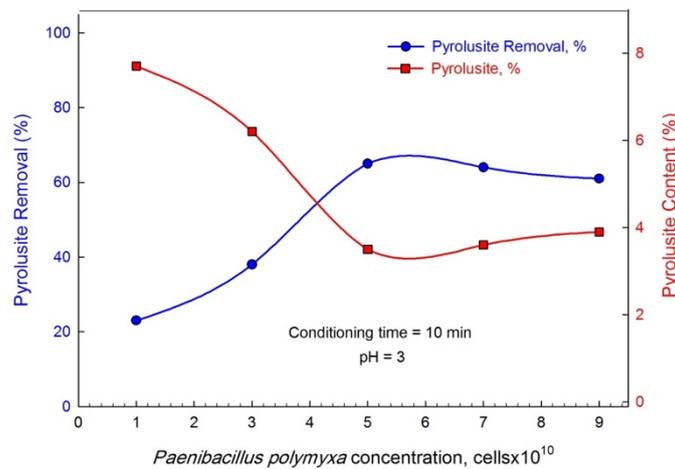

Fig. 11. Bio-flotation of binary mixture as a function of *Paenibacillus polymyxa* concentration
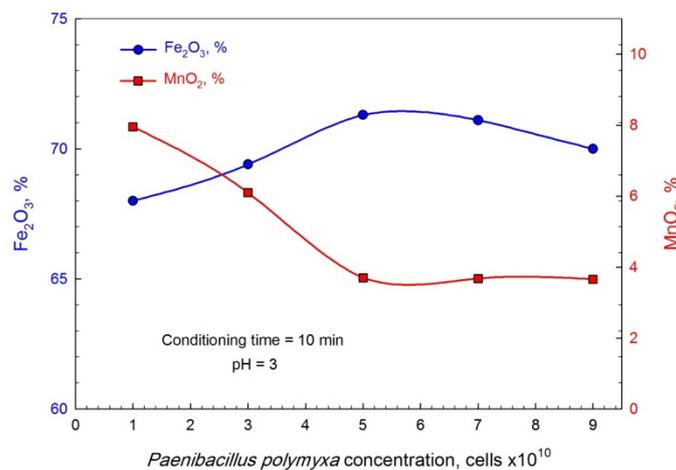

Fig. 12. Bio-flotation of iron ore as a function of *Paenibacillus polymyxa* concentration

Fe_2O_3. The results indicated obviously that the *P. polymyxa* has a high selectivity for upgrading El-Gedida iron ores, Bahariya Oasis of high manganese content for utilization. In the presence of 5×10^{10} cells/ml of *P. polymyxa* at pH 3, a concentrate contains 3.7% MnO_2, 0.5% SiO_2 and 71.30% Fe_2O_3 with a hematite recovery of 72.46% is produced. These results indicated obviously that the *P. polymyxa* has a high selectivity for upgrading El-Gedida iron ores, Bahariya Oasis of high manganese content for utilization.

4. Conclusions

A successful adsorption of the *Paenibacillus polymyxa* bacteria strains onto the hematite and pyrolusite minerals system leads to a degree of surface modification and thus a change in their floatability. The El-Gedida iron ore is composed of hematite and goethite (iron bearing minerals) and pyrolusite (the main manganese bearing mineral). It contains 67.9% Fe_2O_3 and 8.79% MnO_2 with minor amounts of silica and alumina.

The isoelectric point (IEP) of *Paenibacillus polymyxa*, hematite and pyrolusite are occurring at pH 2.4, 2.2 and 2.5, respectively. The (IEP) of the hematite and pyrolusite has shifted as a result of bacteria treatment to 2.6 and 3.3, respectively. Although, *Paenibacillus polymyxa* showed higher adsorption by pyrolusite mineral but FTIR results proved that the type of adsorption occurred on hematite is mainly chemical adsorption which makes its surface more hydrophobic than that of pyrolusite.

The bacteria adsorption is pH dependent and the optimum floatability for hematite and pyrolusite occurs at pH 3. The conditioning time has an important effect on the bacteria adsorption. The bio-flotation of a hematite-pyrolusite binary mixture at pH 3 for 10 min in the presence of 5×10^{10} cells/ml, floated hematite with manganese reduction by 65%. Flotation of a natural iron ore containing 8.79% MnO_2, 0.49% SiO_2 and 67.90% Fe_2O_3 using latter conditions yielded a concentrate containing 3.7% MnO_2, 0.5% SiO_2 and 71.30% Fe_2O_3, with a hematite recovery of 72.46%.

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