

Received November 4, 2019; reviewed; accepted March 25, 2020

Investigating flotation behavior and mechanism of modified mineral oil in the separation of apatite ore

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Abstract: In order to enhance the separation floatation of apatite ore, one mineral oil (MO), a petroleum base oil, as a raw material was modified to obtain a novel high-efficiency collector. The optimized modified mineral oil collector (MPBO) was obtained by systematically modified experiments. The results showed that the optimized condition of modification was air-flow rate 0.15 m³/h, potassium permanganate 0.2% (0.04 g), the reaction time 24 h and the temperature 140 °C. The flotation performance and mechanism of MPBO were further studied by flotation tests, zeta potential measurements, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The results of flotation tests showed that MPBO had a higher selectivity than oxidized paraffin soap. When 400 g/t MPBO was used as collector, the concentrate with 96.89% P₂O₅ recovery and 26.08% P₂O₅ grade was obtained. It also indicated that MPBO as the collector not only significantly improved the separation index of apatite ore flotation, but also greatly shortened and simplified the flotation process. The analysis of zeta potential, FTIR spectra and XPS revealed that carboxyl group was presented in the MPBO, which could form calcium carboxylate with calcium ion on the apatite surface by chemisorption.

Keywords: mineral oil, modification, apatite flotation, adsorption mechanism

1. Introduction

Phosphorus is one of the most common elements on earth and an indispensable mineral resource in life (Sørensen et al., 2015). Phosphate ore is the dominating natural resource for phosphorus extraction while apatite is the most common phosphate ore (Cao et al., 2015). The production and utilization of phosphate ore play an important role in economic development (Ge et al., 2008; Oliveira et al., 2011; Zhou et al., 2015). It is a crucial chemical raw material widely used in ceramics, food, medicine, dyes, fertilizers, and so on (Jong et al., 2017). With the depletion of the easy-to-process and high-grade phosphate ores, utilization of low-grade complex and highly disseminated phosphate ores have become inevitable (Abouzeid et al., 2008; Abouzeid et al., 2009).

Depending on the type of phosphate deposit, phosphate ores can be enriched by different techniques, such as gravity separation, fractionation and froth flotation (Abdel et al., 2000; Elshall et al., 2004; Kyzas and Matis, 2016). Among these methods, flotation has been widely applied in industrial production and more than half of the world's phosphate production benefits from this process (Clark et al., 2006; Hacifazlioglu et al., 2007; Salah et al., 2011). In the flotation process, amine collectors and anionic fatty acid are the most frequently used collectors for direct flotation of phosphate ores, but the large dosage of collectors and high cost exist in the actual production (Sevim et al., 2003; Guan et al., 2009). Recycling waste oil has been regarded as an effective method to prepare fatty acid collectors, not only to reduce environmental pollution, but also to reduce the costs of the collector (Maltesh et al., 1996).

Over the past few years, modification of waste oil which could improve the flotation behavior for phosphate ores had attracted the attention of researchers. Tian utilized the hydrolysis method to stratify waste oil to prepare an anionic collector by sulfonation and saponification, which was applied in the flotation test of iron, fluorite, and apatite (Tian, 2011). Yu et al. changed catering waste oil into the fatty acid collector to float iron ore, apatite, and fluorite, and obtained good flotation results (Yu et al., 2013). Yang et al. directly used drainage oil and emulsified drainage oil in the flotation process of coal and found them played good collecting roles (Yang et al., 2013). Yu et al. prepared collectors by hydrolysis method using four types of hogwash oils and compared their differences on apatite flotation (Yu et al., 2018).

Mineral oil was a by-product of the petroleum industry and its main component was the hydrocarbon. Due to the raising awareness of waste oil in the current way of being re-used or disposed, the public had paid ever-increased attention to the utilization of petroleum base oil. Currently, mineral oil was principally used to prepare cable filling grease, various lubricants and rubber industries, etc. (Lu et al., 1998 & Sejidov et al., 2007). However, mineral oil or its ramifications were rarely used as collectors in phosphate rock flotation, while oxidized paraffin soap, one fatty acid mixture, from the oxidation of one paraffin base oil has been widely used as the collector in the flotation of phosphorite.

In view of this, modification of mineral oil was conducted in this work and the application of this modifier in apatite flotation was also involved. Effects of modification conditions such as air flow rate, reaction time, reaction temperature and potassium permanganate dosage on flotation results of apatite were discussed in detail. The adsorption characteristics and mechanism of the modified collector on the apatite surface were also studied by zeta potential measurements, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

The pure mineral of apatite used in the paper was obtained from Mozambique. High grade samples were handpicked, crushed and ground in a porcelain ball mill. And then it was wet-sieved to obtain the $-74 + 15 \mu\text{m}$ particle size components, subsequently, they were soaked 3 times with deionized water. After natural air drying, pure apatite minerals with a purity of higher than 95% were obtained, which was confirmed by chemical analysis and X-ray diffraction analysis (Fig. 1a). As shown in Table 1, the phosphorus pentoxide (P_2O_5) grade of the pure mineral was 40.96%.

The apatite ore was obtained from overflow product of Chaoyang phosphate mine. After air drying, mixing and dividing, the apatite ore was kept in self-sealing bags as the sample of flotation experiments. Chemical compositions of apatite ore were analyzed and the results were shown in Table 2. The results indicated that P_2O_5 grade of this apatite ore sample was relatively low, which was only 1.72%. X-ray diffraction patterns were used to determine the mineral composition of the sample and the results were shown in Fig. 1b.

Table 1. Chemical analysis of pure apatite (wt.%)

Composition	P_2O_5	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O
Grade	40.96	1.08	0.04	0.23	54.31	0.13	3.25

Table 2. Chemical analysis of apatite ore (wt.%)

Composition	P_2O_5	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Grade	1.72	47.47	7.68	14.03	7.19	4.76	3.25	2.08	0.26

2.2. Reagents

Potassium permanganate, sodium silicate, sodium carbonate, ethanol, dimethicone and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Pine oil and oxidized

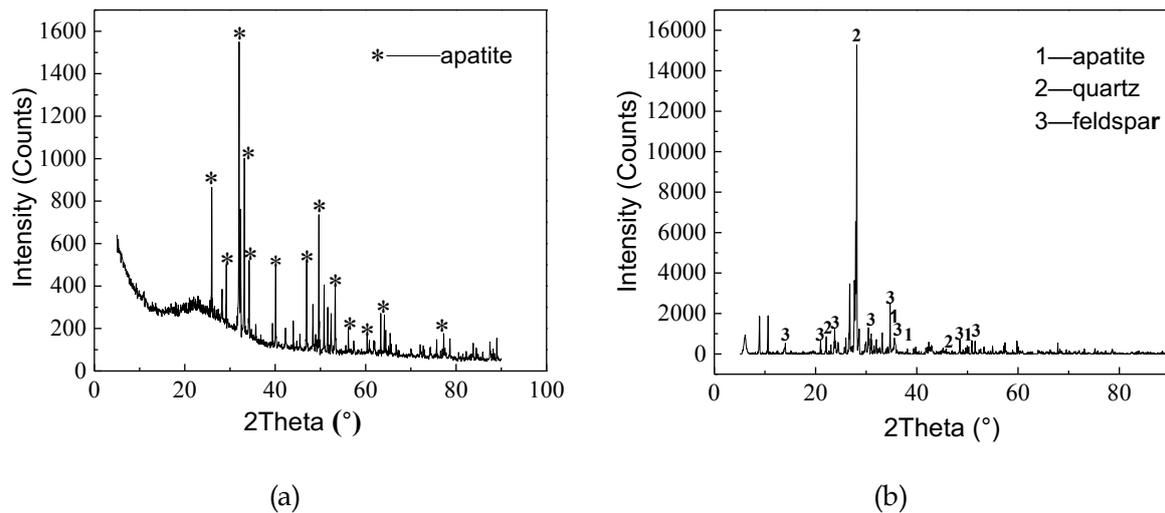


Fig. 1. The X-ray diffraction patterns of (a) pure apatite and (b) apatite ore

paraffin soap was supplied by Tieling mineral processing pharmaceutical company, China. All reagents were used as received without further purification. Pine oil was used as the frother. HCl and Na_2CO_3 solutions were used to adjust pH of the slurry. Na_2SiO_3 solution was used as the depressant and dispersant. Potassium permanganate was used as the oxidant. Sodium hydroxide was used as a catalyst in the modification process (saponification reaction). Mineral oil (MO) was the raw material for the modified collector. MPBO and oxidized paraffin soap were used as collectors. MO (mainly composed of $\text{C}_{19}\text{-C}_{22}$ saturated alkanes) provided by China national offshore oil corporation, had a density of 0.844 g/cm^3 with $5.179 \text{ m}^2/\text{s}$ kinematic viscosity. The results of the mass spectrometry approach in Fig. 2 showed that the main components of the MO were organic substances with a relative molecular weight of 274.5, 303.5 and 318.4. Tap water was used throughout the flotation experiments, while deionized was used for the inspection test.

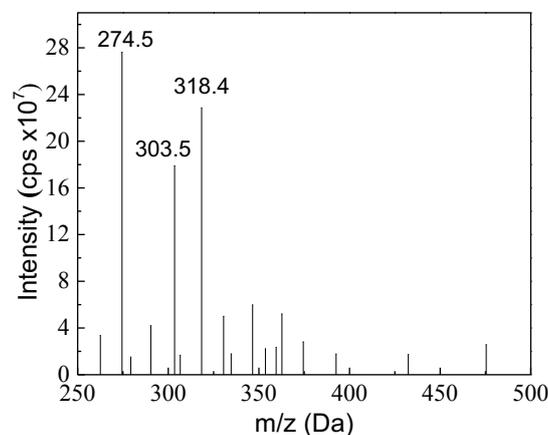


Fig. 2. Mass spectrum of MO

2.3. Methods

2.3.1. Flotation

The flotation tests were carried out in a 0.75 L flotation cell by adding 200 g of mineral samples to adjust the slurry concentration to 26.60%. Flotation cell was suspended on a laboratory XFD_{III} single tank flotation machine. And the slurry was agitated with a mechanical impeller at a speed of 1620 r/min. All flotation tests were carried out at room temperature ($20 \pm 2 \text{ }^\circ\text{C}$), while Na_2SiO_3 and pine oil were used in amounts of 2000 g/t and 50 g/t, respectively. The pH of flotation was 9 ± 0.5 . After flotation tests, both the concentrate and tailings were dried, sampled and analyzed, respectively. The flowsheet for flotation experiments is shown in Fig. 3.

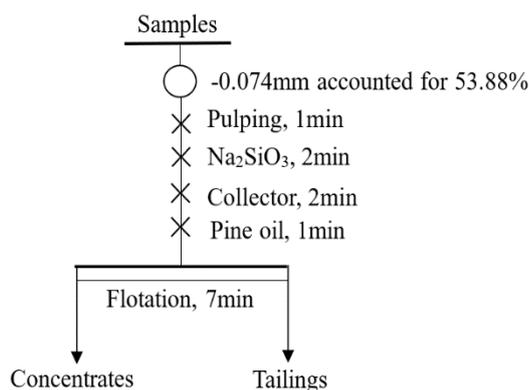


Fig. 3. The flotation flowsheet of apatite

2.3.2. FTIR analysis

Fourier transform infrared spectra (FTIR) were inspected by Nicolet FTIR-740 spectrometer, and they were recorded in the range of 400.0 to 4000.0 cm^{-1} . The mineral slurry ($-10.0 \mu\text{m}$) was stirred with/without MPBO in the flotation cell for 30 min, and the suspension was then centrifuged. The precipitates were gently washed three times with deionized water, and dried thoroughly in a vacuum oven at room temperature. And then, 1.0 mg of the mineral was mixed with 100.0 mg of KBr powder in an agate mortar. The mixture was further ground to reduce the particle size and mix thoroughly. The powdered mixture was then pressed into a sheet for FTIR analysis (Liu et al., 2020).

2.3.3. Zeta potential measurement

Zeta potential analysis was conducted with a Nano-ZS90 zeta potential analyzer from Malvern Instruments Ltd. Britain. Apatite samples (10.0 mg, $-5.0 \mu\text{m}$), conditioned with 40.0 mL of deionized water were stirred 5 min by a magnetic stirrer. A series of pH values were adjusted with HCl and NaOH solutions. At each condition, the average value of at least three individual measurements was accredited as the measured value (Liu et al., 2019).

2.3.4. XPS measurement

X-ray photoelectron spectroscopy (XPS) experiments were performed using an American Thermo VG ESCALAB 250 equipped with an Al target. The sample preparation was similar to the samples for FTIR measurements. The standard C1s binding energy (286.4 eV) was adjusted based on all spectra, and the surface composition was further analyzed (Liu et al., 2019).

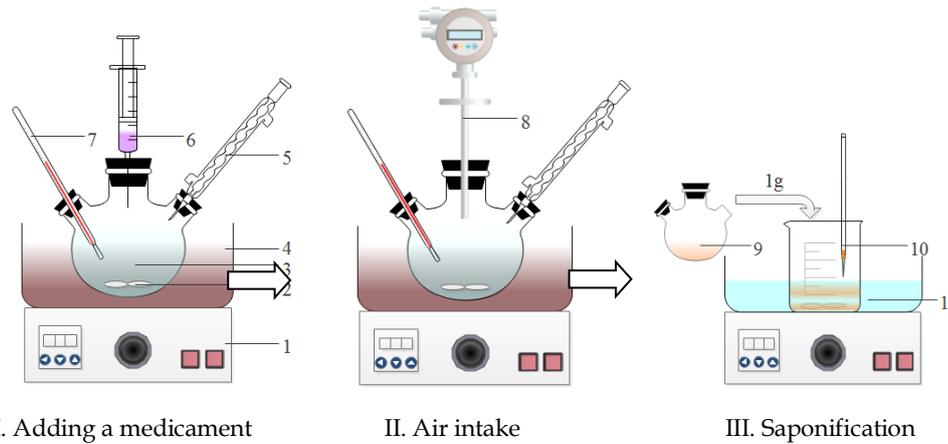
3. Results and discussion

3.1. Preparation and characterization of MPBO

The novel collector was modified using MO as the raw materials. 20.0 g MO and 0.02~0.06 g potassium permanganate was weighed. MO was stirred into a 250.0 mL three-necked round bottomed flask and heated. Potassium permanganate was added to the flask when it was completely dissolved in deionized water. Then the air was introduced at a high temperature for a while to obtain a target product. Lastly, 1.0 g MPBO and 200.0 mL deionized water were added to a 500.0 mL beaker. When the temperature reached 65 $^{\circ}\text{C}$, 0.45 g of a 10% sodium hydroxide solution was added dropwise. The solution was thoroughly stirred until dispersed. The solution was cooled and the emulsion product was obtained. Preparation of MPBO process is shown in Fig. 4.

Characterization of MPBO by FTIR spectroscopy was given in Fig. 5. For PBO, IR (KBr, cm^{-1}): 3423.40 (-OH), 2924.00 (-CH₂), 2853.65 (-CH), 1652.84 (-C=C-), 1463.63 (-CH₂-), 1377.17 (-CH₃), 1095.05 (C-OH), 986.13 (-CH), 721.50 ((-CH₂-)_n) (Reynard et al., 2015 & Filippov et al., 2019). It was worth noting that the modified collector generated several new characteristic peaks. Wavenumbers of 1718.53 cm^{-1} and 1616.58 cm^{-1} were characteristic absorption peaks of the C=O group in R-COOH, and the 1263.18 cm^{-1}

absorption peak indicated the stretching vibration of C-OH (Hope et al., 2010). One peak disappeared in this spectrum: C-OH stretching vibration peak at 1095.05 cm^{-1} . As described above, the collector obtained by the modification contained a functional group such as a hydroxyl group or a carboxyl group, so it was regarded as a fatty acid collector.



1-Heating magnetic stirrer, 2-Magnetic rotor, 3-MO, 4-Dimethicone, 5- Condenser, 6-Potassium permanganate, 7-Thermometer, 8- Electromagnetic flowmeter, 9-MPBO, 10- Sodium hydroxide, 11- Tap water

Fig. 4. Preparation of MPBO process

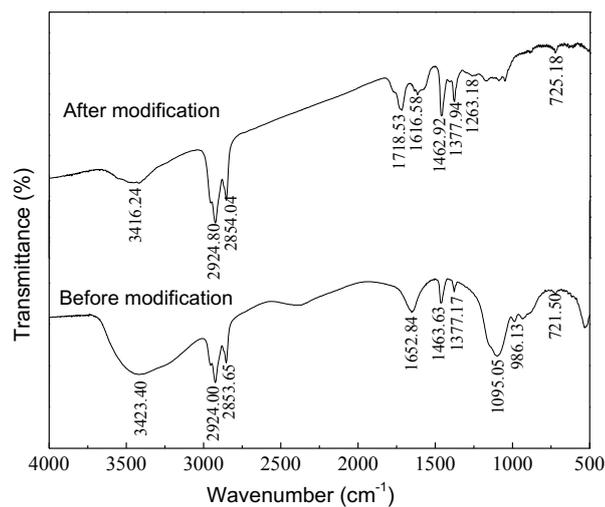


Fig. 5. FTIR spectra of MPBO

3.2. Effect of modification conditions on apatite flotation

In this section, MO was modified to get satisfied flotation separation results of phosphate ore. The single-factor experiments of air-flow rate, reaction time, reaction temperature, and potassium permanganate amount were separately conducted to determine the optimized modification condition. The results were shown in Fig. 6.

Fig. 6a indicates that the recovery of P_2O_5 changed significantly with the air-flow rate increasing. When the air-flow rate was $0.15\text{ m}^3/\text{h}$, the highest flotation recovery of P_2O_5 with 94.80% was obtained, while P_2O_5 grade of the concentrate was the lowest of only 27.59%. The effect of reaction time was also shown in Fig. 6b. It was observed that in general, the P_2O_5 recovery increased with the reaction time, and reached maximum (90.00%) when the reaction time was 24 h. It was evident from Fig. 6c that the increase of the reaction temperature resulted in the increase of P_2O_5 recovery, but the grade of P_2O_5 was almost invariant with the temperature of the reaction. The results of potassium permanganate dosage on flotation index were given in Fig. 6d. When the potassium permanganate dosage was 0.20% of the PBO quality, the recovery was higher (94.80%) than that of 0.10% and 0.30%.

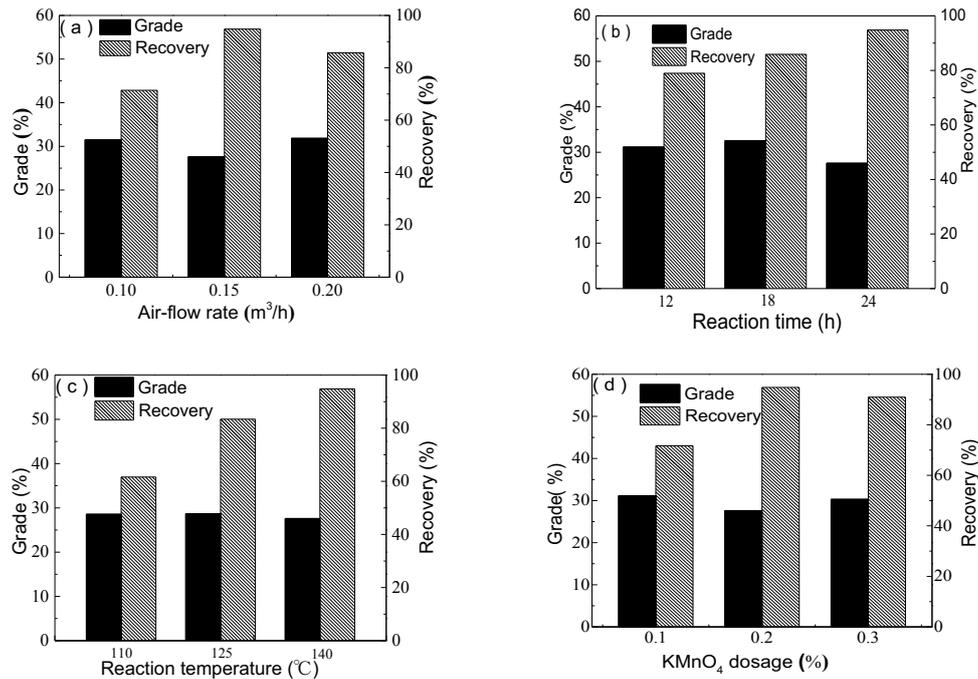


Fig. 6. Effect of modification condition on MPBO in the separation flotation of apatite ore: (a) - effect of air-flow rate, (b) - effect of reaction time, (c) - effect of reaction temperature, and (d) - effect of potassium permanganate amount, MPBO = 400 g/t

From the foregoing, the recovery of P_2O_5 varied notably, but the grade of concentrate was slightly changed. Hence, the recovery of P_2O_5 was the most significant factor considered in the modifier flotation test. The optimal collector for apatite flotation was determined by the tests to be 0.15 m³/h air-flow rate, 24 h reaction time, 140 °C temperature and 0.20% potassium permanganate, and concentrate with 94.80% recovery rate and 27.59% grade was obtained.

3.3. Flotation of apatite ore

The P_2O_5 recovery process for the MPBO was used as a representative to compare with that for conventional reagent oxidized paraffin soap. As described in Fig. 7, at the same dosage of the collector, while the results of the grade obtained in the presence of oxidized paraffin soap were somewhat inferior to the results obtained in the presence of MPBO, the recovery of P_2O_5 differed significantly between those two agents. It could generally be noted that when the MPBO was used as the collector, with the dosage increasing from 200.0 to 400.0 g/t, the recovery increased sharply up to 96.89%, and the grade of P_2O_5 fluctuated slightly around 26.0%. However, the increase of the P_2O_5 recovery was marginal if the collector dose was extended beyond 400.0 g/t, and the grade of P_2O_5 had a slight downward trend. This could be due to the addition of excess collector in the flotation, which caused a small number of silicate minerals to entrain into the foam product.

In addition, when oxidized paraffin soap was used as the collector, the recovery of mineral at the same dosage was significantly reduced. Particularly when the dosage of oxidized paraffin soap was 400.0 g/t, the recovery of P_2O_5 was only 70.32%, which was 26.57% less than that with MPBO as the collector. And the grade of P_2O_5 also dropped from 26.08% to 20.25%. The present results revealed that MPBO exhibited better flotation performance than oxidized paraffin soap.

The closed-circuit flotation tests could investigate the effect of the reagent on the flotation index, and verify the proposed flotation process as well as the simulated production. The closed-circuit flotation tests of apatite ore using MPBO as the collector was indicated in Fig. 8. The results showed that the final concentrate with 31.94% of P_2O_5 grade and 90.43% of P_2O_5 recovery could be obtained via one roughing and one cleaning. While, with the same dosage of oxidized paraffin soap as the collector, the apatite concentrate with 29.04% of P_2O_5 grade and 76.56% of recovery could be produced in a closed-circuit of once roughing, twice scavenging, four cleanings and middling orderly return (Liu et al., 2014). It could

be concluded that, as compared to oxidized paraffin soap, MPBO, used as the collector of apatite ore flotation, not only significantly improved the separation index, but also greatly shortened and simplified the flotation process.

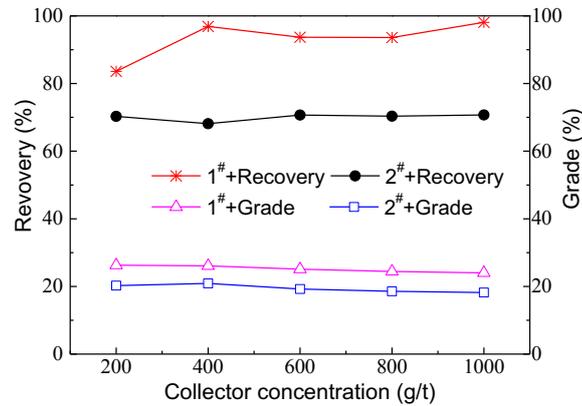


Fig. 7. Effect of collector dosage on apatite ore flotation (1#- MPBO, 2#- oxidized paraffin soap)

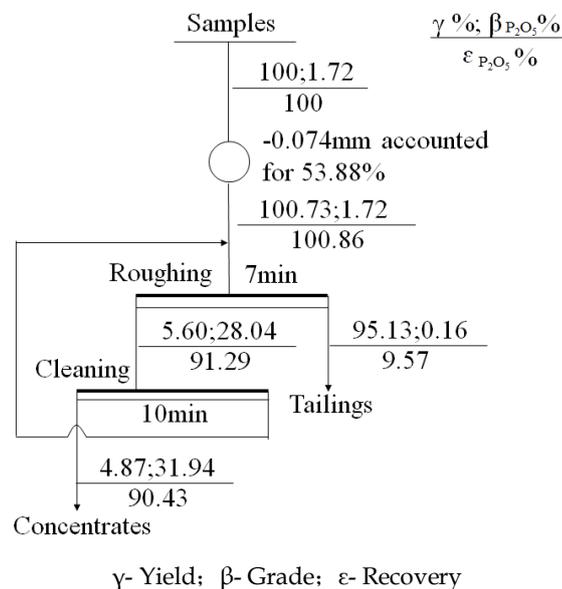


Fig. 8. Flow chart of closed-circuit experiment quantity and quality

3.4. FTIR analysis

Adsorption of MPBO on the apatite surface was investigated by FTIR. FTIR spectra of apatite, MPBO and apatite treated with MPBO were shown in Fig. 9. The vibration and lattice vibration of the PO_4 tetrahedron inside the apatite was the primary origin of the apatite spectrum. The peaks at 1044.38 cm^{-1} and 602.37 cm^{-1} were attributed to the asymmetric stretching vibration of P-O-P bond in PO_4^{3-} , the peak at 574.37 cm^{-1} indicated the in-plane bending vibration of P-O-P in PO_4^{3-} (Lu et al., 1998; Ren et al., 2017). Meanwhile, apatite also had an infrared characteristic peak of carbonate and hydroxyl groups. The double peaks at 1456.71 and 1428.82 cm^{-1} could be assigned to the asymmetric vibration of carbonate substitution of apatite which was ubiquitous in natural apatite (Fleet, 2009). In the spectrum of apatite treated with MPBO, the position and relative intensity of three infrared peaks for its mineral surface were detected (2957.53 cm^{-1} , 2925.27 cm^{-1} and 2855.34 cm^{-1}). They were characteristic for the stretching vibration of -CH in the methylene group. The C=O stretching vibration peak at 1702.66 cm^{-1} disappeared in this spectrum. Apparently, two peaks generated in this spectrum: the COO^- asymmetric stretching vibration peak at 1560.26 and 1541.35 cm^{-1} (Hope et al., 2010). The analysis indicated that the

MPBO was chemically adsorbed on the apatite surface by carboxylate generated, which was beneficial to the flotation of the apatite.

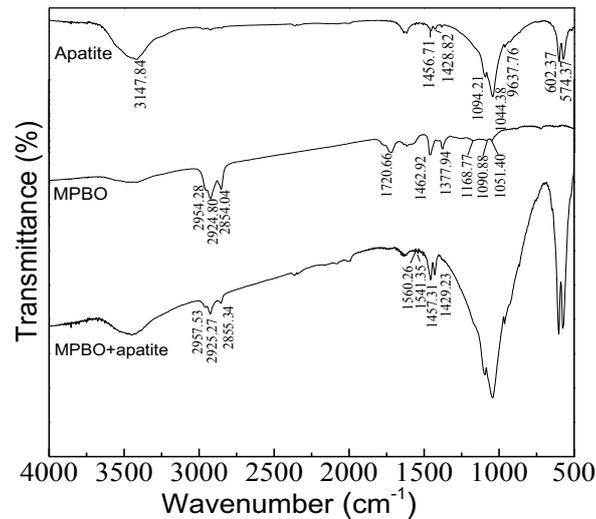


Fig. 9. FTIR spectra of apatite, MPBO, apatite treated with MPBO

3.5. Zeta potential measurement

In order to understand the adsorption of MPBO on apatite surface, the electrokinetic phenomenon of mineral suspensions was investigated. The zeta potentials of apatite in the absence or presence of the reagents, as a function of pH, were presented in Fig. 10. The iso-electric point (IEP) of apatite was determined at about 2.20, which was in accordance with previously reported values (Kou et al., 2010).

When the pH was less than 2.20, the surface of the apatite was positively charged, which was caused by the dissolved anions of the apatite itself, and the negative ions on the surface of the mineral adsorbed the calcium and hydrogen ions in the solution. Conversely, if the pH was greater than 2.20, the surface of the apatite was negatively charged, which was attributed to the adsorption of phosphate ions and hydroxides on the positive electrode (Dorozhkin, 1997). In parallel, according to previous reports, a mixture of long-chain fatty acids were weak acids with a pK_a value of 4.7 ± 0.5 (Nan et al., 2019). When the pH of the slurry was greater than 4.7, MPBO would ionize the anion. Inversely, when the pH was less than 4.7, MPBO was present in the molecule (RCOOH) form in solution. This means that if the pH was higher than 4.7, both the apatite surface and the MPBO were negatively charged, and there was an electrostatic repulsive force between them. Hence, in the presence of MPBO (100 mg/L), zeta potentials of apatite were obviously shifted to more negative. And the IEP of apatite moved to a pH of about 1.54. These clearly indicates that the MPBO was chemisorbed on the apatite surface rather than relying on electrostatic force adsorption. The zeta potential analysis results were consistent with the infrared spectrum analysis.

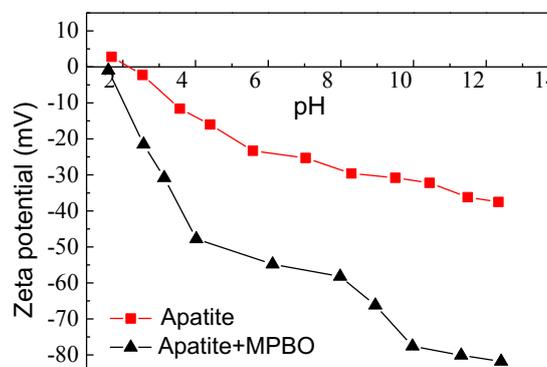


Fig. 10. Zeta potential of apatite as a function of pH

3.6. XPS analysis

The interaction mechanism between the apatite and MPBO was measured by XPS detection, and the apatite treated with and without the collector was separately conducted. The results were shown in Figs. 11-14.

Based on the results in Fig. 11, the apatite treated with and without MPBO only contained four elements which were C, O, P and Ca. The peak intensity and binding energy (BE) of the four elements changed marginally, but no new peaks were found in the apatite spectrum after treatment with the collector. In Fig. 12, the contents were reported for the principal elements C1s, O1s, Ca2p, P2p of the investigated samples. It could be noted that the relative content of C element in the apatite sample increased from 17.92% to 49.96% after treated with MPBO, while the other three elements were slightly reduced. This change could be due to the adsorption of the collector on the apatite surface.

Fig. 13a presented that the C1s spectrum of apatite treated with MPBO contains three different carbon species: C-C/C-H, C-O, C=O and O=C-O at the BE values 284.58 eV, 286.38 eV, 288.58 eV and 289.18 eV, respectively (Paredes et al., 2008; Wu et al., 2009). In addition, there is no peak at 288.30 eV of the apatite sample in Fig. 13b. However, the peak appeared at 288.30 eV after the sample was treated by MPBO, which was a carboxyl peak (-COO). Thus, it could be inferred that the carboxyl group of the collector was adsorbed on the apatite surface.

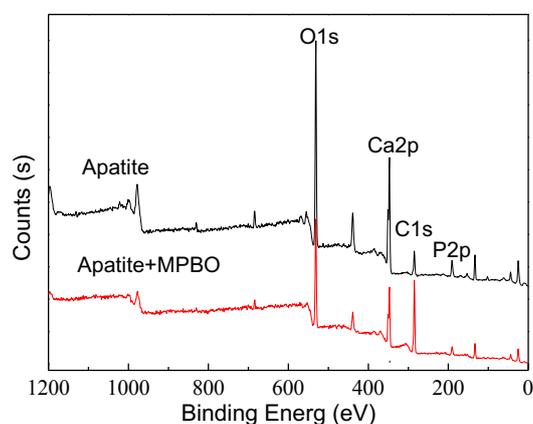


Fig. 11. XPS scan spectra of apatite treated with or without MPBO

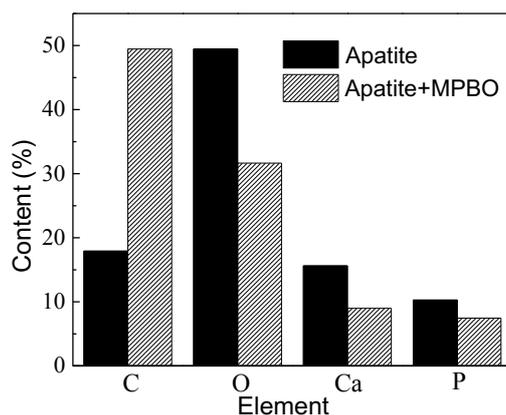


Fig. 12. XPS characterization of reference compounds on the samples

The O1s spectrum of apatite acted with MPBO (Fig. 14) showed that the oxygen element had two different chemical states. There were two peaks at 531.18 eV and 532.28 eV, corresponding to Ca-O-P and Ca-O-C, respectively (Nan et al., 2019). Among them, 532.28 eV was the newly generated peak. In combination with the previous analysis, XPS analysis results demonstrated chemical adsorption between the carboxylate of MPBO and the calcium of the apatite.

Based on the above results of the experiments and analysis, a possible model for the flotation separation process of apatite ore with MPBO as the collector was presented in Fig. 15. The novel collector MPBO with the carboxyl group, would selectively adsorb on apatite surface by chemisorption, which could form calcium carboxylate between MPBO with the calcium on the surface of the apatite.

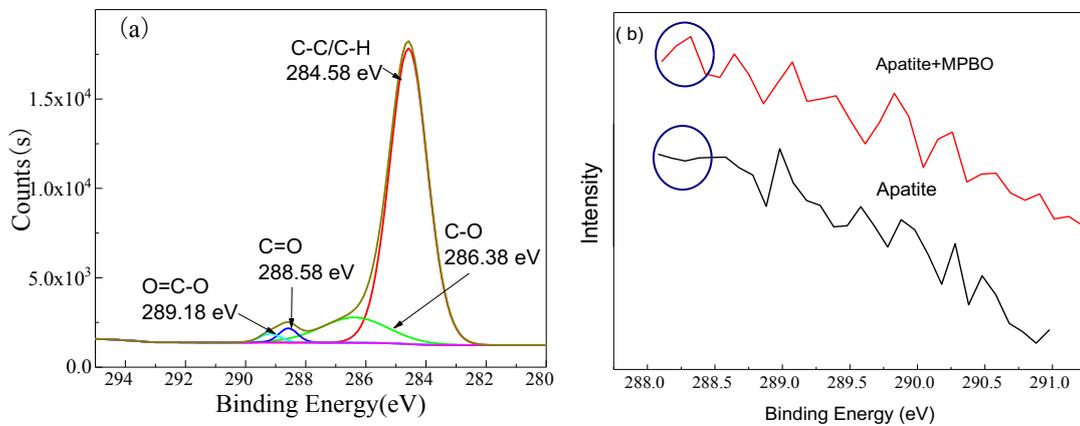


Fig. 13. XPS C1s spectra of apatite treated with MPBO

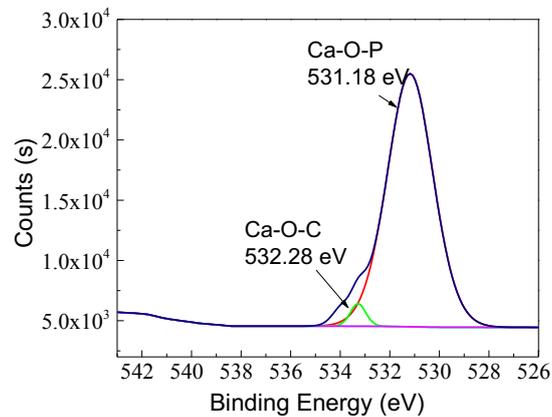


Fig. 14. XPS O1s spectra of apatite treated with MPBO

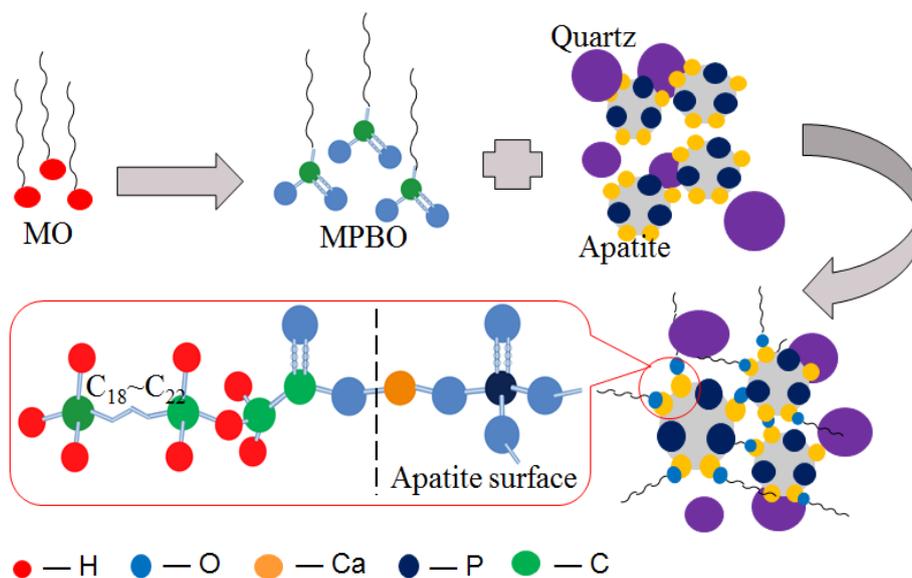


Fig. 15. Schematic diagram of adsorption models of reagents on the apatite surface

4. Conclusions

The composition of MO, with C₁₉-C₂₂ saturated alkanes, is an intermediate waste product in industrial petroleum. Hence, this study provides a novel method of the rational exploit and recovery about waste oil, which contributes to apatite flotation in industry. The optimized MPBO with the best separation index of apatite ore flotation was achieved through the modified condition experiments. According to the infrared analysis, the MPBO contained a functional group such as a hydroxyl group or a carboxyl group, and was regarded as a fatty acid collector.

The results of flotation showed that the MPBO had better collection ability and selectivity to apatite ore than the oxidized paraffin soap under the same flotation conditions. The results also indicated that MPBO, used as the collector of apatite ore flotation, not only significantly improved the separation index, but also greatly shortened the flotation process, which could obtain the qualified concentrate products via one roughing and one cleaning. The results of zeta potential measurements, FTIR and XPS analyses verified that chemisorption existed between the novel collector and the surface of the apatite – the carboxyl group in MPBO with the calcium on the surface of the apatite form calcium carboxylate.

Mineral oil has underutilized industrial application until now. In this sense, Mineral oil shows great potential to be used as a source for flotation collectors, especially in substitution for traditional oils.

Acknowledgments

The authors gratefully thank the young and middle-aged science and technology innovation talent support program of Shenyang (RC170556) and the National Natural Science Foundation of China (No. 51874168) for financial support.

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