The effect of various surfactants on fatty acid for apatite flotation and their adsorption mechanism

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Abstract: The synergistic effect of surfactants, i.e., Tween-80 (polyethylene glycol sorbitan monooleate), Span-80 (sorbitanoleate), and MES (fatty acid methyl ester sulfonates), on fatty acid collectors were investigated using single mineral flotation experiments, surface tension measurement, Fourier transform infrared spectrum, and contact angle measurements. The single mineral flotation experiments showed that it was possible to efficiently separate apatite from magnetite, quartz, and biotite by mixing fatty acids with surfactants. The surface tension measurement showed that the surfactants could significantly reduce the surface tension and Critical Micelle Concentration (CMC) of fatty acids. Fourier transform infrared spectroscopy analysis indicated that all of the surfactants did not react with the fatty acids, but only physically adsorbed on the surface of apatite, thus promoting the chemical adsorption of fatty acids on apatite. However, the surfactant chemisorbed on magnetite and competing with a fatty acid, which led to a decrease in the flotation recovery. The results for contact angle measurement showed that the contact angle difference between apatite and magnetite increased with the addition of surfactant, and resulted in an efficient separation.

Keywords: synergism effect, surfactant, flotation, apatite, magnetite

1. Introduction

Phosphate ore is an important industrial and agricultural raw material (Bata et al., 2013; Horta et al., 2016), and widely used in essential medicine, military industry, and other fields, and has significant strategic value for food security and industrial development. However, the grade of phosphate ore is relatively low in China, with an average grade of 16.85% (P$_2$O$_5$). Phosphate ore resources with ω (quality percentage) (P$_2$O$_5$) ≥ 30% account for only 12%, and most of the rest are low-grade refractory ores, which can only be used economically after treated with mineral processing technologies (Li et al., 2016; Loutou et al., 2019).

Flotation is one of the most common methods used to purify phosphate ore from the purities and improve its grade (Guimarães et al., 2004; Ruan et al., 2017; Oliveira, et al., 2019). Anionic fatty acids, which are mainly composed of a hydrophobic carbon chain and a hydrophilic carboxyl group, are often selected as collectors in phosphate ore flotation. The carboxyl group is easy to react with calcium ions on the apatite surface to form calcium carboxylate (Rao et al., 1990), which adsorb on the mineral surface, thus making the apatite mineral surface hydrophobic. However, fatty acid collectors have some disadvantages, such as low solubility, poor dispersity, poor temperature resistance, and poor selectivity. Therefore, the heating process is often used in the phosphate ore flotation, i.e., heating flotation, which dramatically increases the beneficiation cost.

Recent researches have mainly focused on the following directions to improve the separation index of phosphate ore and reduce the flotation cost: One is mixed-use of different reagents (Kou et al., 2010), i.e., adding surfactants to fatty acids for making a blending reagent; another one is the modification of fatty acid reagents (Apling, 1992; Lane, 2011), including the introduction of various polar functional

groups, polycarboxylic acid groups, sulfonic acid groups, sulfuric acid, hydroxyl groups, ethoxy groups, etc. However, it is challenging to obtain the ideal flotation indexes simply using the modified fatty acids, and some other flotation reagents still need to be added to the flotation system. Therefore, the mixed-use of reagents receives more and more attention for the development of phosphate flotation.

The surfactants are the critical factor for the blending reagents for archiving a high-efficiency apatite flotation. It is generally composed of the non-polar lipophilic (hydrophobic) hydrocarbon chain and polar lipophilic (hydrophobic) groups. Consequently, the surfactant can not only be used as a frother that adsorbed at the liquid/gas interface to reducing the bubble size and forming a stable bubble phase; but also could adsorb at the solid/liquid phase to enhance the surface wettability of the mineral that after interacted with the collector (Farrokhpay, 2011; Khoshdast, 2011). In apatite flotation, there are mainly two kinds of surfactants added to fatty acids forming the blending reagents; one is an anionic surfactant (sulfonic or carboxylic polar group), the other is a non-ionic surfactant (polyoxyethylene type, polyol type, alkanol amide type, polyether type, oxidized amine type, etc.). Oliveira et al. (2011) found that the mixed-use of sulfosuccinate acid and rice oil soap could improve the grade of phosphate concentrate, while the recovery remains constant, indicating that the surfactant could improve the selectivity of the collector. Sis et al. (2003) measured the contact angle between oleate and non-ionic surfactant hydroxy ethylated nonylphenol (NP-4) in pure apatite. Their results showed that the contact angle of apatite in the presence of oleate increased with the addition of NP-4, hence enhancing the hydrophobicity of apatite and increasing the recovery. Rao et al. (2011) investigated the effects of fatty acids, non-ionic surfactants (ethoxynonylphenol), and their mixtures on the separation of apatite and magnetite. The results showed that the addition of non-ionic surfactant could promote the flotation of apatite but did not affect the flotation of magnetite. Depending on those findings, it can be seen that surfactants could enhance the collecting capacity of fatty acids or enhance their selectivity to target minerals, i.e., significantly improving the flotation performance of fatty acids.

Therefore, in this study, to study the effect of fatty acid with surfactant addition on flotation performance of target minerals, single mineral flotation of pure apatite, magnetite, quartz, and biotite were investigated along with the surface tension measurement and contact angle measurements, and Fourier transforms infrared spectroscopy (FTIR) analysis under various conditions.

2. Materials and methods

2.1. Materials

Pure minerals used in this study, i.e., apatite, magnetite, quartz, and biotite, were obtained from Yunnan, China. The samples were first dry-crushed to below 10 mm, and then the crushed mineral was hand-picked to reject any pieces containing visible impurities. Then, the minerals were wet-screened to a size fraction of -74+38 µm after the dry-grinding using a BFA sealed ceramic mill (Changchun Keguang Electromechanical Co., Ltd). The -74+38 µm size fraction samples were used for direct flotation of each pure mineral. X-ray diffraction (XRD, D8 Advance, Bruker Inc., Germany) and X-ray fluorescence (XRF, EDX8300, Suzhou Sanzhi Precision Instrument Co., Ltd., China) were used to determine the crystalline phases and chemical compositions, and the results are shown in Fig. 1 and
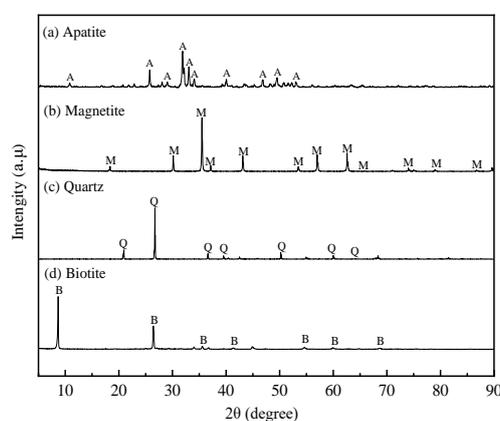
Fig. 1. XRD patterns of (a) apatite, (b) magnetite, (c) quartz, and (d) biotite

Table 1, respectively, which indicated that all the prepared samples had good quality and high purity.

The chemical reagents used in this study include anionic fatty acid collectors, surfactants, and pH regulators. The anionic fatty acid collector was produced in the Laboratory. Tween-80 & Span-80 and MES surfactants were obtained from Liaoning Quanrui Reagent Co. Ltd and Shanghai Youshuo Chemical Technology Co. Ltd., respectively. The molecular weights of Tween-80, Span-80, and MES were 428.60, 428.61, and 198 g/mol, respectively. The pulp pH of the flotation was adjusted with 0.1% sodium carbonate ($NaCO_3$, Analytical reagent, Liaoning Quanrui Reagent Co., Ltd., China) or 0.1% hydrochloric acid (HCl, Guaranteed reagent, Sinopharm Chemical Reagent Co., Ltd., China) solution when the required pH of the suspension was basic or acidic, respectively. The deionized (DI) water was obtained by a laboratory water purification system (Spring-R10, 18.25 MΩ·cm, Research Water Purification Technology Co., Ltd., China) and used in all experiments.

Table 1. Chemical compositions of apatite, magnetite, quartz, and biotite

Sample	Composition (wt.%)									
	Fe	SiO_2	MgO	Al_2O_3	P_2O_5	CaO	Fe_2O_3	K_2O	Na_2O	F
Apatite	-	-	0.08	4.20	39.56	53.35	1.69	-	-	1.12
Magnetite	71.95	2.77	-	0.43	-	0.14	-	-	0.0001	-
Quartz	-	99.37	-	0.21	0.04	0.36	0.01	-	-	0.01
Biotite	-	5.56		19.44	-	0.03	9.48	5.56	0.73	-

2.2.   Methods

2.2.1.   Micro-flotation experiments

The Micro-flotation experiments for the single minerals were conducted in an XFG II type flotation machine (5-35, Shicheng Guobang Mining Machinery Co., Ltd., China). First, 2 g of the -74+38 μm pure minerals and 20 cm³ of DI water were added into the flotation cell, then conditioned for 1 min with a stirring speed of 1500 r/min. Then, pH regulators were added, collector, and surfactant in turn at an interval of 2 min, followed by a 3 min flotation time to obtain the concentrate and tailing. Once the concentrate and tailing dried in an oven at 100°C for 20 min, the flotation recovery of each mineral was calculated using their weight.

2.2.2.   Surface tension measurements

The surface tension measurements for the surfactants were carried out by the pendant drop method using the contact angle measurement instrument (JC2000C, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd., China). The surface tension of DI water at room temperature (25°C) is 72.15 mN/m. Different concentrations of fatty acid and surfactant solutions were prepared for the surface tension measurement at room temperature. Each test was repeated 3 times, and the average value was taken while the results error within 8%.

2.2.3.   Fourier transform infrared spectroscopy analysis

The spectra analysis as a widely used method in studying the interaction mechanism between reagents and minerals was performed using a Fourier Transform Infrared Spectrometer (VERTEX 80v, Bruker Inc., Germany) at a condition of scan resolution 4 cm⁻¹, 256 scans, and wavenumber ranging from 400 to 4000 cm⁻¹. 2 g of pure mineral samples (-74+38 μm) was mixed with 20 cm³ surfactant solution at a specific pH value. Then, the mixed sample was stirred for 10 min followed by filtrating and rinsing 3 times with DI water. After that, the sample was dried in a vacuum oven at 40°C for 30 min. The dried samples were mixed and ground with KBr in an agate mortar and then used for FTIR reflection spectra measurement.

2.2.4.   Contact angle measurements

Surface wettability has been known to affect the floatability of minerals, i.e., minerals with high surface wettability tend to have lower floatability, and vice versa. Surface wettability is usually estimated from

the surface contact angle; therefore, the contact angle measurements were conducted to investigate the effect of reagent treatments on the surface wettability of samples. The experimental method was similar to that used by Sadeghinezhad et al. (2020) the pendant drop method. The contact angle was measured by a dynamic contact angle measuring instrument produced (JC2000C, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd., China) The prepared square sample (1×1×1 cm) with a smooth surface was put into a specific concentration of the solution and soaked for 5 min. The sample was placed on the workbench of the contact angle measurement instrument and put a drop of DI water on the sample surface by a capillary with a diameter of 0.5 mm after the sample was dried at room temperature. Once the water drop is being stable, the images were collected and the contact angle was determined. The measurements were repeated (3×) at different spots on the mineral surface, and the average value of the contact angle readings was reported. The measurement was carried out at room temperature (25°C), and three consecutive averages were taken for each data point (error ± 8%).

3.   Results and discussion

3.1.   Flotation experiments with single minerals

3.1.1. Effect of the pH

The effects of pH on the floatability of apatite, magnetite, quartz, and biotite were investigated under the conditions of the collector (fatty acid) dosage of 200 mg/dm^3 while the pH was in a range of 6.0-10.0. The results are shown in Fig. 2 in which the flotation recovery of apatite slightly increased from pH 6.0 to 9.0, whereas it decreased when the pH was over 9.0. These results may be due to there are a large number of RCOOH under weakly alkaline conditions, which can form molecular ion complexes with RCOO$^-$ (Somasundaran et al., 1984; Martińez et al., 1995). At this time, the surface electronegativity of apatite becomes weak, and the electrostatic repulsion between collector molecules or ions and mineral surface decreases, which is beneficial to the physical adsorption of collector molecules or ions on the mineral surface. On the other hand, fatty acids mainly exist in the forms of RCOO$^-$ or (RCOO)$_2$$^{2-}$ under alkaline conditions; therefore, chemical adsorption occurs on the surface of apatite with Ca^{2+} (Fa et al., 2004). However, when the pH at the high alkali condition, because OH$^-$ ions strongly compete with RCOO$^-$ ions on the mineral surface, resulting in decreased fatty acid anion adsorption and the apatite recovery.

In the case of magnetite, the recovery slightly increased with the increase of pH in a range of pH 6.0-7.0. That was due to the increase of negative charge on the surface of magnetite, resulting in a high level of the RCOO$^-$ concentration, which is conducive to the chemical adsorption between the anion in fatty acid and the Ca^{2+} on the surface of magnetite. However, when the suspension pH was over 7.0, the flotation recovery of magnetite decreased sharply, while it was 0.06% at pH 10.0. The reason was that under alkaline conditions, the adsorbed ions falling off from the magnetite surface due to the competitive adsorption took place between the RCOO$^-$, (RCOO)$_2$$^{2-}$, and RCOOHRCOO$^-$ in fatty acid solution with OH$^-$, resulting in a decrease in adsorption capacity. There was no change in the recovery for quartz and biotite when the pH was between 6.0 and 10.0 because fatty acids almost have a non-collecting effect on quartz and biotite. It can be seen from the data in Fig. 2 that the difference of recovery of apatite and magnetite was most significant at pH 8.0, 9.0, and 10.0. However, relatively high pH requires more pH regulator addition, i.e., more OH$^-$ ions in the pulp and adsorbed on the mineral surface, making the surface of the sample hydrophilic and hindering the adsorption of fatty acids. Therefore, the optimal pH was determined to be 8.0 in the following experiments.

3.1.2. Effect of the collector dosage

The effects of fatty acid dosage on the floatability of apatite, magnetite, quartz, and biotite were investigated under the conditions of pH 8.0, while the collector dosage was in a range of 50-200 mg/dm^3. The results are shown in Fig. 3. The recovery of apatite increased from 15.25% to 93.53% when the fatty acid dosage increased from 50 to 200 mg/dm^3 at pH 8.0, whereas it remained almost constant when further increases the collector exceeds 200 mg/dm^3. On the other hand, the magnetite recovery reached 33.41%, while the fatty acid dosage increased from 50 mg/dm^3 to 250 mg/dm^3. However, the recovery of quartz and biotite did not change anymore when the collector dosage was adjusted to be 50-250

mg/dm^3. The results showed that fatty acids did not affect collecting quartz and biotite (Li et al., 2002; Xu et al., 2013). As shown in Fig. 3, the most efficient separation of apatite and the other three pure minerals was obtained at a fatty acid dosage of 200 mg/dm^3, which was therefore determined as the optimal condition.
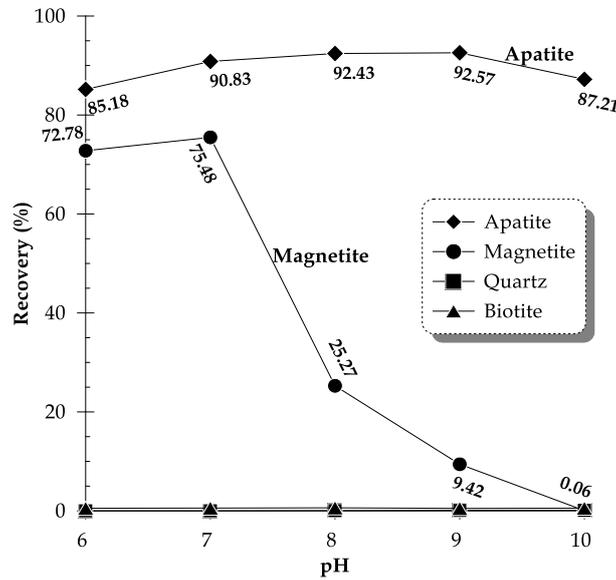
Fig. 2. The effect of pH on the single minerals flotation (Pulp density: 10%, fatty acid dosage: 200 mg/dm^3, surfactant dosage: 0 mg/dm^3, temperature: 25°C, flotation time: 3 min, and pH 6.0-10.0)
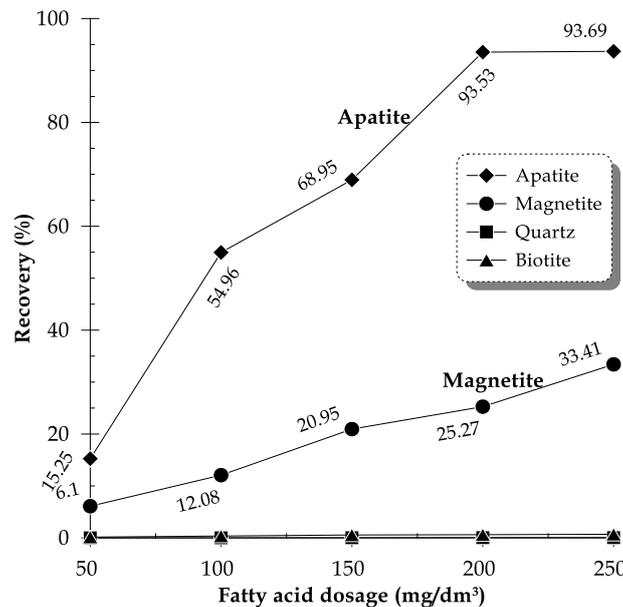
Fig. 3. The effect of fatty acid dosage on the single minerals flotation (Pulp density: 10%, pH 8.0, surfactant dosage: 0 mg/dm^3, temperature: 25°C, flotation time: 3 min, and fatty acid dosage: 50-200 mg/dm^3)

3.1.3. Effect of the surfactant under various pH

The effect of the surfactant (Tween-80, Span-80, and MES) under various pH on the single minerals (apatite, magnetite, quartz, and biotite) flotation was investigated under the conditions of 200 mg/dm^3 collectors and 15 mg/dm^3 surfactants, while the pH was adjusted in a range of 6.0-10.0. The results are shown in Fig. 4. The recovery of apatite slightly increased when injecting the surfactant and increasing the suspension pH, which indicated that the surfactant could promote the adsorption of fatty acids on the apatite surface (Filippova et al., 2014). At pH 8.0 with 15 mg/dm^3 of Tween-80, Span-80, and MES, the apatite recovery increased to 94.83%, 94.64%, and 93.48%, respectively. As seen from Fig. 4 that the

magnetite recovery decreased dramatically with the addition of surfactant compared with the condition of non-surfactant, especially to MES in which the recovery decreased from 25.27% to 12.28% at pH 8.0. For quartz and biotite, there were no differences with the addition of surfactant and adjusting the pH.
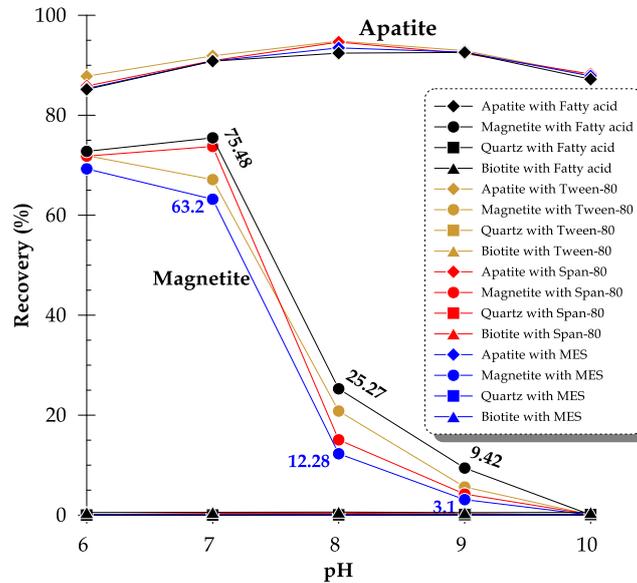
Fig. 4. The effect of the surfactant under various pH on the single minerals flotation (Pulp density: 10%, fatty acid dosage: 200 mg/dm³, surfactant dosage: 15 mg/dm³, temperature: 25°C, flotation time: 3 min, and pH 6.0-10.0)

3.1.4.   Effect of the surfactant dosage

The effect of surfactant on the single minerals flotation was conducted at pH 8.0 and 200 mg/dm³ fatty acid, and surfactant dosages in a range of 0-100 mg/dm³. As seen in Fig. 5, the recovery of apatite slightly increased when the surfactant dosage was adjusted from 0 to 15 mg/dm³, whereas it decreased dramatically with a further increase in 100 mg/dm³. That was maybe due to the competitive adsorption between the surfactant and fatty acid, preventing the precipitation of calcium carboxylate ions in the form of calcium carboxylate. In the case of magnetite, the recovery decreased with the increasing surfactant dosage, and it was found that there was no significant difference between Tween-80, Span-80, and MES. As can be seen from Fig. 5, the most efficient separation of apatite and magnetite was obtained at the condition of 15 mg/dm³ MES, in which the recovery difference was 83.47%.
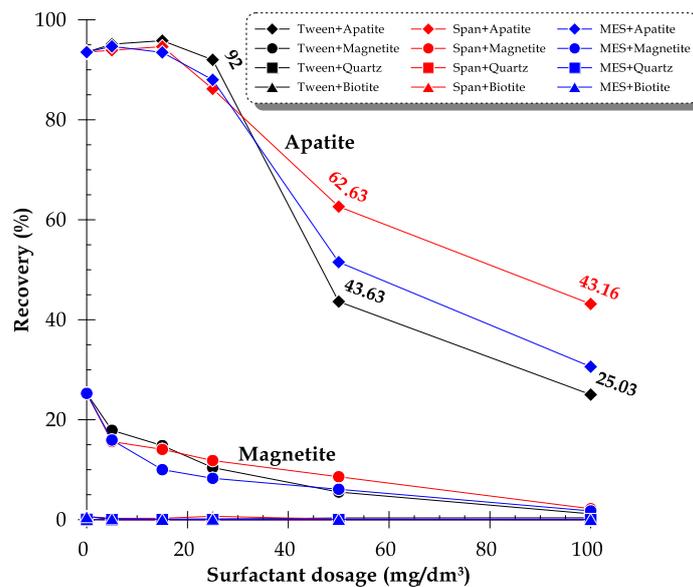
Fig. 5. The effect of the surfactant dosage on the single minerals flotation (Pulp density: 10%, fatty acid dosage: 200 mg/dm³, pH 8.0, temperature: 25°C, flotation time: 3 min, and surfactant dosage: 0-100 mg/dm³)

3.2. Surface tension experiments

The surface tension measurement was conducted at various reagents and their dosages to understand the interaction mechanism between surfactants and collectors (fatty acids). The results are shown in Fig. 6. It should be noted that Tween-80 and Span-80 is a non-ionic surfactant and MES is an anionic surfactant. As shown in Fig. 6 that the CMC (Critical Micelle Concentration) of the fatty acid was 320 mg/dm^3, in which the surface tension was 35 mN/m. However, the CMC and surface tension of the tested solution dramatically decreased when the coexisting with fatty acid and surfactant in contrast to the condition with a single reagent, e.g., the collector only and surfactant only, which indicated that the surfactants had synergistic effects on fatty acids. That was because surfactants addition helped to form a more stable foam, thus reducing the bubbles bursting and improving the flotation probability of the ore particles. It was found that the ability to reduce the surface tension of fatty acid was MES > Tween-80 > Span-80. The synergistic effect of Tween-80 and Span-80 on fatty acids was mainly because the portion of oxygen atoms in the molecules of those surfactants are partially protonated in an aqueous solution and generate positive electricity resulting in strong interaction with anionic fatty acid collectors (Schwuger, 1973; Hua et al., 1982; Hanumantha Rao et al., 1997). Additionally, the non-ionic surfactant molecules could enter between the fatty acid ions, which weakens the electrical repulsion between the fatty acid molecules (Vold, 1964). Therefore, the surface activity of the compound system, i.e., surfactant with a fatty acid, is better than that of the collector only. The synergistic effect of MES on fatty acids is mainly due to the inductive interaction between the carbonyl group and the sulfonic acid group in the solution, leading to the electrostatic repulsion between the hydrophilic ions to be buffered and reducing the CMC of fatty acid.
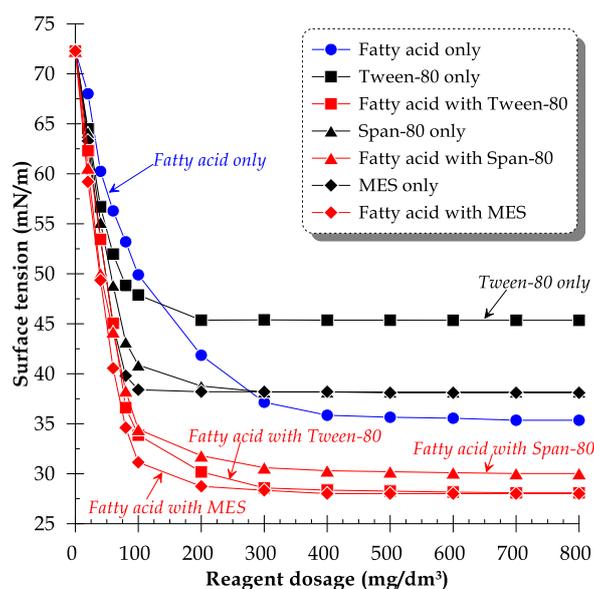
Fig. 6. The surface tension of the tested solution with various reagents and concentrations (Fatty acid dosage: 200 mg/dm^3, surfactant dosage: 15 mg/dm^3, temperature: 25°C, and pH 8.0)

3.3. Fourier transform infrared (FTIR) analysis

Fourier transform infrared (FTIR) spectra of apatite and magnetite minerals before and after fatty acids and the surfactants treated were obtained to investigate the interaction mechanism between the reagents and minerals, and the results are shown in Figs. 7-9. The wavenumber of 1560.89 cm^{-1} in Fig. 7 (a) is due to the stretching vibration of COOH$-$. The characteristic absorption peaks 2922.37 cm^{-1} and 2857.86 cm^{-1} in Fig. 7 (b) are due to the stretching vibration of $-CH_2-$. The peaks located at 1248.37 cm^{-1} and 1111.29 cm^{-1} are assigned to the asymmetrical and symmetrical stretching vibration of $C-O-C$, while the peak at 947.25 cm^{-1}, 850.53 cm^{-1}, and 1735.26 cm^{-1} are due to $C-H$ out-of-plane bending vibration and C=O stretching vibration, respectively. The peak of 1465.24 cm^{-1}, 1373 cm^{-1}, and 1725.30 cm^{-1} in Fig. 7 (c) belongs to $-CH_2-$ bending vibration, $-CH_3$ symmetrical deformation vibration, and C=O stretching vibration, respectively. The characteristic absorption peaks at 1725.30 cm^{-1}, 620.43 cm^{-1}, and

553.6 cm^{-1} are due to the C=O stretching vibration, S=O stretching vibration, and COO$^-$ formation vibration. The peaks located at 1218.44 cm^{-1} and 1124.67 cm^{-1} are assigned to the asymmetrical and symmetric stretching vibration of SO$_3^-$, respectively.

The peaks of 1095.51 cm^{-1}, 604.03 cm^{-1}, 1042.34 cm^{-1}, and 567.76 cm^{-1} in Fig. 8 (a) are the characteristic absorption peaks of PO$_4^{3-}$ (Eslami et al., 2009). The infrared spectrum of apatite with fatty acid is given in Fig. 8 (b). With the addition of the collector, some new peaks of 2922.71 cm^{-1} and 2857.58 cm^{-1} appeared in the infrared spectrum, while the peak at 1042.34 cm^{-1} shifted about 4 cm^{-1} (to 1047.59 cm^{-1}), indicating that the chemical adsorption between apatite and fatty acid occurs, which also accords with our earlier observations. In the case of the infrared spectrum apatite treated with fatty acid and surfactant (see Fig. 8 (c), (d), and (e)), the characteristic absorption peaks of Tween-80, Span-80, and MES did not appear, indicating that the surfactants did not react with fatty acids and generate new compounds, i.e., the surfactant only physically adsorbed on the surface of apatite (Luo et al., 2000). Because of that, the chemical environment of calcium on the surface of apatite was improved, which could promote the collector's chemical adsorption on apatite. This finding is consistent with the flotation results given in section 3.1.4, which showed that the recovery of apatite increased slightly with the addition of surfactant at pH 8 compared with that of the collector only.
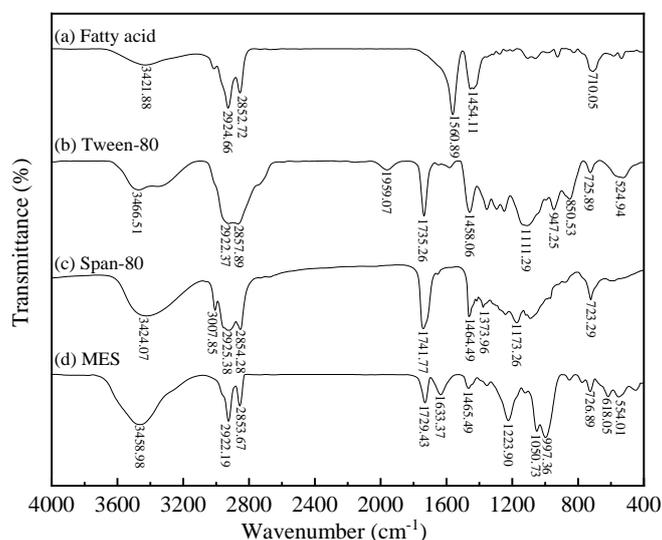
Fig. 7. FTIR spectra of the reagents at pH 8 and 25°C
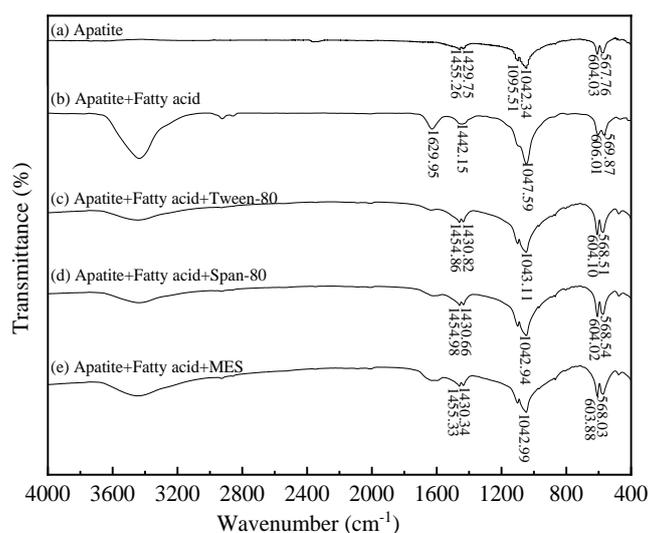
Fig. 8. FTIR spectra of apatite treated by the reagents at pH 8 and 25°C (Fatty acid dosage: 200 mg/dm^3, surfactant dosage: 15 mg/dm^3)

It can be seen from Fig. 9 (a), the peaks located at 1104.66 cm^{-1} and 470.5 cm^{-1} are due to the bending vibration peak of Fe-O, and the peak of 572.67 cm^{-1} is assigned to the stretching vibration of Fe-O. It was found that the characteristic peak which referring to the bending vibration of Fe-O, red-shifted from 1104.66 cm^{-1} to 1045.21 cm^{-1}, indicating that fatty acid chemical adsorbed onto the apatite. The infrared spectrum peaks assigned to Fe-O bending vibration shifted from 1045.21 cm^{-1} to 1039.82 cm^{-1}, 1040.09 cm^{-1}, and 1040.15 cm^{-1} when the magnetite and fatty acid were treated with Tween-80, Span-80, and MES, respectively, indicating that all of the three surfactants could chemically be adsorbed onto magnetite surface. Therefore, the surfactants might form hydrophilic substances and reject the adsorption of the collector on the mineral surface, resulting in a decreasing magnetite recovery discussed in section 3.1.4.
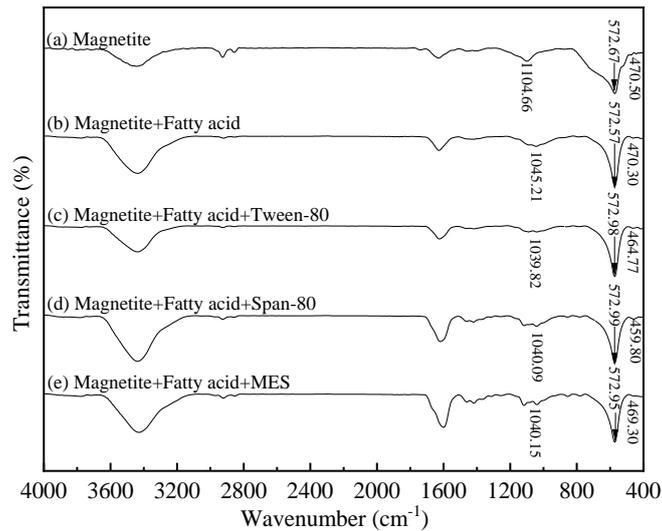
Fig. 9. FTIR spectra of magnetite treated by the reagents at pH 8 and 25°C (Fatty acid dosage: 200 mg/dm^3, surfactant dosage: 15 mg/dm^3)

3.4. Contact angle measurements

The activity of the mineral surface is related to the flotation reagent and depends on the force acting on its surface. When a liquid comes into contact with a solid in bulk, gaseous phase, according to Young's equation, there is a relationship between the contact angle θ, the surface tension of the liquid γ_{LG}, the interfacial tension γ_{SL} between liquid and solid, and the surface free energy γ_{SG} of the solid as follows:

$$\gamma_{SG} = \gamma_{LG} \cdot \cos\theta + \gamma_{SL} \tag{1}$$

The value $\theta=90°$ can be used as the boundary between wetting and non-wetting, in which between $0°<\theta<90°$ the solid is wettable and above 90° it is not wettable (Zhu et al., 2020).

The contact angle measurements of the minerals in the absence and presence of reagents were carried out at pH 8, 200 mg/dm^3 fatty acid, and the surfactant dosage of 15 mg/dm^3. As can be seen from Fig. 10 that the contact angles of the apatite and magnetite surface that prepared without reagents addition were 35.64° and 28.33°, respectively. With the addition of fatty acid, the contact angle values increased sharply to 56.64° and 50.11°, respectively. However, the floatability between the two minerals was not much different, even treated with the collector. The contact angle dramatically increased to around 75° when the apatite treated with fatty acid and surfactants, and the most excellent angle of 76.32° was obtained at the condition of MES addition. In the case of magnetite, the contact angle slightly decreased with the addition of surfactant compared with that of fatty acid only. The order of the contact angle difference between apatite and magnetite with collector and surfactant was Tween-80 (26.21) < Span-80 (26.25) < MES (30.65), which agree with the previous results (see Figs. 4 and 5).

4.   Conclusions

This study aimed to assess the synergistic effects of surfactants on fatty acid collectors and establish their interaction mechanism. The findings can be summarized below:
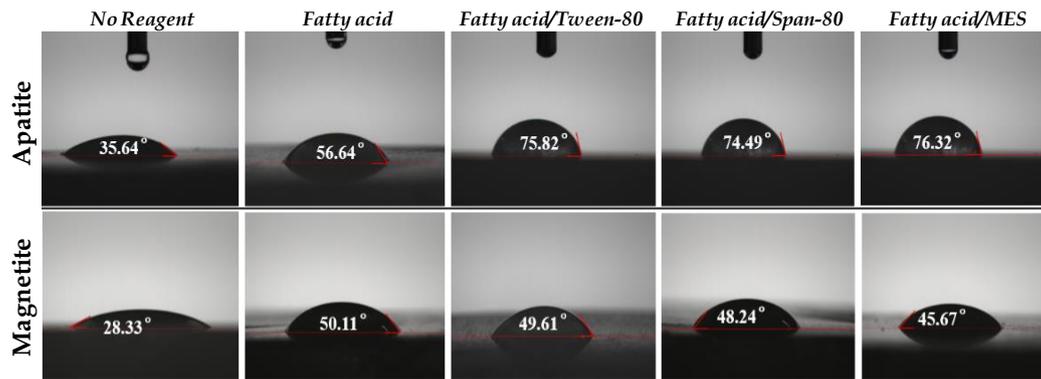
Fig. 10. The contact angle of the minerals before and after treated with reagents (Fatty acid dosage: 200 mg/dm³, surfactant dosage: 15 mg/dm³)

1) With the addition of surfactant with a fatty acid, apatite and magnetite can be effectively separated compared with fatty acid only.

2) The surfactant can significantly reduce the surface tension and CMC of fatty acids, thus affecting apatite flotation indexes. However, it should be noted that the surfactant dosage is a critical factor for apatite flotation, i.e., adding a small amount of surfactant can promote apatite to float up; on the contrary, it will reduce the recovery.

3) The results of infrared spectrum analysis showed that apatite and magnetite could be effectively separated by adding surfactant into fatty acid. For apatite, the surfactants physically adsorbed on it, promoting the chemical adsorption of fatty acids on apatite, thereby improving the recovery. For magnetite, the surfactant chemisorbed on magnetite, and competed with a fatty acid, resulting in a decrease of recovery.

4) The results of contact angle measurements showed that with the addition of surfactant, the contact angle of apatite increased significantly. At the same time, that of magnetite decreased slightly, and the contact angle difference between the two minerals increased, leading to different floatability and resulting in an efficient separation of apatite from magnetite.

Therefore, the results of this study indicate that the mixed-use of surfactant with fatty acid could significantly improve the separation efficiency of apatite and magnetite.

Acknowledgments

References

APLING, A., 1992. *Flotation: theory, reagents and ore testing: Ronald D. Crozier, Pergamon Press, Oxford. ISBN 0-08-041864-3, 343 pages.* Corros. Sci, 33(12), 1997-1998.

BADA, S., GCANGA, S., FALCON, L., FALCON, R., MAKHULA, M., 2013. *Electrostatic concentration of phosphate flotation concentrate.* Int. J. Min. Sci. Techno, 23(3), 403–406.

ESLAMI, H., SOLATI-HASHJIN, M., TAHRIRI, M., 2009. *The comparison of powder characteristics and physicochemical, mechanical and biological properties between nanostructure ceramics of hydroxyapatite and fluoridated hydroxyapatite.* Mat. Sci. Eng. C-Mater, 29(4), 1387–1398.

FA, K., JIANG, T., NALASKOWSKI, J., MILLER, J.D., 2004. *Optical and spectroscopic characteristics of oleate adsorption as revealed by FTIR analysis.* Langmuir, 20(13), 5311–5321.

FARROKHPAY, S., 2011. *The significance of froth stability in mineral flotation – A review.* Adv. Colloid. Interfac, 166(1-2), 1–7.

FILIPPOVA, I.V., FILIPPOV, L.O., DUVERGER, A., SEVEROV, V.V., 2014. *Synergetic effect of a mixture of anionic and non-ionic reagents: Ca mineral contrast separation by flotation at neutral pH.* Miner. Eng, 66-68, 135–144.

GUIMARAES, R.C., ARAUJO, A.C., PERES, A.E.C., 2005. *Reagents in igneous phosphate ores flotation.* Miner. Eng, 18(2), 199–204.

HANUMANTHA RAO, K., FORSSBERG, K.S.E., 1997. *Mixed collector systems in flotation*. Int. J. Miner. Process, 51(1-4), 67–79.

HORTA, D., DE MELLO MONTE, M.B., DE SALLES LEAL FILHO, E.L., 2016. *The effect of dissolution kinetics on flotation response of apatite with sodium oleate.* Int. J. Miner. Process, 146, 97–104.

HUA, X.Y., ROSEN, M.J., 1982. *Calculation of the coefficient in the Gibbs equation for the adsorption of ionic surfactants from aqueous binary mixtures with non-ionic surfactants.* J. Colloid. Interf. Sci, 87(2), 469–477.

KHOSHDAST, H. and SAM, A., 2011. *Flotation frothers: Review of their classifications, properties and preparation.* Open Mineral Processing Journal, 4(1), 25-44.

KOU, J., TAO, D., XU, G., 2010. *Fatty acid collectors for phosphate flotation and their adsorption behavior using QCM-D.* Int. J. Miner. Process, 95(1-4), 1–9.

LANE, G.S., 2011. *Flotation Reagents.* Patent Cooperation Treaty, International Publication Number: WO 2011/085445 A1, https://www.freepatentsonline.com/wo2011085445.html.

LI, Y., LEI, D.S., & XU, S., 2002. *Effect of metal ions in pulp on flotation separation of sillimanite from quartz.* Journal of The Chinese Ceramic Society, 03, 362-365.

LI, M.D., CONG, X., ZHU, L., KONG, L., ZHANG, Z., TIAN, A., LI, L., 2016. *Experimental study on recycling dredged marine sediment and phosphate tailing to produce earth fill.* Mar. Georesour Geotec, 35(4), 586–591.

LOUTOU, M., MISRAR, W., KOUDAD, M., MANSORI, M., GRASE, L., FAVOTTO, C., HAKKOU, R., 2019. *Phosphate mine tailing recycling in membrane filter manufacturing: Microstructure and filtration suitability.* Minerals-Basel, 9(5), 318.

LUO, H.H., ZHONG, K.N., WEI Y.H., 2000. *Effects of synergism on the flotation performance of apatite at environmental temperature.* Industrial Minerals & Processing, 05, 8-10.

MARTINEZ, A.L., URIBE, A.S., 1995. *Interfacial properties of celestite and strontianite in aqueous solutions.* Miner. Eng, 8(9), 1009–1022.

OLIVEIRA, M.S., SANTANA, R.C., ATAÍDE, C.H., BARROZO, M.A.S., 2011. *Recovery of apatite from flotation tailings.* Sep. Purif. Technol, 79(1), 79–84.

OLIVEIRA, P.D., MANSUR, H., MANSUR, A., SILVA, G.D., PERES, A.E.C., 2019. *Apatite flotation using pataua palm tree oil as collector.* J. Mater. Res. Technol, 8(5), 4612–4619.

RAO, K.H., ANTTI, B.M., FORSSBERG, E., 1990. *Mechanism of oleate interaction on salt-type minerals, Part II. Adsorption and electrokinetic studies of apatite in the presence of sodium oleate and sodium metasilicate.* Int. J. Miner. Process, 28(1-2), 59–79.

RAO, K.H., DWARI, R.K., LU, S., VILINSKA, A., SOMASUNDARAN, P., 2011. *Mixed anionic/non-ionic collectors in phosphate gangue flotation from magnetite fines.* Open Mineral Processing Journal, 4(1), 14.

RUAN, Y., ZHANG, Z., LUO, H., XIAO, C., ZHOU, F., CHI, R., 2017. *Ambient temperature flotation of sedimentary phosphate ore using cottonseed oil as a collector.* Minerals-Basel, 7(5), 65.

SADEGHINEZHAD, E., QADEER SIDDIQUI, M.A., ROSHAN, H., REGENAUER-LIEB, K., 2020. *On the interpretation of contact angle for geomaterial wettability: Contact area versus three-phase contact line.* J. Petrol. Sci. Eng, 107579.

SCHWUGER, M., 1973. *Mechanism of interaction between ionic surfactants and polyglycol ethers in water.* J. Colloid. Interf. Sci, 43(2), 491–498.

SIS, H., CHANDER, S., 2003. *Adsorption and contact angle of single and binary mixtures of surfactants on apatite.* Miner. Eng, 16(9), 839–848.

SOMASUNDARAN, P., ANANTHAPADMANABHAN, K., IVANOV, I., 1984. *Dimerization of oleate in aqueous solutions.* J. Colloid. Interf. Sci, 99(1), 128–135.

VOLD, M.J., 1964. *Colloidal Surfactants. Some Physicochemical Properties.* J. Am. Chem. Soc, 86(7), 1461–1461.

XU, L., WU, H., DONG, F., WANG, L., WANG, Z., XIAO, J., 2013. *Flotation and adsorption of mixed cationic/anionic collectors on muscovite mica.* Miner. Eng, 41, 41–45.

ZHU, Z., WANG, D., YANG, B., YIN, W., ARDAKANI, M.S., YAO J., DRELICH, J.W., 2020. *Effect of nano-sized roughness on the flotation of magnesite particles and particle-bubble interactions.* Miner. Eng, 151, 106340.