# Effect of food-grade guar gum on flotation separation of chalcopyrite and monoclinic pyrrhotite in low-alkali systems

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**Abstract:** The flotation separation of chalcopyrite from monoclinic pyrrhotite using food-grade guar gum (FGG) as a depressant was studied through micro flotation and flotation kinetics experiments, zeta potential, adsorption measurements and scanning electron microscope (SEM) analysis as well as infrared spectroscopy analysis. The flotation tests showed that the reagent scheme of depressant FGG 40 mg/dm³, collector PAX (potassium amyl xanthate) 10 mg/dm³ and frother MIBC (Methyl isobutyl carbinol) 10 mg/dm³ at pH 8.0 could achieve selective flotation separation of chalcopyrite from monoclinic pyrrhotite (a concentrate with Cu grade of 22.35% and recovery of 82.52% was achieved from the mixed minerals flotation), which indicated that FGG exhibited a selective depression effect on monoclinic pyrrhotite The kinetics, zeta potential, adsorption, SEM and infrared studies revealed that the depressant FGG could absorb more strongly on the surface of monoclinic pyrrhotite than chalcopyrite. Additionally, the results revealed that the interaction of FGG with the monoclinic pyrrhotite surface was governed primarily by strong chemisorption, whereas FGG mainly bonded to chalcopyrite through hydrogen bonding. This property was the reason why FGG had excellent depression selectivity toward monoclinic pyrrhotite and weak depression effect on chalcopyrite flotation.

*Keywords*: food-grade guar gum, chalcopyrite, monoclinic pyrrhotite, flotation depressant

## 1. Introduction

Refractory copper sulfide ores are typically characterized as being low grade with complex mineralogy and with the valuable Cu sulfide minerals being fine-grained (Qiu et al., 1997). The objective of copper-sulfur flotation is to achieve separation of copper minerals from iron sulfide as well as other gangue minerals. Chalcopyrite ($CuFeS_2$) is the most important copper bearing mineral; it represents the major source of copper. Among the sulfide minerals, iron sulfide ($FeS_2$ and $Fe_{1-x}S$) is the most common gangue (Waters et al., 2008). Numerous researchers have indicated that the selective separation of chalcopyrite and iron sulfides (like pyrrhotite) is difficult because electrochemical interactions occur at the minerals' surfaces during the grinding and flotation conditioning processes.

Pyrrhotite ($Fe_{1-x}S$, $0 \leq x \leq 0.125$), which is one of the most abundant iron sulfide gangue minerals, is commonly associated with deposits of other sulfides. It mainly occurs as two crystalline structures in nature: hexagonal and monoclinic (Díaz-López et al., 2001; Tukel and Kelebek, 2010; Allison and O'Connor, 2011). The characteristics of the hexagonal form differ from those of the monoclinic form; for example, the hexagonal form is nonmagnetic and exhibits low floatability, enabling it to be easily depressed by CaO addition. By contrast, the monoclinic pyrrhotite is generally ferromagnetic and exhibits excellent floatability. Because of the complex separation schemes, the separation of monoclinic pyrrhotite from polysulfide has rarely been realized. In practice, the separation of chalcopyrite from pyrrhotite is achieved by depressing pyrrhotite under a highly alkaline medium. Therefore, selective depressants that strongly inhibit the flotation of pyrrhotite but hardly affect the floatability of chalcopyrite under low-pH conditions are needed (Chandra and Gerson, 2009; Wang et al., 2015).

Many traditional depressants have been widely used in the flotation separation between copper sulfide minerals and pyrrhotite, including cyanide, lime, calcium hypochlorite, potassium permanganate, sulfite, sodium sulfide and sodium carbonate (Qiu et al., 2011). Studies have indicated that the depressant cyanide shows the best inhibition efficiency in the flotation separation of copper sulfide minerals and pyrrhotite. However, cyanide, which exhibits high natural toxicity, poses an environmental pollution hazard. Therefore, the use of cyanide has been gradually limited in recent years (Zhang et al., 2004a; Gül et al., 2008; Lu, 2011). Lime is a good inhibitor of both pyrrhotite and pyrite in chalcopyrite flotation, however, it needed in large dosage for highly alkaline pulps. Besides, the use of lime as a depressant not only affects the recovery of associated precious metals but also causes difficulty in the activation of iron sulfides as well as problems associated with wastewater disposal. In a word, each of the aforementioned inorganic depressants brings different negative consequences when used in the flotation separation process. Therefore, it is urgently needed for seeking clean, efficient and environmentally friendly depressants.

Compared with inorganic depressants, organic depressants exhibit better selectivity and pose less pollution risk. Thus, the use of organic depressants in flotation separation has been an active research topic. For example, thioglycolic acid (Chmielewski et al., 1991) and diethylenetriamine (Kelebek et al., 1995; Yoon et al., 1995) have been used to depress iron sulfide minerals. Polymers, which are well-known depressants of both sulfide and non-sulfide minerals commonly used to depress pyrite (Bolin and Laskowski, 1991; Bogusz et al., 1997). Xu et al (2003) found that the new organic depressant RC had a strong depression effect on both pyrite and pyrrhotite. Sun et al (2006) found that copper-activated marmatite could be separated efficiently from pyrrhotite using DMPS as depressant. Polyamines such as DETA and TETA have shown good depression ability on iron sulfide when used in the processing of a nickel ore (Kim, 1998; Kelebek and Tukel, 1999). Subsequently, their combined use with $SO_2$ or sodium metabisulfite ($Na_2S_2O_5$) was found to lead to much better performance than the use of polyamine alone (Cai et al., 2005; Chen et al., 2006). In addition, new depressants such as corn starch, carboxymethylcellulose (CMC), lignosulphonates (LS), humic acid, and sodium humate have been used in the processing of iron ore (Pearse ,2005; Liu et al.,2006; Turrer and Peres,2010; Chen et al.,2011).

Guar gum is an environmental friendly chemical reagent the same as dextrin, starch and CMC, which has higher depression capacity than CMC. In previous research, the interaction mechanisms of guar gum with several hydrophobic and sulfide minerals, such as talc, mica, galena, sphalerite, pyrite and pyrophyllite have been investigated. The reported findings suggest that it exhibits high depressing ability on iron sulfides, which gives an idea for realizing the chalcopyrite separation (Frollini et al., 1995; Shortridge et al., 2000; Gong et al., 2011; Chen et al., 2012; Castro et al., 2016; Zhao et al., 2017). Compared with common guar gum, food-grade guar gum (FGG) (shown in Fig. 1) has the advantage of higher purity and stronger depressing action and few works have been done on the separation of chalcopyrite and monoclinic pyrrhotite. Thus, it was used as the depressant in the study.
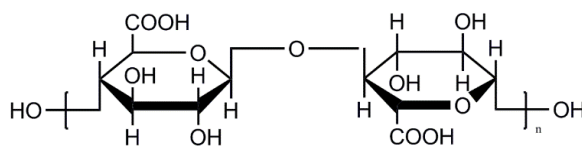


Fig. 1. Molecular structure of food-grade guar gum

The purpose of this study was to investigate the efficiency of FGG as a depressant in the flotation separation between chalcopyrite and monoclinic pyrrhotite. The experiments include single mineral flotation tests and artificial mixed mineral flotation experiments. The adsorption mechanism of FGG on mineral surface is investigated by flotation kinetics, dynamic potential, adsorption and infrared spectrum analysis.

## 2. Materials and methods

### 2.1. Pure minerals and reagents

Chalcopyrite and monoclinic pyrrhotite pure minerals were purchased from the Geological Museum of China. The two minerals were both handpicked to obtain high-purity samples, and then ground and

screened to collect the −0.074 mm to +0.038 mm size fractions for the following flotation tests (Fig. 2 and Table 1). The purity of chalcopyrite and monoclinic pyrrhotite was as high as 95.54% and 93.67%, determined by X-ray diffraction (XRD) analysis and chemical analysis, respectively (Fig. 3 and Table 2).

Potassium amyl xanthate (PAX) was used as a collector. The food-grade guar gum (FGG) $(C_{18}H_{29}O_{15})_n$, obtained from commercial companies with purity above 92% was used as a depressant in the study. Methyl isobutyl carbinol (MIBC) was chosen as a frother bought from Sinopharm Chemical Reagent Co., Ltd, China. Solutions of $H_2SO_4$ and NaOH were used to adjust the pH of the pulp. All water used in the experiments was distilled water.
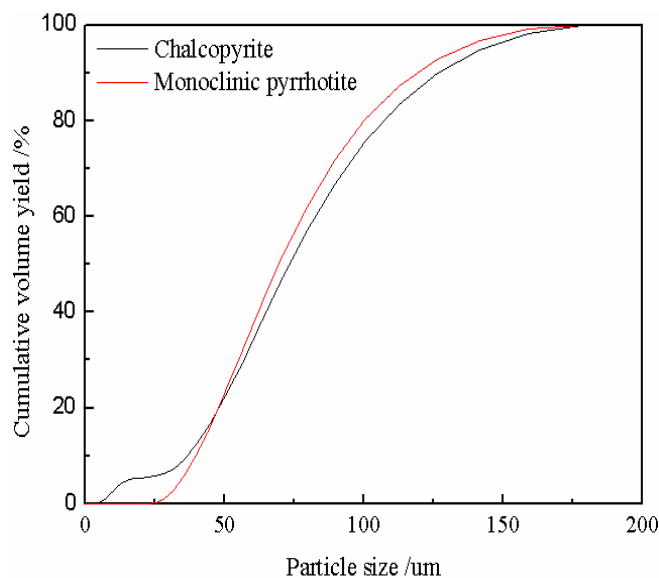


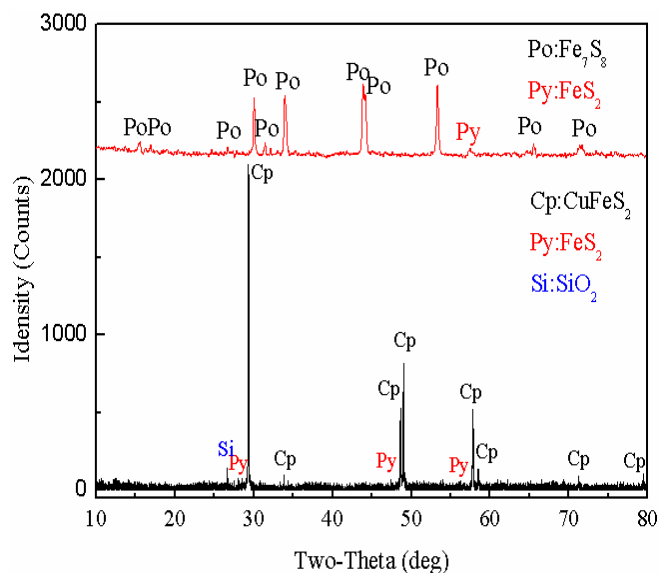Fig. 2. -0.074~+0.037 mm chalcopyrite and monoclinic pyrrhotite particle size distribution



Fig. 3. XRD diagrams of chalcopyrite and monoclinic pyrrhotite

## 2.2. Flotation experiment

Flotation experiments were carried out in a mechanical agitation flotation machine with a volume of 40 $cm^3$. The impeller speed was fixed at 1860 r/min. For each test, 2 g of sample was taken, and the mineral surface was cleaned for 5 min using an ultrasonic cleaner to remove any oxide. The sample was allowed to settle, and the upper liquid layer was decanted. And then add 2 g of pure minerals to 40 $cm^3$ of solutions. The pH of the mineral suspension was adjusted to a needed value by adding NaOH or $H_2SO_4$ stock solutions. The prepared FGG and PAX solution was added at a desired concentration and

conditioned for 3 min. Each flotation experiment was carried out for 3 min. For mixed minerals flotation, the flotation recovery was calculated based on yield and Cu grade between the concentrates and tailings.

Table 1. Grain size composition of mineral samples

| Sample | Particle size distributions (mm) | Distribution rate (%) | Average diameter (μm) | Specific surface area (m²/g) |
|---|---|---|---|---|
| Chalcopyrite | +0.1 | 24.42 | 77.06 | 0.118 m²/g |
| | -0.1～+0.074 | 28.25 | | |
| | -0.074～+0.037 | 35 | | |
| | -0.037 | 12.33 | | |
| Monoclinic pyrrhotite | +0.1 | 19.89 | 84.02 | 0.0844 m²/g |
| | -0.1～+0.074 | 28.14 | | |
| | -0.074～+0.037 | 41.85 | | |
| | -0.037 | 10.12 | | |

Table 2. Chemical analysis of chalcopyrite and monoclinic pyrrhotite (%)

| Species | Cu | Fe | S |
|---|---|---|---|
| Chalcopyrite | 32.50 | 30.11 | 32.93 |
| Monoclinic pyrrhotite | - | 57.97 | 37.08 |

## 2.3. Flotation kinetics

It had been widely accepted that most flotation systems could be described by means of a first-order reaction rate equation (Eq. (1)).

$$\varepsilon = \varepsilon_\infty (1 - e^{-Kt}) \tag{1}$$

where, $\varepsilon$ was the recovery in the flotation, t was time, $K$ was the flotation rate constant, $\varepsilon_\infty$ was the max concentrate recovery in infinitely flotation time.

The constant $K$ depended on a large variety of variables which included factors related to ore characteristics such as mineralogy, factors defined through the flotation medium such as the type and quantity of reagents (Kelebek andNanthakumar, 2007; Rodriguez et al., 2009).

## 2.4. Zeta potential measurements

The zeta potential measurements were conducted with a Malvern Zetasizer Nano ZS90 (England) equipped with a rectangular electrophoresis cell. The suspensions were prepared by adding 20 mg of purified minerals that were ground to -5 μm in an agate mortar and 40 cm³ of ultrapure water. After magnetic stirring for 5 min and settling for 10 min, the supernatant of the dilute fine-particle suspension was obtained for the zeta potential measurement. During stirring, the suspension was conditioned with corresponding reagents at different pH values. Each sample was measured at least three times, and the averages were used as the final result.

## 2.5. Adsorption experiments

The adsorption measurements were completed on a TU-1810 UV–Vis spectrophotometer (Purkinje General, Beijing, China). 2 g of mineral powder and 40 cm³ of distilled water were transferred into a 100 cm³ Erlenmeyer flask. After the reagent addition to the solution, the Erlenmeyer flask was stirred on a magnetic mixer for 10 min, allowing the adsorption process to reach equilibrium. After centrifuged, the concentration of FGG in the supernatants was determined using UV spectrometry analysis. And the adsorption of the reagent on the mineral surface can be calculated as follows:

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$$\Gamma = \frac{(C_0 - C) \times V}{1000 \times 2 \times Vs} \tag{2}$$

where $\Gamma$ is the adsorption quantity (mg/m$^2$), $C_0$ is the initial reagent concentration (mg/dm$^3$), $C$ is the tested concentration in the supernatant, V is the pulp volume (dm$^3$), $V_s$ is the specfic surface area (m$^2$/g).

### 2.6. Scanning electron microscope (SEM) analysis

The surface morphological characteristics of mineral interacting with FGG were observed with a scanning electron microscope (SEM) (MIRA3 LMU, Tescan, Czech) operated at 20 kV. For each test, 2 g of pure mineral powder less than 38 μm and 40 cm$^3$ of distilled water were placed in a flotation cell, after adding the desired reagents with 5 min of conditioning time, washing for one time using distilled water, and then vacuum-dried below 30 °C. Finally, taking a minor amount of sample paving and spraying gold to observe.

### 2.7. Infrared spectrometry measurement

Fourier transform infrared (FT-IR) spectroscopy was conducted at an environmental temperature of 25°C with a Spectrum One (version BM) FT-IR (USA) spectrometer. The samples were prepared by adding the desired reagents and 1 g of pure minerals that had been ground to less than 2 μm to a Plexiglas cell with 40 min of conditioning time. After the samples had been washed three times with distilled water, they were vacuum dried at a temperature below 30°C and used for subsequent FT-IR analysis. The spectra of the solids were collected via the KBr pellet method. The data were collected from 4000 to 400 cm$^{-1}$.

## 3. Results and discussion

### 3.1. Single mineral flotation

Fig. 4 presents the effect of pH on the floatability of chalcopyrite and monoclinic pyrrhotite in the presence of depressant FGG using PAX as a collector. As illustrated in Fig. 4, without the addition of FGG, chalcopyrite and monoclinic pyrrhotite both showed excellent floatability with recovery above 90% over the tested pH range. The flotation recovery had a slight decline except for the high-alkaline pH conditions, which mean that the separation of chalcopyrite from monoclinic pyrrhotite cannot be realized by adding the anionic collector PAX alone. However, in the presence of FGG, the flotation recovery of monoclinic pyrrhotite decreased significantly and remained below 20% at the pH value of 8.0. On contrary, the recovery of chalcopyrite was affected slightly by FGG. Especially, the chalcopyrite recovery was exceeded 80% as pH less than 9.0. It is clear that an excellent selectivity could be obtained through using the FGG in a weak alkaline condition.

Fig. 5 presents the effect of FGG dosage on the floatability of chalcopyrite and monoclinic pyrrhotite. It can be seen from Fig. 5 that the recovery of chalcopyrite and monoclinic pyrrhotite both decreased with increasing FGG dosage. When FGG dosage increased from 0 to 60 mg/dm$^3$, the chalcopyrite recovery decreased from 97.52% to 70.05%, while the monoclinic pyrrhotite recovery dramatically dropped from 94.23% to 11.37%. Comparing the floatability of chalcopyrite and monoclinic pyrrhotite with different FGG dosages, it is clear that the optimal separation range of FGG dosage is 30 mg/dm$^3$- 50 mg/dm$^3$. FGG dosage of 40 mg/dm$^3$ is chosen for the next separation experiments.

### 3.2. Mixed minerals flotation

The single mineral flotation results suggest that it is possible to separate chalcopyrite from monoclinic pyrrhotite by FGG. Therefore, the flotation separation tests of mixed minerals (a chalcopyrite to monoclinic pyrrhotite mass ratio of 1:2) were conducted under the condition of MIBC 10 mg/dm$^3$ and PAX 10 mg/dm$^3$ at pH 8.0 using different dosage of FGG and the best results achieved are shown in Table 3. It can be seen from Table 3 that a concentrate with Cu grade of 22.35% and recovery of 82.52% was achieved with the addition of 40 mg/dm$^3$ FGG. When the FGG dosage increased to 60 mg/dm$^3$, the Cu concentrate grade increased but the recovery decreased from 82.52% to 78.35%. The results in Table 3 illustrate that the FGG shows a straining influence on the depression of monoclinic pyrrhotite

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in the mixed minerals flotation and the flotation separation between chalcopyrite and monoclinic pyrrhotite can be achieved with FGG as the depressant.
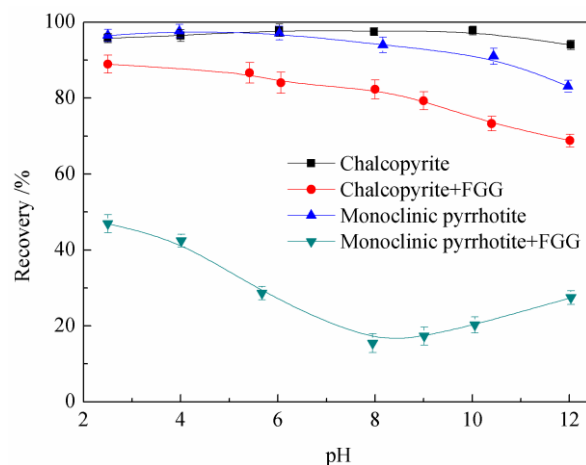


Fig. 4. Flotation recovery of chalcopyrite and monoclinic pyrrhotite as a function of pH in the absence and presence of FGG ([PAX] = 10 mg/dm³, [FGG] = 40 mg/dm³, [MIBC] = 10 mg/dm³)
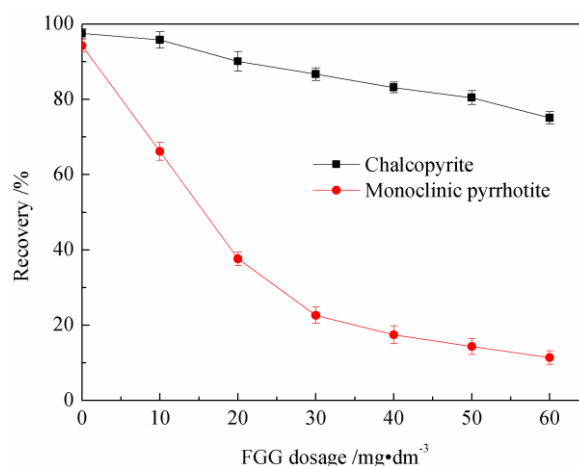


Fig. 5. Effects of FGG dosage on the flotation recovery of chalcopyrite and monoclinic pyrrhotite (pH 8.0, [PAX] = 10 mg/dm³, [MIBC] = 10 mg/dm³)

### 3.3. Flotation kinetics

It can be seen from Fig. 6 and Table 4 that with the increasing FGG dosage, the max concentrate recovery of monoclinic pyrrhotite was reduced from 93.89% to 16% and the flotation rate was reduced from 2.03% to 0.55%. While chalcopyrite still remained a good floatability (recovery above 80%), although the flotation rate constant of chalcopyrite decreased from 3.77 to 1.16. This illustrates that FGG has stronger depressing effect on monoclinic pyrrhotite than on chalcopyrite.

Table 3. The results of flotation separation of mixed minerals

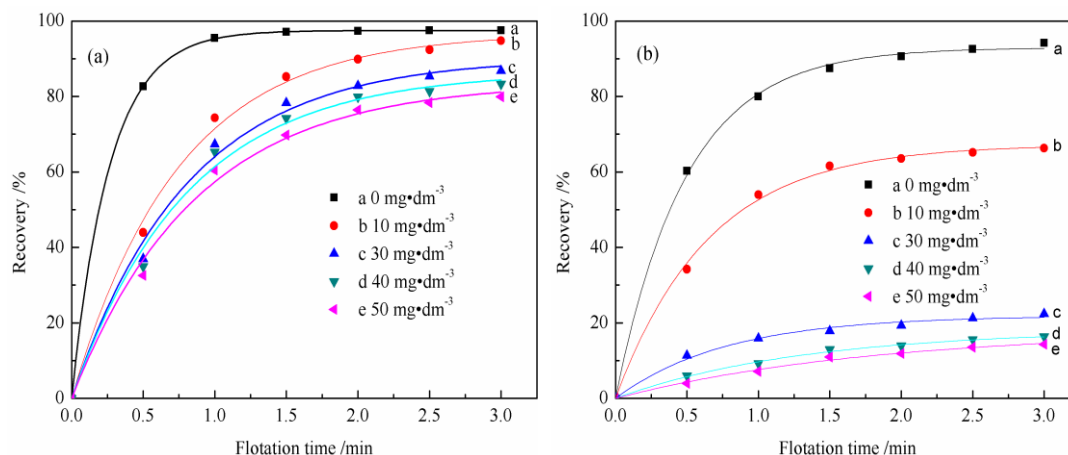| Dosage of FGG (mg/dm³) | Product | Ratio (w/%) | Cu grade (%) | Cu recovery (%) |
|---|---|---|---|---|
| 40 | Cu concentrations | 41.32 | 22.35 | 82.52 |
| | Tailings | 58.68 | 3.33 | 17.48 |
| | Feed | 100 | 11.19 | 100 |
| 60 | Cu concentrations | 35.76 | 24.56 | 78.35 |
| | Tailings | 64.24 | 3.78 | 21.65 |
| | Feed | 100 | 11.21 | 100 |

Fig. 6. Effect of FGG dosage on (a) chalcopyrite and (b) monoclinic pyrrhotite recovery versus flotation time in the presence of PAX (pH 8.0, [PAX] = 10 mg/dm³, [MIBC] = 10 mg/dm³)

Table 4. Effect of FGG dosage on parameters of first-order flotation rate model of chalcopyrite and monoclinic pyrrhotite

| Species | FGG dosage /mg.dm⁻³ | $K$ /(min⁻¹) | $\varepsilon_\infty$ | $R^2$ |
|---------|---------------------|--------------|----------------------|-------|
| Chalcopyrite | 0 | 3.77 | 97.48 | 0.999 |
| | 10 | 1.34 | 96.31 | 0.996 |
| | 30 | 1.23 | 90.28 | 0.993 |
| | 40 | 1.21 | 86.47 | 0.991 |
| | 50 | 1.16 | 83.73 | 0.993 |
| Monoclinic pyrrhotite | 0 | 2.03 | 93.89 | 0.999 |
| | 10 | 1.53 | 67.20 | 0.998 |
| | 30 | 1.29 | 21.87 | 0.990 |
| | 40 | 0.75 | 18.20 | 0.996 |
| | 50 | 0.55 | 16.00 | 0.992 |

### 3.4. Zeta potential measurement

The zeta potentials of chalcopyrite and monoclinic pyrrhotite in the absence and presence of FGG are shown in Fig. 7. In the absence of any reagents, the iso-electric point (IEP) for monoclinic pyrrhotite was approximately 7.1, which was slightly higher than the reported value pH 6.5 (Miller et al., 2005). The IEP of chalcopyrite couldn't be found in the tested pH range of 2.0-12.0. According to the literature, the IEP of elemental sulfur was at pH 1.6 (Fairthorne et al., 1998). In the presence of FGG, the zeta potential of chalcopyrite decreased by approximately 2 mV, whereas the monoclinic pyrrhotite had a drop of 15 mV at pH 8.0. The results suggest that FGG was adsorbed more strongly on the negatively charged monoclinic pyrrhotite surface than on chalcopyrite surface.

### 3.5. Adsorption analysis

The adsorption behaviors of FGG on chalcopyrite and monoclinic pyrrhotite surfaces as a function of FGG dosage are given in Fig. 8. It is clear that the adsorption ability of FGG on the surface of monoclinic pyrrhotite was significantly higher than chalcopyrite, the adsorption amount of FGG on monoclinic pyrrhotite surface increased rapidly with the increasing FGG dosage, while the adsorption of FGG on chalcopyrite surface was weak and the adsorption dosage of chalcopyrite growed slowly. The results obtained in the dosage range of 40-50 mg/dm³ FGG were consistent with the flotation results presented in Fig. 5. At a dosage of 40 mg/dm³ FGG, the adsorption amount of FGG on chalcopyrite and monoclinic pyrrhotite surface were 7.69 mg/m⁻² and 0.92 mg/m⁻² respectively.
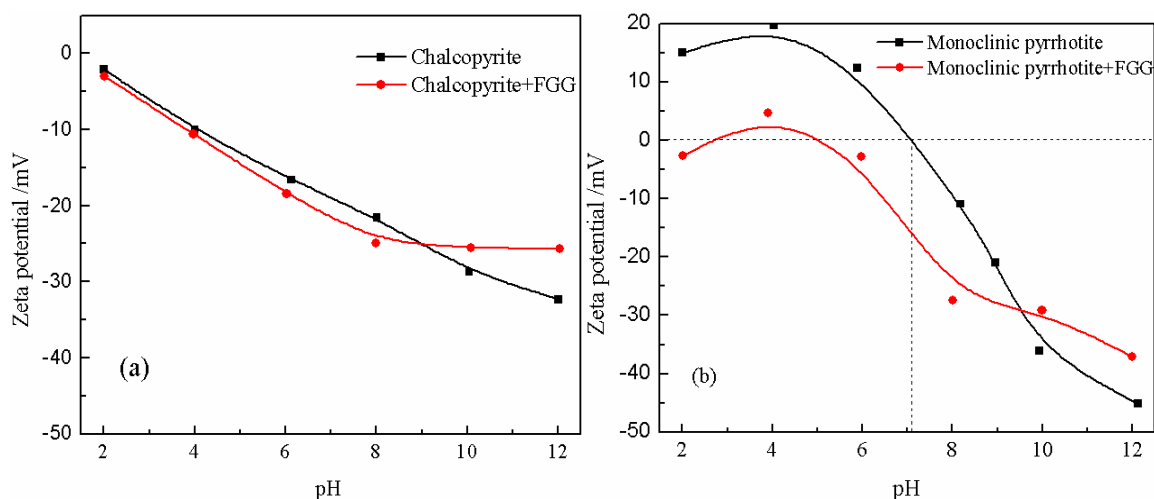
Fig. 7. Zeta potentials of (a) chalcopyrite and (b) monoclinic pyrrhotite as a function of pH ([FGG] = 40 mg/dm³)
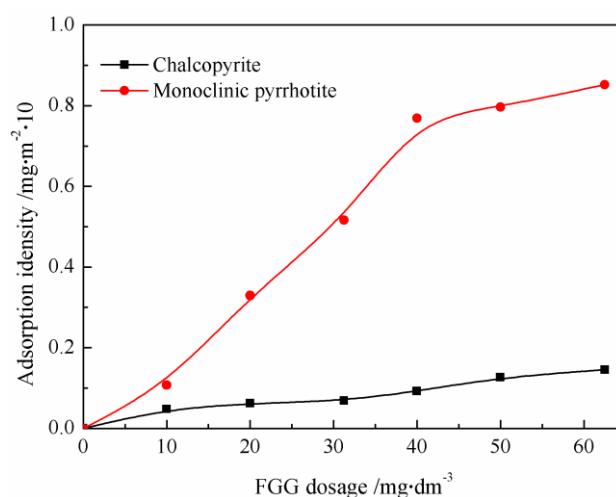


Fig. 8. Effects of FGG dosage on adsorption of chalcopyrite and monoclinic pyrrhotite (pH 8.0)

### 3.6. SEM (scanning electron microscope) analysis

The microstructural changes of chalcopyrite and monoclinic pyrrhotite after interacting with FGG (40 mg/dm³) are shown in Fig. 9. It can be seen that there exists a great difference in the surface topography of monoclinic pyrrhotite, after interacting with FGG, the monoclinic pyrrhotite surface become rough and covered by one layer of puffy floccule in various locations. On the contrary, the surface topography of chalcopyrite had no obvious change and the chalcopyrite surface remained smooth and clean in different magnifications. These results indicate that FGG occurs a stronger adsorption on monoclinic pyrrhotite than chalcopyrite.

### 3.7. FTIR spectra analysis

In the aforementioned analysis, we demonstrated that the depressant FGG could selectively adsorb onto monoclinic pyrrhotite. However, the adsorption mechanism remains unclear. Therefore, the FTIR spectra of these two minerals before and after interacting with FGG were subjected to infrared spectroscopic study in order to further uncover the underlying adsorption mechanism (shown in Fig. 10).

The FTIR spectrum of monoclinic pyrrhotite after interacting with depressant FGG is shown in Fig. 10(a). Several new bands appeared near 3419.08 cm$^{-1}$, 1091.49 cm$^{-1}$ and 951.43 cm$^{-1}$. The characteristic sharp bands of monoclinic pyrrhotite near 3445.3 cm$^{-1}$ shifted to 3419.08 cm$^{-1}$ due to -OH stretching vibration (Rath et al., 2000), and the bands near 1111.1 cm$^{-1}$ and 1049.72 cm$^{-1}$ shifted to 1091.49 cm$^{-1}$ and
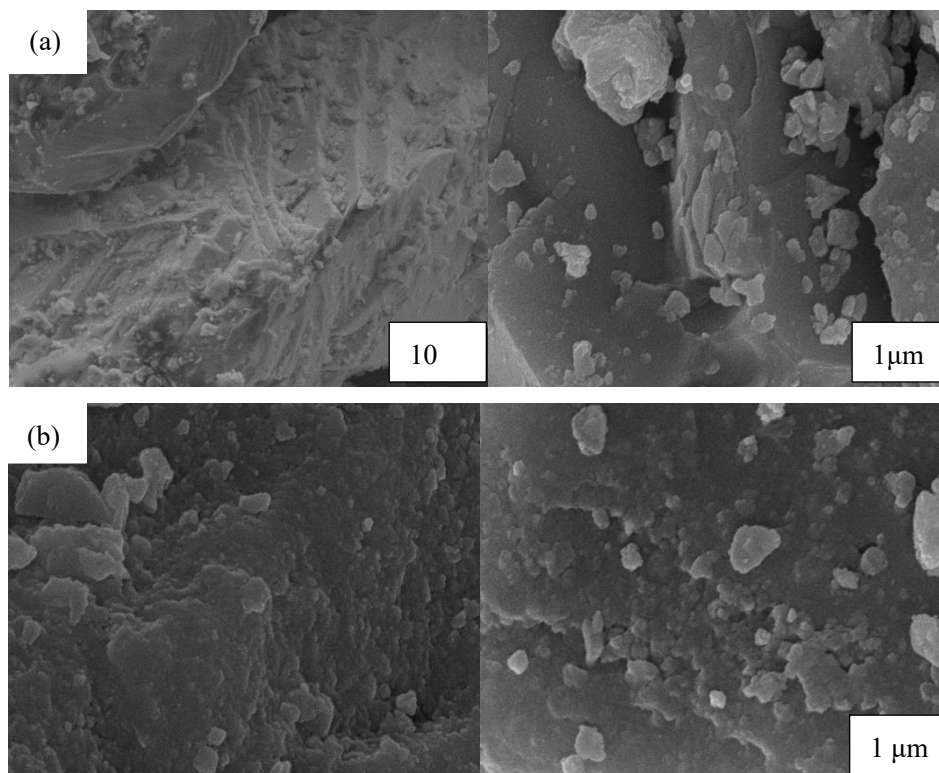
Fig. 9. SEM micrographs of (a) chalcopyrite and (b) monoclinic pyrrhotite after interacting with FGG ([FGG] = 40 mg/dm³)

951.43 cm⁻¹ respectively attributed to C-O stretching vibration (Messali et al., 2017), indicating that a strong chemisorption of FGG on the monoclinic pyrrhotite surface occurred. The adsorption of -OH, and C-O were the functional groups between monoclinic pyrrhotite and FGG.

Fig. 10(b) shows the FTIR spectrum of chalcopyrite after interacting with FGG. It is clear from Fig. 10(b) that FGG had a negligible effect on the spectrum of chalcopyrite. After interacting with FGG, the characteristic adsorption bands of chalcopyrite shared no obvious changes and no new bands appeared. Except for the characteristic peaks at 1100.16 and 1016.86 cm⁻¹ were slightly lowered in intensity and appeared at 1086.11 and 1021.11 cm⁻¹ after adsorption. These results were attributed to the hydrogen bonding between FGG and chalcopyrite surface. Additionally, some literatures reported that guar gum may occur chemisorption on chalcopyrite surface in the form of hydroxyl groups (Rath et al., 1999). It comes to the conclusion that the depressant, FGG, adsorbs stronger on monoclinic pyrrhotite surface
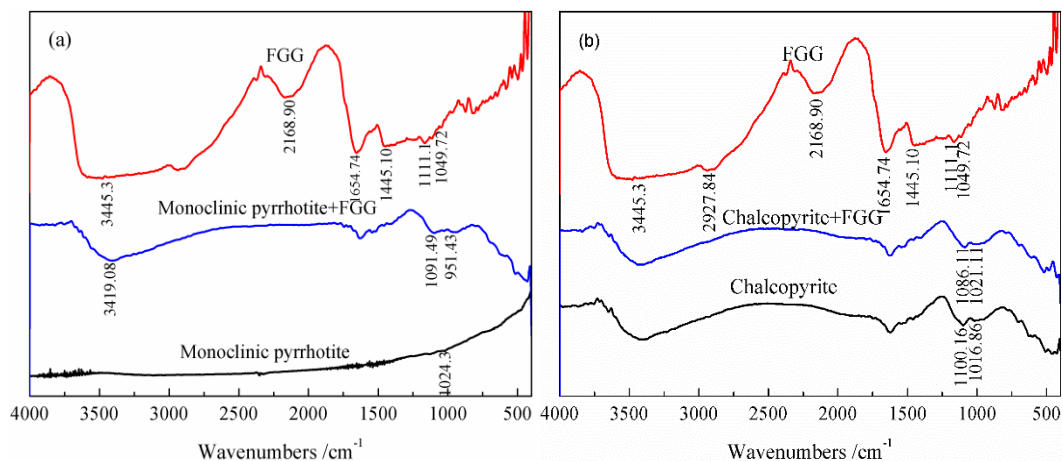


Fig. 10. The IR spectra of (a) monoclinic pyrrhotite and (b) chalcopyrite before and after interacting with FGG

than chalcopyrite, and the strong chemical adsorption process may dominate the interaction of depressant FGG with monoclinic pyrrhotite while having a weak adsorption on chalcopyrite, which are confirmed by kinetics, dynamic potential, adsorption, SEM studies and FTIR analysis respectively. This may be the reason why FGG has high depression selectivity for monoclinic pyrrhotite and little effect on chalcopyrite flotation.

## 4. Conclusions

In this work, FGG was used as a depressant in the flotation of a chalcopyrite-monoclinic pyrrhotite system. The flotation separation could not be realized without the addition of depressant as monoclinic pyrrhotite had a good floatability in a wide pH range. A novel reagent scheme, i.e., 40 mg/dm$^3$ of FGG depressant, 10 mg/dm$^3$ of PAX collector and 10 mg/dm$^3$ of MIBC frother at pH 8.0, was proved to achieve the selective flotation separation between chalcopyrite and monoclinic pyrrhotite. It is indicated that FGG has good depression ability and high depression selectivity to monoclinic pyrrhotite. Analyzing through the flotation kinetics, dynamic potential, adsorption, SEM and FTIR spectra measurements results, it is concluded that the FGG could absorb stronger on monoclinic pyrrhotite surface than chalcopyrite, and the chemical adsorption process may dominate the interaction of FGG with monoclinic pyrrhotite while hydrogen bonding as the main interaction of FGG with chalcopyrite.

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