

Pullulan Polysaccharide as an Eco-Friendly Depressant for Flotation Separation of Chalcopyrite and Molybdenite

Wenhui Yang, Tingsheng Qiu, Xianhui Qiu,* Huashan Yan, Qinghao Jiao, Kaiwei Ding, and Guanfei Zhao



Cite This: *ACS Omega* 2024, 9, 29557–29565



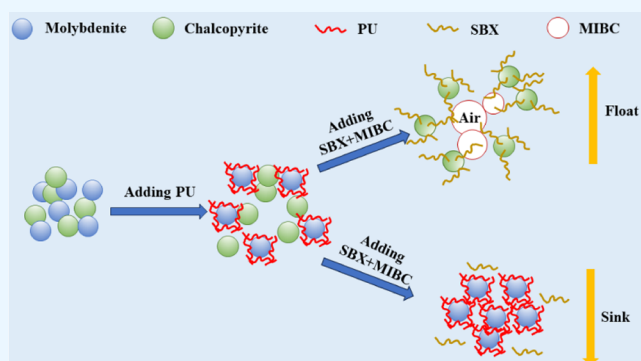
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: It is difficult to separate molybdenite and chalcopyrite by froth flotation due to the good floatability of the two minerals. In this paper, the separation of copper–molybdenum sulfide minerals was realized by using pullulan polysaccharide (PU) as the depressant. The flotation test results showed that the copper concentrate grade increased from 16.24 to 29.86%, and the copper concentrate recovery reached 83.55% under low alkali conditions. The selective separation mechanism of the two minerals by PU was revealed through contact angle measurements, ζ -potential measurements, Fourier transform infrared (FTIR) spectroscopy analyses, and X-ray photoelectron spectroscopy (XPS) analyses. The ζ -potential and contact angle results showed that PU is more easily adsorbed on molybdenite to strengthen the hydrophilicity of molybdenite. The FTIR and XPS results showed that PU is adsorbed on molybdenite by physical interactions, and hydrophobic interactions and hydrogen bonding play a major role.



1. INTRODUCTION

Copper and molybdenum are important energy sources, mainly derived from copper and molybdenum sulfide minerals. Copper and molybdenum minerals are usually co-associated, and flotation is one of the best ways to separate them. However, the good floatability of the two minerals makes it difficult to separate.^{1,2} Various depressants have been studied for the depression of target minerals during molybdenite and chalcopyrite separation. The main depressants of chalcopyrite are the inorganic depressants sodium sulfide (Na_2S) and sodium hydrosulfide (NaHS), and the organic depressant sodium thioglycolate is also widely used.^{3,4} However, these reagents have many disadvantages; for example, Na_2S and NaHS will produce H_2S in the flotation process, which will damage the ecological environment. Although sodium thioglycolate has high selectivity, low dosage, and low environmental pollution, its wide application is restricted by its high production cost.^{5,6} The agents used to depress molybdenite are usually hydrophilic polymers, such as lignosulfonate, carboxymethyl cellulose, humic acid, and xanthan gum.^{7,8} Although these agents have promoted the separation of copper–molybdenum, there are many drawbacks, such as high assumptions, poor selectivity, and high cost. Therefore, it is still necessary to look for a copper–molybdenum flotation depressant with excellent characteristics,

such as environmental protection, high selectivity, and great stability.

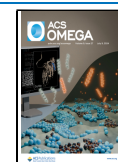
An extensive range of environmentally friendly and low-cost depressants have received significant attention. *O*-Carboxymethyl chitosan (*O*-CMC) can be adsorbed on molybdenite and chalcopyrite, but the interaction between *O*-CMC and chalcopyrite is basically a weak physical interaction, and the *O*-CMC adsorbed on chalcopyrite can be washed off or replaced by a collector. *O*-CMC is mainly adsorbed on molybdenite through hydrophobic interactions and electrostatic adsorption and is basically not affected by washing or collectors, so molybdenite can be effectively depressed by *O*-CMC.⁹ In the selective separation of copper and molybdenum sulfide minerals, galactomannan can selectively depress molybdenite but has no effect on chalcopyrite. The interaction between molybdenite and galactomannan is mainly hydrophobic, and galactomannan can be used as an environment-friendly reagent to separate molybdenite and chalcopyrite.¹⁰ Pectin was mainly adsorbed on Cu–Mo sulfide minerals through electrostatic and

Received: March 13, 2024

Revised: May 6, 2024

Accepted: May 16, 2024

Published: June 25, 2024



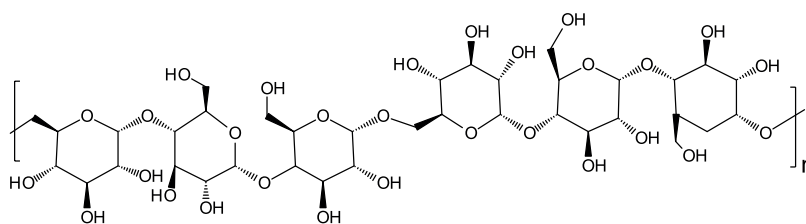


Figure 1. Structural formula of PU.

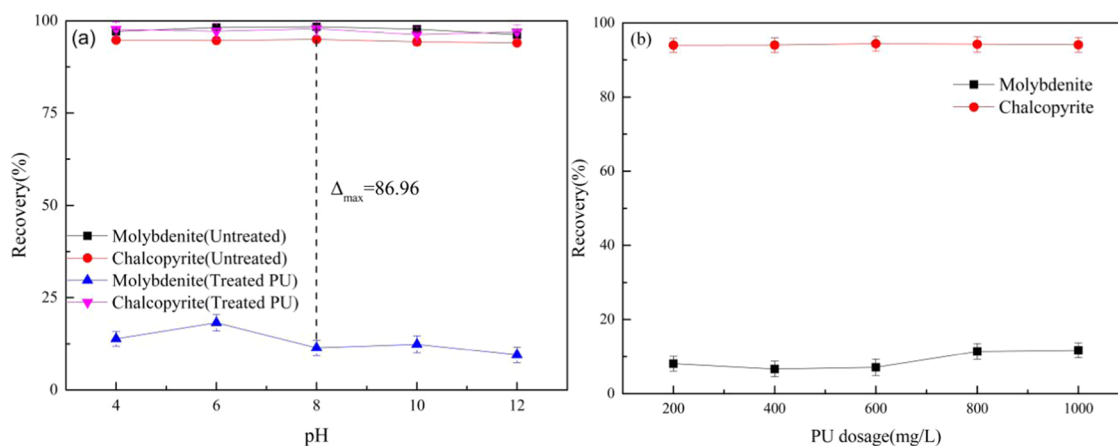


Figure 2. (a) Effect of pH on the recovery of molybdenite and chalcopyrite (SBX = 10 mg/L, MIBC = 20 mg/L, PU = 800 mg/L). (b) Effect of PU dosage on the recovery of molybdenite and chalcopyrite (pH = 8, SBX = 10 mg/L, MIBC = 20 mg/L).

hydrophobic interactions. The preadsorbed pectin on the chalcopyrite surface can be replaced by xanthate, but almost no xanthate is adsorbed on molybdenite which has reacted with pectin. The separation of Cu–Mo can be achieved by using kerosene or xanthate as collectors and pectin as a depressant.¹¹ In the pH range of 3–8, tragacanth gum had obvious selective depression behavior on chalcopyrite flotation but had little effect on molybdenite. Tragacanth gum may be chemically adsorbed on chalcopyrite through the hydrogen bond between –COOH and the hydrophilic substance of iron and the chemical bond between –COOH and iron sites on chalcopyrite. The adsorption of tragacanth gum on chalcopyrite prevents the further reaction of xanthate on its surface, so the separation of Cu–Mo minerals is realized.¹² Tiopronin has a good depression of chalcopyrite but almost no depression of molybdenite. The –SH and C–O groups in the tiopronin molecule form a complex ring by bonding with Cu atoms on the chalcopyrite surface.¹³

Pullulan polysaccharide (PU) is a natural degradable and safe macromolecular polymer with the chemical formula $(C_6H_{10}O_5)_n$, which is the most widely used in food and medicine and has great economic value and development prospects.^{14,15} There are many hydroxyl hydrophilic groups in PU molecules (Figure 1), which can be adsorbed on minerals to make them hydrophilic. However, its utilization as a depressant for molybdenite in copper–molybdenum sulfide flotation systems has rarely been reported in previous studies. The aim of this work was to investigate the possibility of PU as an environmentally friendly molybdenite depressant for the separation of copper and molybdenum. In the case of flotation with PU, the test results depicted that the copper grade of concentrate increased from 16.24 to 29.86%, and the recovery of copper concentrate reached 83.55% under low alkali conditions. The depression mechanism of molybdenite by

PU was studied by Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), contact angle, and ζ -potential.

2. RESULTS AND DISCUSSION

2.1. Single Mineral Flotation Test Results. To investigate the flotation behavior of molybdenite and chalcopyrite in the PU system, the effects of pH conditions and different PU concentration conditions on the flotation behavior of the two minerals were studied in detail. Figure 2a depicts the flotation recovery of molybdenite and chalcopyrite under different pH conditions. The experimental conditions were that the concentration of SBX was 10 mg/L, the concentration of MIBC was 20 mg/L, and the dosage of PU was 800 mg/L. In the test pH range, the recoveries of molybdenite and chalcopyrite without PU treatment remain above 96 and 94%, respectively. The results reveal that molybdenite and chalcopyrite have excellent floatability over a wide pH range with PU treatment. In the presence of PU, the molybdenite recovery was kept below 20% of the experiment. When the pH was 6–8, the molybdenite recovery reduced from 20% to approximately 10%, and in the pH range of 8–12, the molybdenite recovery was approximately 10%. Within the scope of the test pH, the recovery rate of chalcopyrite was kept above 94%. These results prove that PU has a better depressive behavior on molybdenite in pH 8–12, and the low alkali condition with pH 8 is selected for subsequent experiments, which is environmentally friendly and has less equipment wastage. In addition, the difference in the recovery of molybdenite before and after PU treatment is 86.96% when the pH is 8.

The flotation condition of pulp pH 8 was selected to explore the influence of PU concentration on the two minerals recovery, and the results are described in Figure 2b. The

experimental conditions were as follows: the consumption of SBX was 10 mg/L, and the concentration of MIBC was 20 mg/L. Within the entire dosage range of the test, the recovery of molybdenite was below 20%. The recovery of molybdenite is less than 10% when the consumption of PU is below 600 mg/L. With the increase of PU consumption, the chalcopyrite recovery was basically maintained at around 94%. The results confirmed that the depressive ability of PU on molybdenite was much stronger than that on chalcopyrite.

2.2. Mixed-Mineral Flotation Tests Results. The separation effect of PU on molybdenite and chalcopyrite was further explained by the tests of artificial mixed minerals. The experimental conditions were as follows: the consumption of SBX was 10 mg/L, the consumption of MIBC was 20 mg/L, the consumption of PU was 800 mg/L, and the pH was 8. The results are displayed in Table 1. The mass recovery rate of the

Table 1. Results of Molybdenite-Chalcopyrite Mixed Minerals

	products	mass recovery	grade (%)		recovery (%)	
		(Wt/%)	Cu	Mo	Cu	Mo
without Pu	concentrate	97.14	16.24	29.77	93.43	96.49
	tailing	2.86	5.75	36.78	6.57	3.51
with Pu	concentrate	42.95	29.86	1.56	83.55	2.52
	tailing	57.05	4.43	45.44	16.45	97.48

flotation concentrate obtained was 97.14%, and the copper grade was 16.24% in the absence of PU. After adding PU, the mass recovery of the concentrate decreased from 97.14 to 42.95%, while the copper concentrate grade increased from 16.24 to 29.86%, and the copper concentrate recovery reached 83.55%. The recovery of Cu in tailings was 16.45%, and the grade was only 4.43%. After adding PU, the molybdenum grade in the concentrate reduced from 29.77 to 1.56%, and the molybdenum recovery of the concentrate was only 2.52%. The recovery of molybdenum in tailings was 97.48%, while the grade was 45.44%. The results demonstrate that PU has a selective depressive effect on molybdenite and can be used as a new depressant with high efficiency to reach the selective separation of copper and molybdenum.

2.3. Effect of PU Treatment on the Wettability of Chalcopyrite and Molybdenite. To observe the influence of PU on the hydrophobicity of molybdenite and chalcopyrite, the contact angles of the two minerals were tested. The stronger the hydrophilicity of the mineral is, the smaller the contact angle, which leads to the hydrophilic sinking of the mineral; in contrast, the mineral is hydrophobic and floats.^{16,17} Therefore, the hydrophobicity and hydrophilicity of a mineral surface are usually represented by the contact angle. The influence of PU on the contact angle of the two minerals is depicted in Figure 3. Without any reagents, the contact angle of natural molybdenite was 85.1° and that of chalcopyrite was 75.5°, indicating that both minerals have good floatability.

With the increase in the dosage of PU added, the contact angle of chalcopyrite was almost unchanged and remained above 70°. As the consumption of PU increased, the contact angle of molybdenite reduced significantly. The contact angle of molybdenite reduced sharply from 85.1 to 46.1° when the amount of PU increased to 200 mg/L, and then with increasing dosage, the contact angle continued to decrease. The amount of PU was 800 mg/L, and its contact angle was

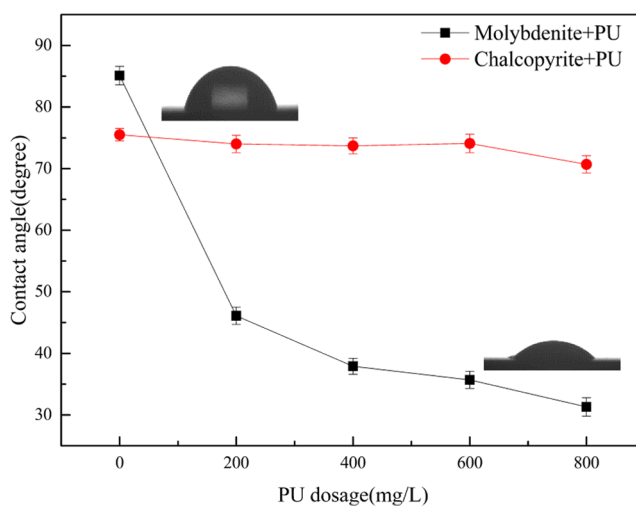


Figure 3. Effect of PU dosage on the surface contact angle of molybdenite and chalcopyrite (pH = 8).

31.3°. The results indicate that PU can significantly change the surface contact angle of molybdenite, making the surface hydrophilic, but has no significant influence on the hydrophobicity of chalcopyrite. These results are consistent with the flotation results. It can be considered that PU is more easily adsorbed on molybdenite and reduces the hydrophobicity of molybdenite. PU is difficult or weakly adsorbed on chalcopyrite, and the attached PU can be easily removed by rinsing. The difference between the contact angles of molybdenite and chalcopyrite is obvious when the dosage of PU is 800 mg/L, which provides favorable conditions for the selective depression of molybdenite.

2.4. Effect of PU Treatment on the ζ -Potential of Chalcopyrite and Molybdenite. The influence of PU on the surface charge of the two minerals was studied by detecting the ζ -potential of molybdenite and chalcopyrite before and after PU treatment (Figure 4). In the test pH range, the ζ -potential of chalcopyrite was negative, and its ζ -potential showed a negative shift with pH increasing, which corresponds to previous research.^{18,19} Within the entire test pH range, its ζ -potential moved in a positive direction after treating

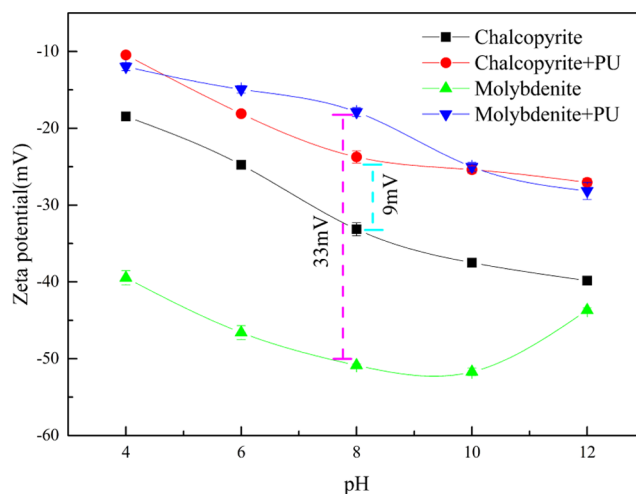


Figure 4. ζ -Potential of molybdenite and chalcopyrite before and after PU treatment (pH = 8, PU = 200 mg/L).

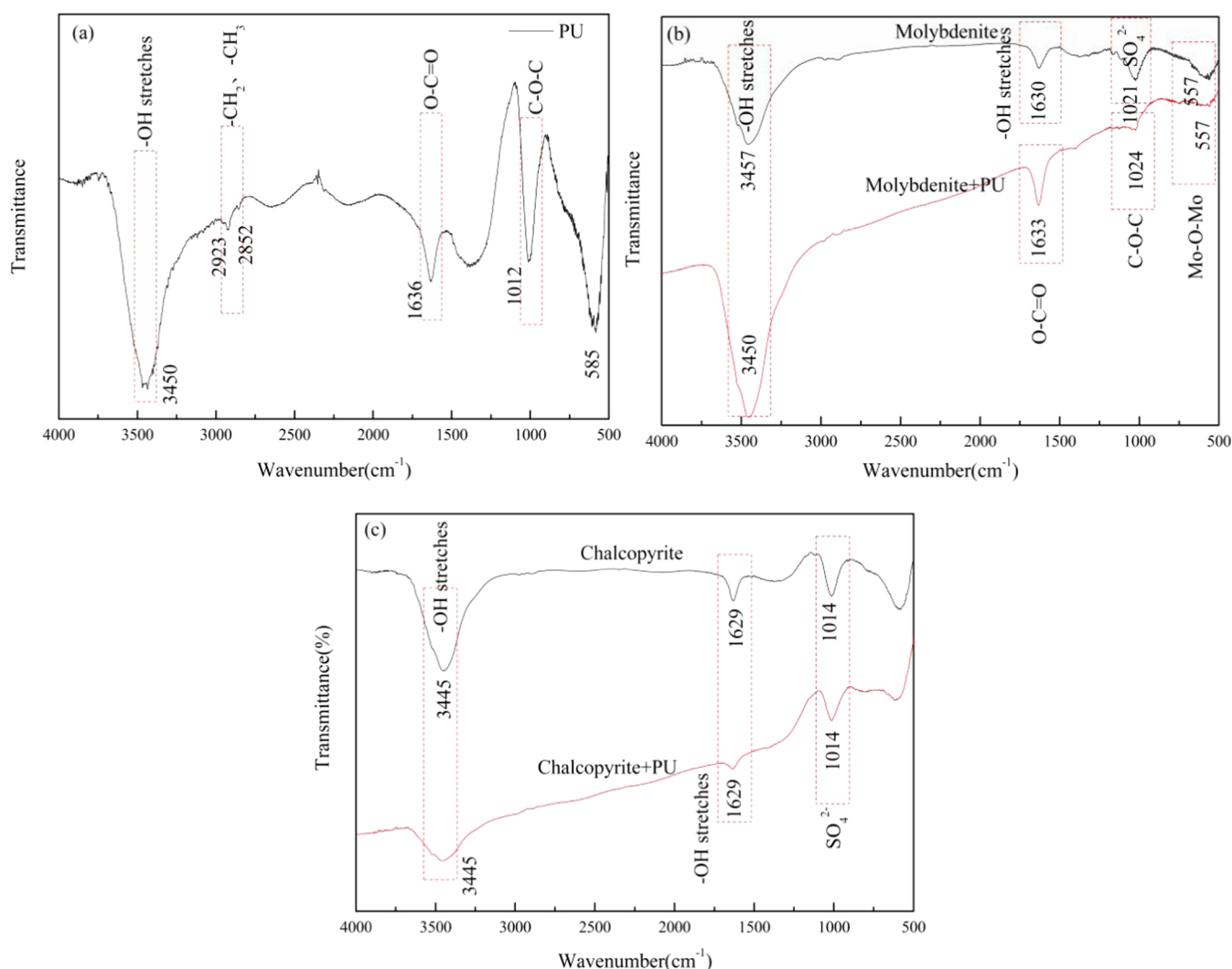


Figure 5. (a) Infrared spectra of PU; (b) infrared spectra of molybdenite; and (c) infrared spectra of chalcopyrite.

chalcopyrite with PU, which indicated that PU had an effect on chalcopyrite. The adsorption of PU reduces the negative ζ -potential of chalcopyrite.

The ζ -potential of molybdenite is negative in pH 4–12, and its ζ -potential shows a negative shift in the pH 4–9 range, while it displays a positive shift in pH 10–12, which is consistent with previous research.^{11,20} After PU treatment, the ζ -potential of molybdenite shifted in a positive direction, and the adsorption of PU also reduced the negative ζ -potential of molybdenite. Because PU is nonionic, it can be assumed that the movement of ζ -potential is due to the adsorption of PU on the minerals, which makes the sliding surface of the double electric layer deviate from the mineral surface, causing the absolute value of ζ -potential to decrease.^{10,21} The difference in ζ -potential is the most obvious when the pH is 8, where the difference in ζ -potential of molybdenite is 32.98 mV, while that of chalcopyrite is only 9.42 mV, which demonstrates that the amount of PU adsorbed on molybdenite is much larger than that on chalcopyrite and the ζ -potential of molybdenite moves more in the positive direction. This difference in adsorption capacity can be considered a weaker interaction between PU and chalcopyrite, while the interaction between PU and molybdenite is stronger, and PU is more easily adsorbed on molybdenite.^{22–24}

2.5. FTIR Analyses of Chalcopyrite and Molybdenite Surface before and after PU Treatment.

FTIR was used to illustrate the adsorption mechanism of PU on molybdenite and chalcopyrite. The infrared spectra of PU and minerals with and without PU treatment are presented in Figure 5. The infrared spectrum of PU is displayed in Figure 5a. The band appearing at 3450 cm⁻¹ belongs to the stretching vibration of -OH, the bands at 2852 and 2923 cm⁻¹ are -CH₃ and -CH₂, and the peak intensity at 1012 cm⁻¹ is C-O-C and at 1636 cm⁻¹ is O-C=O.^{25,26}

Figure 5b depicts the infrared spectrum of molybdenite. The bands at 3457 and 1630 cm⁻¹ are tensile vibrations of -OH, and the peak observed at 1021 cm⁻¹ may belong to asymmetric S-O stretching of sulfate formed by oxidation of molybdenite. The band at 557 cm⁻¹ belongs to the symmetrical stretching peak of Mo-O-Mo.^{27,28} In the PU-treated molybdenite spectrum, the peak at 1630 cm⁻¹ moved to 1633 cm⁻¹, which was obviously the O-C=O peak of PU, the -OH peak at 3457 cm⁻¹ shifted to 3450 cm⁻¹, belonging to the -OH peak of PU, and the peak at 1021 cm⁻¹ shifted to 1024 cm⁻¹ representing the stretching vibration of C-O-C in PU. In the infrared spectrum of molybdenite, the characteristic peaks of PU appeared, while the bands at 1630 and 1021 cm⁻¹ of molybdenite disappeared. The result indicated that PU can be

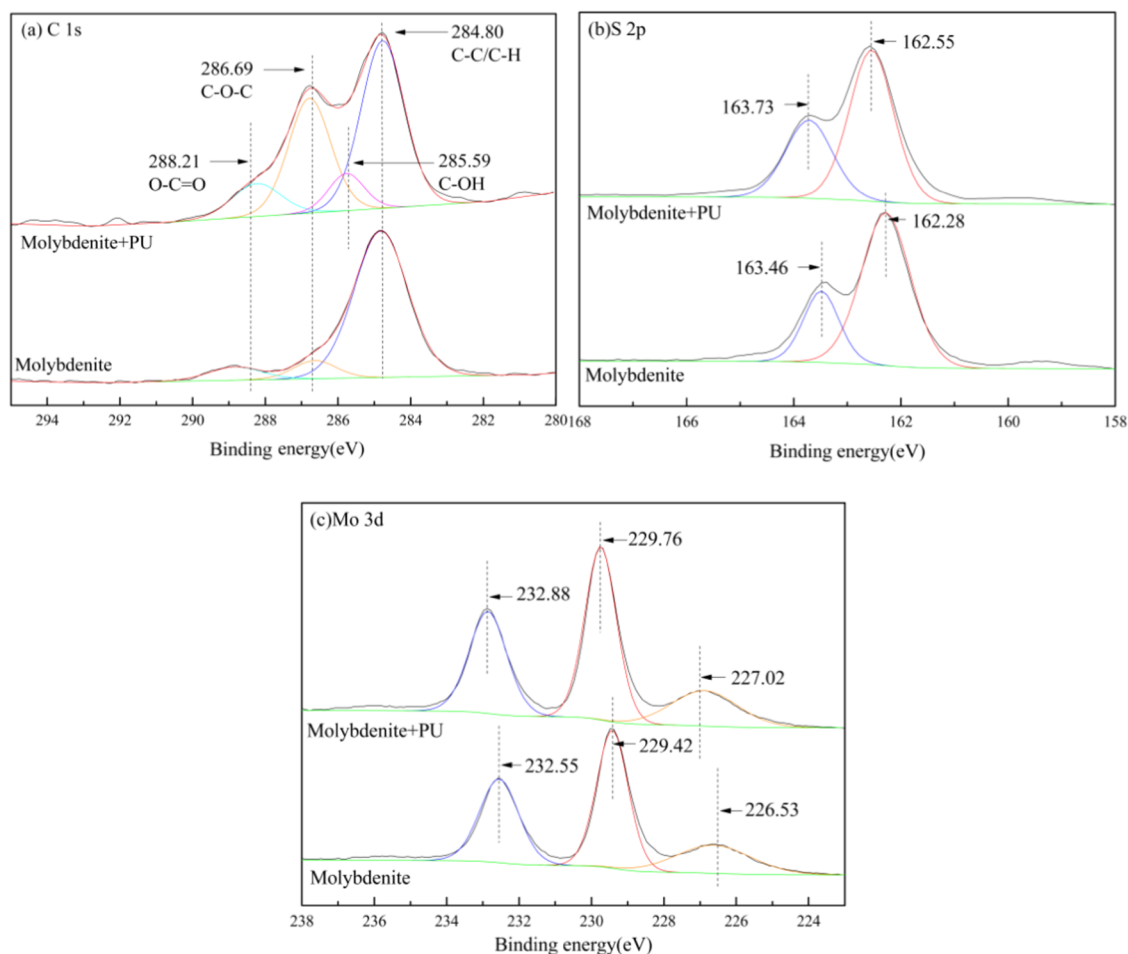


Figure 6. High-resolution (a) C 1s, (b) S 2p, and (c) Mo 3d spectra of molybdenite.

physically adsorbed on the molybdenite surface through hydrogen bonds between hydroxyl groups or other groups. Then, whether the adsorption of PU on molybdenite involves chemical reactions can be further analyzed through XPS.

The infrared spectrum of chalcopyrite is displayed in Figure 5c. The band at 3445 cm^{-1} is the tensile vibration of $-\text{OH}$, and the peaks at 1629 and 1014 cm^{-1} are the characteristic peaks of chalcopyrite.^{23,29} Chalcopyrite treated with PU showed no obvious offset at 3445 , 1629 , 1014 , and 590 cm^{-1} , indicating that PU hardly adsorbed on chalcopyrite.

2.6. XPS Analyses of Chalcopyrite and Molybdenite Surface before and after PU Treatment. XPS analysis was adopted to detect the chemical state and elemental composition of the mineral sample surface. The XPS spectra of Mo 3d, S 2p, and C 1s of molybdenite with and without PU are depicted in Figure 6. As depicted in Figure 6a, in the absence of PU, the peaks of 288.21 , 286.69 , and 284.8 eV belong to $\text{O}-\text{C}=\text{O}$, $\text{C}-\text{O}-\text{C}$, and $\text{C}-\text{C}/\text{C}-\text{H}$, respectively, due to external contamination.^{30,31} It can be clearly seen from the C 1s peak that the surface carbon species of molybdenite without PU treatment is mainly $\text{C}-\text{C}/\text{C}-\text{H}$ of 284.8 eV . After PU treatment, it is clear that a new $\text{C}-\text{OH}$ peak appears at 285.59 eV , and the peak intensity increases significantly at 286.69 eV ($\text{C}-\text{O}-\text{C}$) and 288.21 eV ($\text{O}-\text{C}=\text{O}$), which indicates that most of the carbon species on the treated molybdenite surface are provided by PU. As depicted in Figure 6b, the components at 162.28 and 163.46 eV in the S 2p spectrum belong to S 2p_{3/2} and S 2p_{1/2}, respectively.^{32,33}

After PU treatment, the binding energy of S 2p in molybdenite moved from 162.28 and 163.46 eV to 162.55 and 163.73 eV . As shown in Figure 6c, the components at 232.55 and 229.42 eV belong to Mo 3d_{3/2} and Mo 3d_{5/2}, respectively.³⁴ After treatment with PU, the binding energy of molybdenite Mo 3d shifted from 229.42 , 232.55 , and 226.53 eV to 229.76 , 232.88 , and 227.02 eV , the binding energy moved in a higher direction, and the sulfur and molybdenum atoms on molybdenite lost electrons. It could be seen that no new peaks appeared in the Mo 3d and S 2p spectra of molybdenite with or without PU, which further proved that the reaction between PU and molybdenite did not include chemical interactions. Therefore, PU and molybdenite should be physical adsorption, and mainly the adsorption of hydrophilic hydroxyl in PU molecules on the surface of molybdenite.

The XPS high-resolution spectra of chalcopyrite with and without PU are depicted in Figure 7. The XPS spectra of C 1s, S 2p, Fe 2p, and Cu 2p of chalcopyrite are depicted in Figure 7a–d, respectively. The C 1s spectra of chalcopyrite before and after PU treatment are almost unchanged, and the carbon species is consistent with that of untreated molybdenite. In the S 2p spectrum, the components at 161.20 and 162.34 eV belong to the sulfides of chalcopyrite, and the peaks at 163.56 eV are attributed to disulfides on chalcopyrite.³⁵ The peaks in the Fe 2p spectra are mainly attributed to iron and iron oxides and ferric sulfate.^{36,37} The peaks in the Cu 2p spectra of chalcopyrite mainly belong to the Cu(I)-S of chalcopyrite and the Cu 2p of CuO and CuS.³⁸ With the addition of PU, the

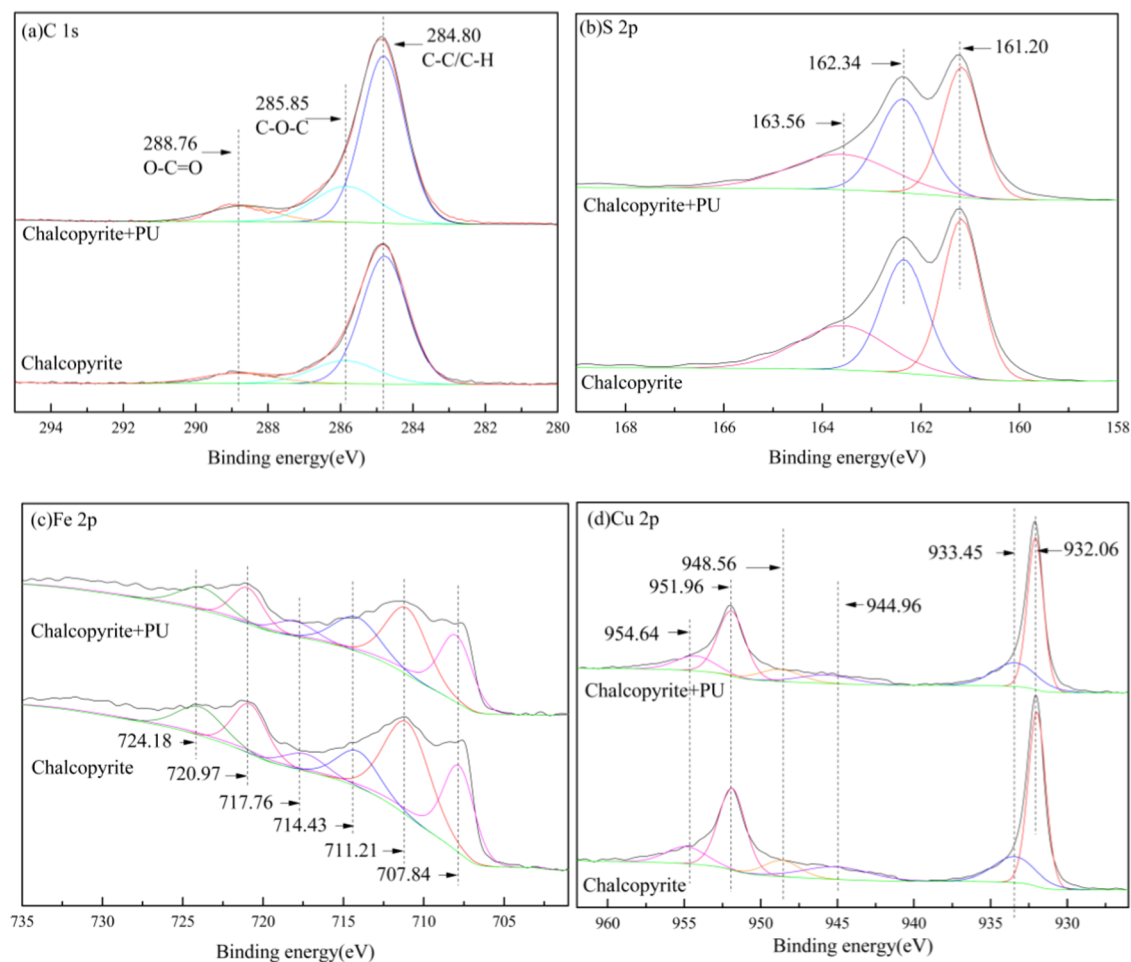


Figure 7. High-resolution (a) C 1s, (b) S 2p, (c) Fe 2p, and (d) Cu 2p spectra of chalcopyrite.

peaks of all spectra of chalcopyrite have no shift, and the binding energy is unchanged, indicating that PU had no obvious adsorption on the chalcopyrite surface.

In summary, PU is mainly adsorbed on molybdenite by hydrogen bonding, but XPS and FTIR analysis results indicate that the surface of molybdenite is slightly oxidized, and the surface hydroxyl components are less. Therefore, PU may be adsorbed on the molybdenite surface by hydrophobic interaction. Previous studies have shown that the adsorption of hydroxyl groups of polysaccharides and natural hydrophobic minerals is more hydrophobic interaction.^{10,39} PU contains hydrophilic groups such as $-\text{OH}$ and $\text{C}-\text{O}-\text{C}$ (Figure 1). Molybdenite has two different surfaces, a strong hydrophobic surface and a hydrophilic edge, so molybdenite is a typical anisotropic mineral. Because the crystal surface area accounts for approximately 90% of the total specific surface area, the nature of the crystal surface plays a leading role in the natural floatability of molybdenite.^{11,40} Therefore, the hydrophobic interaction between PU and molybdenite is easy to occur. The adsorption of PU on molybdenite is not only caused by hydrogen bonding but also by hydrophobic interaction.

3. CONCLUSIONS

In this work, the depression and mechanism of separation of molybdenite and chalcopyrite in flotation was investigated by adopting PU as a depressant. The main research conclusions are summarized as follows:

- (1) The mixed-mineral flotation test results showed that the copper grade of the concentrates increased from 16.24 to 29.86%, and the recovery reached 83.55% under low alkali conditions with PU as molybdenite depressant.
- (2) PU was more easily adsorbed on molybdenite to strengthen the hydrophilicity of molybdenite. Therefore, PU had a greater impact on the surface wettability of molybdenite, while it had little impact on chalcopyrite.
- (3) PU was adsorbed on molybdenite by physical interactions, hydrophobic interactions, and hydrogen bonding played a major role.
- (4) The results facilitate suggestions for the depression performance of PU on molybdenite and have reference value for the study of improving the quality of chalcopyrite and molybdenite concentrates.

4. MATERIALS AND METHODS

4.1. Materials and Reagents. High-purity minerals were taken from Guangdong Province, China. After crushing and grinding, particle sizes of $+0.038$ to -0.074 mm were obtained for flotation research. Hydrochloric acid (HCl), sodium hydroxide (NaOH), methyl isobutyl methanol (MIBC), sodium butyl xanthate (SBX), and PU were all of analytical grade and were used as pH regulator, frother, collector, and depressant, respectively, in the test. Potassium bromide (KBr) of spectral grade was used in the infrared test. The experimental water was deionized water. The compositions

of pure minerals were tested by chemical composition analyses, and the results showed that the purities of molybdenite and chalcopyrite were more than 96% (Table 2 and Figure 8).

Table 2. Chemical Constituents of Molybdenite and Chalcopyrite (wt %)

components	Fe	Cu	S	Mo	purity (%)
molybdenite			38.52	59.52	96.31
chalcopyrite	30.39	33.41	36.10		96.06

4.2. Micro-Flotation Tests. The flotation test of single mineral was tested on a trough flotation machine. After ultrasonic cleaning of 2 grams of sample each time, the sample was placed in a 40 mL flotation cell. After pH conditioning with HCl or NaOH, PU, SBX, and MIBC were added for the full reaction. After 4 min of stable flotation, the foam products and tailings were placed in an oven for drying. The recovery was obtained by the weight of the foam product and tailings. Each set of experiments was conducted at least three times, the mean value was calculated as the result, and the error bar was calculated from the standard deviation. The flowchart is shown in Figure 9.

Through the flotation test of mixed minerals, the separation effect of two minerals under the action of PU was verified. The operating steps followed the single mineral flotation test, and the mass ratio of molybdenite to chalcopyrite was 1 (the two minerals were 1.0 g each).

4.3. Contact Angle Measurements. The samples had to be polished to expose a fresh surface before testing. First, the lumpy molybdenite and chalcopyrite were cut into a flat surface and sealed with a fixed proportion of epoxy resin adhesive and curing agent. The obtained adhesive-sealed sample was carefully polished on a polishing machine to ensure that a fresh surface was exposed, and residual particles on the surface of the sample were cleaned with anhydrous ethanol and deionized water. The obtained sample was first thoroughly treated with PU (the pH of the solution was 8), and the sample after chemical treatment was tested using a JY-82C contact angle meter. Each sample was repeated three times, and the mean value was calculated as the result.

4.4. ζ -Potential Measurements. The reaction of molybdenite with chalcopyrite and PU was investigated by the ζ -potential method, and it was determined by a Zetasizer Nano ZS90 (Malvern, U.K.) instrument. Chalcopyrite/

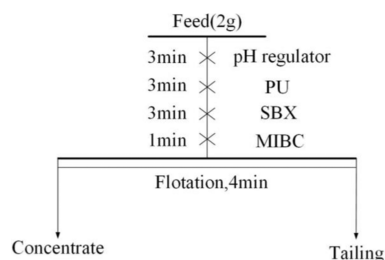


Figure 9. Flowchart of flotation tests.

molybdenite ($-2 \mu\text{m}$) (0.3 g) was put into a beaker, and 40 mL of 1×10^{-4} mol/L KCl solution was introduced. The pH was adjusted to the corresponding value with NaOH and HCl after stirring for 1 min. Then, PU (200 mg/L) was introduced into a beaker and stirred for 5 min, and the supernatant was introduced into the sample pool for detection. Each sample was repeated three times, and the mean value was calculated as the results.

4.5. FTIR Analyses. The reagents and the mineral samples with and without reagents were tested by FTIR. Infrared testing was conducted on an FTIR-740 infrared spectrometer. First, the samples of $-38 \mu\text{m}$ was further processed to $-5 \mu\text{m}$, the 2.0 g mineral sample ($-5 \mu\text{m}$) was added to a 50 mL beaker, and 40 mL PU solution (pH = 8) with a certain concentration was added and fully stirred on the magnetic agitator before being filtered and rinsed at least three times after the reagent interacted with the mineral. The samples were then dried using a vacuum oven, and the temperature was adjusted to 45°C . Finally, the spectral grade of KBr and the prepared sample were mixed evenly at a ratio of 100:1, the appropriate amount was loaded into the mold, and then FTIR detection was carried out.

4.6. XPS Analyses. XPS was performed on an X-ray photoelectron spectrometer model ESCALAB 250XI. First, 2.0 g of the samples with a particle size of 38 to $74 \mu\text{m}$ was weighed, and 40 mL of PU solution (the pH of the solution is 8) with a certain concentration was added, and then stirred thoroughly. After the mineral samples fully react with the reagent, it is filtered and rinsed at least three times. The samples were then dried using a vacuum oven, the temperature was adjusted to 45°C , and finally, the XPS test was carried out. The standard data of C 1s (284.8 eV) were corrected before peak separation and fitting of the XPS spectrum.

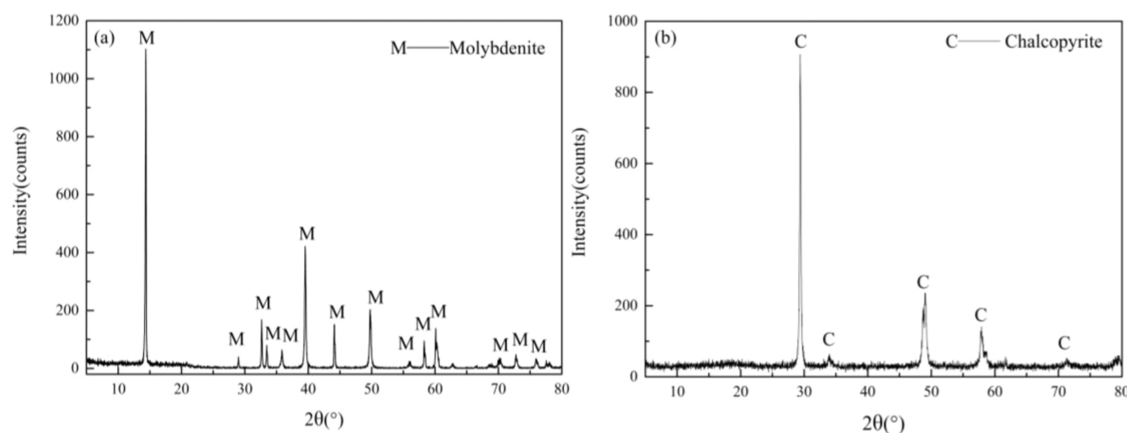


Figure 8. X-ray diffraction patterns of (a) molybdenite and (b) chalcopyrite.

AUTHOR INFORMATION

Corresponding Author

Xianhui Qiu – School of Resource and Environment Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; Jiangxi Province Key Laboratory of Mining Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; orcid.org/0000-0002-2087-8668; Email: qiuxianhui@jxust.edu.cn

Authors

Wenhui Yang – School of Resource and Environment Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

Tingsheng Qiu – School of Resource and Environment Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; Jiangxi Province Key Laboratory of Mining Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

Huashan Yan – School of Resource and Environment Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; Jiangxi Province Key Laboratory of Mining Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; orcid.org/0000-0003-0255-9062

Qinghao Jiao – School of Resource and Environment Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

Kaiwei Ding – School of Resource and Environment Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

Guanfei Zhao – School of Resource and Environment Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.4c02464>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (2022YFC2904502), the National Natural Science Foundation of China (nos. 51974138, 52374267), and The Program of Qingjiang Excellent Young Talents (JXUSTQ-JYX2020021).

REFERENCES

- (1) Hirajima, T.; Miki, H.; Suyantara, G. P. W.; Matsuoka, H.; Elmahdy, A. M.; Sasaki, K.; Imaizumi, Y.; Kuroiwa, S. Selective flotation of chalcopyrite and molybdenite with H₂O₂ oxidation. *Miner. Eng.* **2017**, *100*, 83–92.
- (2) Suyantara, G. P. W.; Hirajima, T.; Miki, H.; Sasaki, K.; Yamane, M.; Takida, E.; Kuroiwa, S.; Imaizumi, Y. Effect of Fenton-like oxidation reagent on hydrophobicity and floatability of chalcopyrite and molybdenite. *Colloids Surf., A* **2018**, *554*, 34–48.
- (3) Yin, Z.; Chen, S.; Xu, Z.; Zhang, C.; He, J.; Zou, J.; Chen, D.; Sun, W. Flotation separation of molybdenite from chalcopyrite using an environmentally-efficient depressant L-cysteine and its adsorption mechanism. *Miner. Eng.* **2020**, *156*, No. 106438.
- (4) YIN, Z.-g.; Sun, W.; Hu, Y.-h.; Guan, Q.-j.; Zhang, C.-h.; Gao, Y.-s.; Zhai, J.-h. Depressing behaviors and mechanism of disodium bis(carboxymethyl) trithiocarbonate on separation of chalcopyrite and molybdenite. *Trans. Nonferrous Met. Soc. China* **2017**, *27*, 883–890.
- (5) Miki, H.; Hirajima, T.; Muta, Y.; et al. Effect of Sodium Sulfite on Floatability of Chalcopyrite and Molybdenite. *Minerals* **2018**, *8*, No. 172, DOI: 10.3390/min8040172.
- (6) Chen, J.-h.; Lan, L.-h.; Liao, X.-j. Depression effect of pseudoglycolthiourea acid in flotation separation of copper–molybdenum. *Trans. Nonferrous Met. Soc. China* **2013**, *23*, 824–831.
- (7) Yin, Z.; Sun, W.; Hu, Y.; Zhang, C.; Guan, Q.; Liu, R.; Chen, P.; Tian, M. Utilization of acetic acid-[(hydrazinylthioxomethyl)thio]-sodium as a novel selective depressant for chalcopyrite in the flotation separation of molybdenite. *Sep. Purif. Technol.* **2017**, *179*, 248–256.
- (8) Ansari, A.; Pawlik, M. Floatability of chalcopyrite and molybdenite in the presence of lignosulfonates. Part I. Adsorption studies. *Miner. Eng.* **2007**, *20*, 600–608.
- (9) Yuan, D.; Liu, K.; Zeng, Q.; Zeng, H. Adsorption characteristics and mechanisms of O-Carboxymethyl chitosan on chalcopyrite and molybdenite. *J. Colloid Interface Sci.* **2019**, *552*, 659–670, DOI: 10.1016/j.jcis.2019.05.023.
- (10) Wang, X.; Gao, P.; Liu, J.; Gu, X.; Han, Y. Adsorption performance and mechanism of eco-friendly and efficient depressant galactomannan in flotation separation of chalcopyrite and molybdenite. *J. Mol. Liq.* **2021**, *326*, No. 126574.
- (11) Yang, B.; Zeng, M.; Zhu, H.; Huang, P.; Li, Z.; Song, S. Selective depression of molybdenite using a novel eco-friendly depressant in Cu-Mo sulfides flotation system. *Colloids Surf., A* **2021**, *622*, No. 126683.
- (12) Zhong, C.; Bo, F.; Hui, W.; Yuan, C.; Meng, G. The depression behavior and mechanism of tragacanth gum on chalcopyrite during Cu-Mo flotation separation. *Adv. Powder Technol.* **2021**, *32*, 2712–2719.
- (13) Bingqiao, Y.; Hai, Y.; Mengyuan, Z.; Huanyu, Z. Tiopronin as a novel copper depressant for the selective flotation separation of chalcopyrite and molybdenite. *Sep. Purif. Technol.* **2021**, *266*, No. 118576, DOI: 10.1016/j.seppur.2021.118576.
- (14) Mitić, Z.; Cakic, M.; Nikolić, G. M.; Nikolić, R.; Nikolić, G. S.; Pavlovic, R.; Santaniello, E. Synthesis, physicochemical and spectroscopic characterization of copper(II)-polysaccharide pullulan complexes by UV–vis, ATR-FTIR, and EPR. *Carbohydr. Res.* **2011**, *346*, 434–441.
- (15) Wani, S. M.; Mir, S. A.; Khanday, F. A.; Masoodi, F. A. Advances in pullulan production from agro-based wastes by *Aureobasidium pullulans* and its applications. *Innovative Food Sci. Emerging Technol.* **2021**, *74*, No. 102846.
- (16) Cui, Y.; Jiao, F.; Wei, Q.; Wang, X.; Dong, L. Flotation separation of fluorite from calcite using sulfonated lignite as depressant. *Sep. Purif. Technol.* **2020**, *242*, No. 116698.
- (17) Chen, C.; Hu, Y.; Zhu, H.; Sun, W.; Qin, W.; Liu, R.; Gao, Z. Inhibition performance and adsorption of polycarboxylic acids in calcite flotation. *Miner. Eng.* **2019**, *133*, 60–68.
- (18) Wang, X.; Zhao, B.; Liu, J.; Zhu, Y.; Han, Y. Dithiouracil, a highly efficient depressant for the selective separation of molybdenite from chalcopyrite by flotation: Applications and mechanism. *Miner. Eng.* **2022**, *175*, No. 107287.
- (19) Hu, J.-c.; Shi, Q. Relationship between rheological behavior and flotation rate in slurry with different chalcopyrite and lizardite concentration. *J. Cent. South Univ.* **2022**, *29*, 1479–1487.
- (20) Wang, X.; Yuan, S.; Liu, J.; Zhu, Y.; Han, Y. Nanobubble-enhanced flotation of ultrafine molybdenite and the associated mechanism. *J. Mol. Liq.* **2022**, *346*, No. 118312.
- (21) Feng, B.; Peng, J.; Zhang, W.; Ning, X.; Guo, Y.; Zhang, W. Use of locust bean gum in flotation separation of chalcopyrite and talc. *Miner. Eng.* **2018**, *122*, 79–83.
- (22) Wang, C.; Liu, R.; Wu, M.; Xu, Z.; Tian, M.; Yin, Z.; Sun, W.; Zhang, C. Flotation separation of molybdenite from chalcopyrite using rhodanine-3-acetic acid as a novel and effective depressant. *Miner. Eng.* **2021**, *162*, No. 106747.
- (23) Liu, D.; Zhang, G.; Chen, Y.; Huang, G.; Gao, Y. Investigations on the utilization of konjac glucomannan in the flotation separation of chalcopyrite from pyrite. *Miner. Eng.* **2020**, *145*, No. 106098.

- (24) Yan, H.; Yang, B.; Zeng, M.; Huang, P.; Teng, A. Selective flotation of Cu-Mo sulfides using xanthan gum as a novel depressant. *Miner. Eng.* **2020**, *156*, No. 106486.
- (25) Zhang, W.; Tao, L.; Xun, L.; Qi, Z.; Pooley, S.; Sun, W.; Cao, J.; Gao, Z. Improved flotation of molybdenite from talc using a selective reagent scheme. *Miner. Eng.* **2022**, *176*, No. 107324.
- (26) Shingel, K. I. Determination of structural peculiarities of dextran, pullulan and γ -irradiated pullulan by Fourier-transform IR spectroscopy. *Carbohydr. Res.* **2002**, *337*, 1445–1451.
- (27) Tang, X.; Chen, Y.; Liu, K.; Peng, Q.; Zeng, G.; Ao, M.; Li, Z. Reverse flotation separation of talc from molybdenite without addition of depressant: Effect of surface oxidation by thermal pre-treatment. *Colloids Surf., A* **2020**, *594*, No. 124671.
- (28) He, T.; Li, H.; Jin, J.; Peng, Y.; Wang, Y.; Wan, H. Improving fine molybdenite flotation using a combination of aliphatic hydrocarbon oil and polycyclic aromatic hydrocarbon. *Results Phys.* **2019**, *12*, 1050–1055.
- (29) Xun, W.; Yi, Z.; Yue, H. Adsorption and depression mechanism of an eco-friendly depressant PCA onto chalcopyrite and pyrite for the efficiency flotation separation. *Colloids Surf., A* **2021**, *620*, No. 126574, DOI: 10.1016/j.colsurfa.2021.126574.
- (30) Ejtemaei, M.; Nguyen, A. V. Kinetic studies of amyl xanthate adsorption and bubble attachment to Cu-activated sphalerite and pyrite surfaces. *Miner. Eng.* **2017**, *112*, 36–42.
- (31) Buckley, A. N.; Woods, R.; Wouterlood, H. J. An XPS investigation of the surface of natural sphalerites under flotation-related conditions. *Int. J. Miner. Process.* **1989**, *26*, 29–49, DOI: 10.1016/0301-7516(89)90041-0.
- (32) Zhao, Q.; Liu, W.; Wei, D.; Wang, W.; Cui, B.; Liu, W. Effect of copper ions on the flotation separation of chalcopyrite and molybdenite using sodium sulfide as a depressant. *Miner. Eng.* **2018**, *115*, 44–52.
- (33) Liu, G.; Qiu, Z.; Wang, J.; Liu, Q.; Xiao, J.; Zeng, H.; Zhong, H.; Xu, Z. Study of N-isopropoxypropyl-N'-ethoxycarbonyl thiourea adsorption on chalcopyrite using in situ SECM, ToF-SIMS and XPS. *J. Colloid Interface Sci.* **2015**, *437*, 42–49.
- (34) Yang, B.; Yan, H.; Zeng, M.; Huang, P.; Jia, F.; Teng, A. A novel copper depressant for selective flotation of chalcopyrite and molybdenite. *Miner. Eng.* **2020**, *151*, No. 106309.
- (35) Harmer, S. L.; Thomas, J. E.; Fornasiero, D.; Gerson, A. R. The evolution of surface layers formed during chalcopyrite leaching. *Geochim. Cosmochim. Acta* **2006**, *70*, 4392–4402.
- (36) Li, Y.; Wei, Z.; Qian, G.; Li, J.; Gerson, A. Kinetics and Mechanisms of Chalcopyrite Dissolution at Controlled Redox Potential of 750 mV in Sulfuric Acid Solution. *Minerals* **2016**, *6*, No. 83, DOI: 10.3390/min6030083.
- (37) da Silva, G. R.; Espiritu, E. R. L.; Mohammadi-Jam, S.; Waters, K. E. Surface characterization of microwave-treated chalcopyrite. *Colloids Surf., A* **2018**, *555*, 407–417.
- (38) Hussain, Z.; Salim, M. A.; Khan, M. A.; Khawaja, E. E. X-ray photoelectron and auger spectroscopy study of copper-sodium-germanate glasses. *J. Non-Cryst. Solids* **1989**, *110*, 44–52.
- (39) Zhong, C.; Wang, H.; Zhang, L.; Guo, M.; Feng, B. Flotation separation of molybdenite and talc by xanthan gum. *Powder Technol.* **2021**, *388*, 158–165.
- (40) Lu, Z.; Liu, Q.; Xu, Z.; Zeng, H. Probing Anisotropic Surface Properties of Molybdenite by Direct Force Measurements. *Langmuir* **2015**, *31*, 11409–11418.