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Selective depression mechanism of ferric chromium lignin sulfonate for chalcopyrite–galena flotation separation

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Abstract: Selective recovery of chalcopyrite–galena ore by flotation remains a challenging issue. The development of highly efficient, low-cost, and environmentally friendly depressants for this flotation is necessary because most of available reagents (e.g., $K_2Cr_2O_4$) are expensive and adversely affect the environment. In this study, ferric chromium lignin sulfonate (FCLS), which is a waste-product from the paper and pulp industry, was introduced as a selective depressant for galena with butyl xanthate (BX) as a collector. Results show that the residue recovery of Pb in Cu concentrate was substantially reduced to 4.73% using FCLS compared with 10.71% using the common depressant $K_2Cr_2O_4$. The underlying mechanisms were revealed using zeta-potential measurements and X-ray photoelectron spectroscopy (XPS). Zeta-potential measurements revealed that FCLS was more efficiently absorbed onto galena than onto chalcopyrite. XPS measurements further suggested that FCLS enhanced the surface oxidation of galena but prevented that of chalcopyrite. Thus, FCLS could be a potential candidate as a depressant for chalcopyrite–galena flotation because of its low cost and its lack of detrimental effects on the environment.

Keywords: chalcopyrite; galena; depressant; flotation separation

1. Introduction

Froth flotation remains as the main method to recover chalcopyrite and galena concentrate from ores. Separation of chalcopyrite and galena is a major concern because of their very similar floatability [1]. Therefore, an effective depressant is critical for the efficient flotation of these compounds. Inorganic depressants, such as dichromate, cyanide, and sulfur dioxide, are the most commonly used depressants for flotation. Effective approaches to separate copper and lead include using cyanide to depress copper and float lead as well as using dichromate to depress lead and float copper [2]. However, these inorganic depressants have limited applications because of their high toxicity, high dosage, poor selectivity, large losses of precious metals, and difficult re-activation, among other shortcomings, even with high reasonable separation effect [1,3].

Therefore, the major problem in the development of methods to separate Cu–Pb sulfide ore lies in the development of an effective depressant for separation. Many studies have reported the application of various depressants. Piao *et al.* [3] showed that sodium 2,3-dihydroxypropyl dithiocarbonate (SGX) can separate chalcopyrite from galena at pH value of 6; however, SGX is expensive and its application requires a high dosage. Piao *et al.* [4] synthesized the novel reagent O,O-bis(2,3-dihydroxypropyl) dithiophosphate. Although satisfactory separation performance was attained in the laboratory, this reagent is difficult to apply industrially because of its expensive synthesis. Liu *et al.* [5] found that a depressant consisting of sodium humate and ammonium persulfate (APS) can remarkably separate chalcopyrite from galena; however, APS is a dangerous and controlled reagent. High-molecular-weight polyacrylamide (PAM) and dextrin were applied as depressants, but chalcopyrite and galena could not be separated by PAM without ethylene diamine tetraacetic acid (EDTA) pretreatment or by dextrin without adding citric acid [6–8]. Several depressants, including sodium pyrophosphate and chitosan, are effective in acidic

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solution [1,9]. In such solutions, the frother exhibits poor performance; in addition, acidic solution necessitate acid-resistant equipment. Hence, the development of a new effective depressant remains a challenge.

In this study, ferric chromium lignin sulfonate (FCLS) was applied as a depressant to separate chalcopyrite from galena. FCLS was first synthesized in the 1960s and used in the petroleum industry as anti-caving drilling mud, which has been the primary use of FCLS for more than 40 years [10–12]. FCLS is a chelate, which is formed by complexation reaction of two or more polar groups of lignin sulfonate with Fe^{2+} and Cr^{3+}. The precursor raw material of FCLS is lignin sulfonate, which is a by-product of wood processing to extract cellulose [13]. Therefore, FCLS has abundant resources and is inexpensive compared with other organic reagents. However, few studies have reported the application of FCLS as a depressant in froth flotation. FCLS was used as depressant for limonite at the Dachang Mine in Guangxi province, China [14]. Liu *et al.* [15] showed that, when FCLS was used as depressant, marmatite was strongly depressed, whereas chalcopyrite was only slightly depressed. In the present study, the ability of FCLS to depress chalcopyrite and galena was examined using microflotation and bench-scale flotation tests. The interaction mechanism was investigated further through zeta-potential measurements and X-ray photoelectron spectroscopy.

2. Experimental

2.1. Materials and reagents

Chalcopyrite and galena samples were obtained from Chenzhou (Hunan, China) and from Fankou Mine (Guangdong, China), respectively. The samples were purified by hand sorting, and chemical analyses showed that their chalcopyrite and galena contents were 72.65% and 92.35%, respectively. The 0.074–0.104 mm fraction, which was stored in sealed glass bottles, was used for the flotation tests. Samples further ground to −0.038 mm in an agate mortar were used for zeta-potential measurements.

Butyl xanthate (BX) and terpineol (2# oil) were industrial-grade products from Zhuzhou Flotation Reagents Factory (Hunan, China). Industrial-grade FCLS was supplied by Renqiu Jia Fu Chemical Co., Ltd. (Hebei, China). The level of pH value was adjusted with sodium hydroxide and hydrochloric acid stock solutions. Deionized water (18 mΩ·cm) was used in all experiments.

2.2. Microflotation tests

Pure mineral and artificial mixed-mineral flotation experiments were performed in an XFG-type flotation machine at an impeller speed of 1600 r/min. To remove any surface oxides, the sample was cleaned using an ultrasonic cleaner. The mineral suspension was prepared by adding 2.0 g (1.0 g of chalcopyrite and 1.0 g of galena for artificial mixed minerals) of mineral samples to 40 mL of deionized water. The pH value was adjusted and recorded. The depressant, collector, and frother were then added sequentially, with corresponding conditioning times of 3, 2, and 1 min, respectively. The flotation lasted for 4 min. For pure mineral flotation, the flotation products were dried and weighed and the recovery rate was calculated. For artificial mixed minerals, the flotation concentrates and tails were assayed for Cu and Pb.

2.3 Bench-scale flotation tests

The experimental runs were conducted in an XFD-type flotation cell with a volume capacity of 1.5 L. The feed was added to the flotation cell with tap water to obtain the required pulp density. The pulp density was adjusted to 33% during flotation. The concentrate and tailings were filtered, dried, weighed, and analyzed.

2.4. Zeta-potential measurements

Zeta-potential measurements were conducted at (25.0 ± 0.5)°C using a Coulter Delsa 440SX zeta-potential analyzer (Beckman Coulter, USA). Mineral samples (50 mg, <2 μm) were added to 50 mL of KCl solution. The ionic strength of the suspension in all tests was maintained at 10^{-3} $mol \cdot L^{-1}$. The pH value was then adjusted by adding HCl or NaOH solutions, and the desired reagent(s) was/were added in the same order as that in the flotation experiment. After being magnetically stirred for 5 min, the suspension was sucked out and used for measurement. The zeta-potential measurement was repeated three times, and the average value was calculated.

2.5. XPS

XPS analyses were performed with a PHI-5300/ESCA (Perkin-Elmer Co., USA) spectrometer equipped with an Al K_α radiation source operated at 3.0 kV and 6 mA. A spectrometer pass energy of 0.8 eV was used for all elemental spectral regions. The pressure in the analyzer chamber was 2.9×10^{-7} Pa. All measurements were performed at a take-off angle of 45°. The tested samples were prepared as follows. The mineral sample (1 g) was added into 20 mL of the aqueous solution with reagents at natural pH value, ground in a carnelian agate mortar for 30 min, filtered, rinsed with distilled water, and then dried under vacuum at room temperature for 24 h. The X-ray photoelectron spectrum was immediately recorded to calculate the surface compositions.

3. Results and discussion

3.1. Effect of pH value level on the flotation of chalcopyrite and galena

The flotation results of galena and chalcopyrite as a function of pH value (pH 2–12) in the presence and absence of FCLS are shown in Fig. 1. The experimental results show that galena and chalcopyrite floated well at pH 2–10 in the absence of FCLS. The recovery of galena decreased sharply under a high-alkali environment, and the results are consistent with those in previous reports [6,16]. Chalcopyrite and galena exhibit excellent natural floatability because of the formation of hydrophobic species, such as elemental sulfur (S^0), on the surface of galena and chalcopyrite through oxidation and electrochemical reaction [17–18]. When FCLS was added, the recovery of galena decreased sharply to 20% in the pH value range of 4–10. At pH value levels greater than 10 or less than 4, the recovery of galena dramatically decreased. By contrast, the recovery of chalcopyrite decreased slightly when FCLS was introduced at pH 3–12. FCLS had a slight depressing effect on chalcopyrite, whereas the recovery of galena decreased dramatically. The maximum recovery difference between chalcopyrite and galena occurred over the pH value range of 8–12.

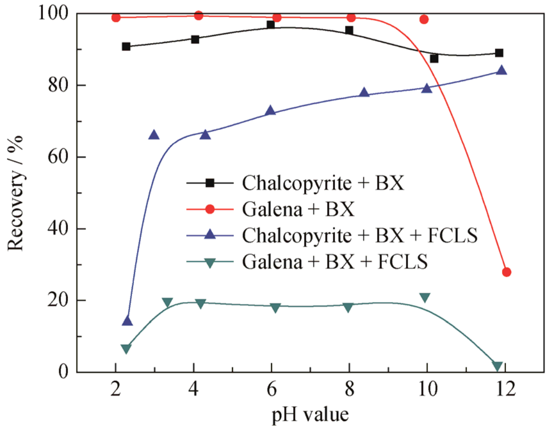

Fig. 1. Flotation recovery of chalcopyrite and galena as a function of pH value in different reagents ($C_{(BX)} = 1 \times 10^{-4}$ mol·L^{-1}, $C_{(FCLS)} = 100$ mol·L^{-1}, $C_{(2\# oil)} = 10$ mol·L^{-1}).

3.2. Flotation of artificial mixed minerals

In mixed-mineral flotation, 2 g of sample was used for each test, and the mass ratio of chalcopyrite and galena was 1:1. The pH value was adjusted to 11.11. In the experiment, the dosages of FCLS, BX, and 2# oil were 100, 1×10^{-4}, and 10 mol·L^{-1}, respectively. The results are shown in Table 1. The chalcopyrite and galena recoveries could be calculated using the yield and grade data in Table 1 because chalcopyrite and galena are the only Cu-bearing and Pb-bearing minerals in this study. Table 1 shows that 76.67% of the chalcopyrite was recovered and 85.33% of the galena was depressed. The flotation tests confirm the feasibility of using FCLS as a selective depressant in chalcopyrite–galena separation.

Table 1. Results of the flotation separation of chalcopyrite–galena artificial mixed minerals

Products	Yield / %	Grade, β / %		Recovery, ε / %	
		Cu	Pb	Cu	Pb
Cu concentrate	45.67	21.21	12.85	76.67	14.67
Pb concentrate	54.33	5.43	62.81	23.33	85.33
Feed	100.00	12.64	40.00	100.00	100.00

3.3. Bench-scale flotation tests

On the basis of the flotation experimental results in Section 3.2, FCLS can be used industrially. Hence, open-circuit flotation experiments were conducted. The feed material containing 0.38wt% Cu and 1.92wt% Pb from Pingjiang Cu–Pb–Zn Mine (Hunan, China) was used for these experiments. Mineralogical data confirmed the complex mineral composition consisting of various mineral species. Cu and Pb mainly existed in the form of chalcopyrite and galena, and the predominant gangue minerals were quartz, calcite, sericite, and chlorite. The spectral analysis results for the ore sample are shown in Table 2.

Table 2. Results of spectral analysis of the ore sample wt%

Cu	Pb	Zn	Fe	Mn	W
0.38	1.92	3.45	1.00	0.01	0.01

In this experiment, Z-200 was used as collector, whereas Na_2S and activated carbon were used to remove the reagents, which were added for Cu–Pb bulk flotation and cleaning flotation. For comparison, FCLS + Na_2SO_3 + Na_2SiO_3 and $K_2Cr_2O_4$ + Na_2SO_3 + Na_2SiO_3 were used as depressants. The detailed flow sheet of the open-circuit flotation is shown in Fig. 2. The results of the experiment are shown in Table 3.

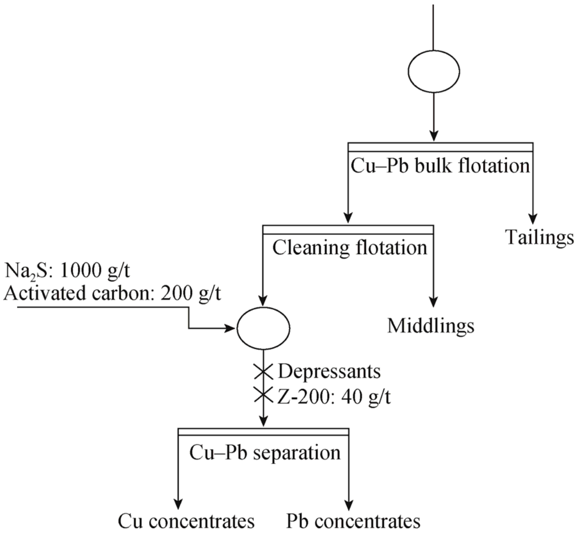

Fig. 2. Copper–lead separation flotation flow sheet.

With $K_2Cr_2O_4$ as depressant, the recovery of Cu and Pb was 86.06% and 77.95%, respectively; however, the recovery of Pb in Cu concentrates was high and reached 10.71%. When FCLS was used as depressant, the recovery of Pb was high, reaching 83.32%; the recovery of Pb in the Cu concentrate decreased from 10.71% to 4.73%. FCLS is superior to $K_2Cr_2O_4$ in depressing galena. In addition, the results show that the chromium in FCLS is trivalent. The toxicity of Cr^{3+}, which is an essential trace element in mammalian metabolism, is 1/500 that of Cr^{6+}; thus, Cr^{3+} is considered non-toxic [19–23]. Moreover, when FCLS is used as the depressant, the dosage of chromium is 1/20 of that when $K_2Cr_2O_4$ is used as the depressant. Hence, FCLS exhibited strong potential for industrial application as a replacement for $K_2Cr_2O_4$ in the separation of chalcopyrite from galena.

Table 3. Comparison of the test results for ferric chromium lignin sulfonate and potassium dichromate

Depressants dosage / (g·t^{-1})	Products	Yield / %	Grade / %		Recovery / %	
			Cu	Pb	Cu	Pb
FCLS, 1000 Na_2SO_3, 500 Na_2SiO_3, 500	Cu concentrates	1.83	18.370	4.54	84.47	4.73
	Pb concentrates	2.17	0.870	67.49	4.75	83.32
	Middlings	2.39	0.540	3.31	3.24	4.50
	Tailings	93.61	0.032	0.14	7.54	7.45
	Feed	100.00	0.398	1.76	100.00	100.00
$K_2Cr_2O_4$, 1000 Na_2SO_3, 500 Na_2SiO_3, 500	Cu concentrates	1.96	17.830	8.79	86.06	10.71
	Pb concentrates	2.15	1.090	59.46	5.76	77.95
	Middlings	1.07	0.550	3.34	1.45	2.17
	Tailings	94.02	0.029	0.16	6.73	9.17
	Feed	100.00	0.406	1.64	100.00	100.00

3.4. Zeta-potential measurements

The zeta potential of galena as a function of pH value with or without FCLS was determined to investigate the interaction mechanism between FCLS and the mineral surface (Fig. 3). Fig. 3 indicates that, with or without reagents, the isoelectric point of galena was not found in the pH value range from 2 to 12. The zeta potential of galena decreased gradually with increasing pH value level at pH value < 10 and then increased slightly at pH value > 10. A previous study showed that, with the change in pH value of the solution, the dissolution of Pb^{2+} and S^{2-} in the mineral surface produced different lead and sulfide species. In an acidic solution, the galena surface metal dissolves and forms a metal-deficient sulfur-rich surface; by contrast, the sulfide species are dominant for zeta potential. Under alkaline conditions, lead hydroxide ($PbOH^-$, $Pb(OH)_2$, $Pb(OH)^{3+}$) was formed and covered the surface, reducing the zeta potential [24–25].

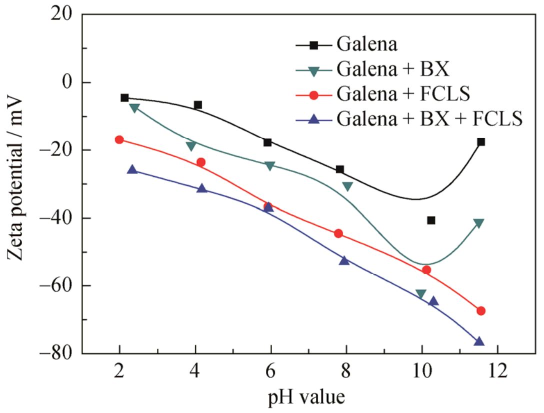

Fig. 3. Zeta potential of galena as a function of pH in different reagents ($C_{(BX)} = 1 \times 10^{-4}$ mol·L^{-1}, $C_{(FCLS)} = 100$ mg·L^{-1}).

In the presence of BX, the zeta potential of galena became negative, indicating that BX was adsorbed onto the surface of galena. After FCLS was added, the zeta potential of galena become more negative, indicating that FCLS was adsorbed onto the galena surface. FCLS is an anionic surfactant that contains a large number of hydroxyl (−OH) and sulfonic acid ($-SO_3H$) groups. The more negative zeta potential of galena might be associated with the adsorption of these groups. Moreover, the zeta potential remarkably decreased and became almost constant at pH value < 10. At pH value > 10, the reduction in the zeta potential became greater. Thus, the adsorption of FCLS on galena at pH value > 10 was stronger than that at pH value < 10. Flotation of galena was depressed more strongly at pH value > 10 (Fig. 1). In the presence of both FCLS and BX, the observed zeta potential of galena was more negative than with FCLS alone. This phenomenon indicates that BX was also adsorbed onto the galena surface and that the presence of FCLS could not completely prevent BX from adsorbing onto the galena surface. However, the adsorption of BX onto the galena surface was weaker than its adsorption onto chalcopyrite. Therefore, when FCLS was used as the depressant, the flotation of galena could be effectively depressed, whereas chalcopyrite was floatable [15].

3.5. XPS analysis

The X-ray photoelectron spectra of the initial and reacted samples of galena and chalcopyrite are presented in Figs. 4–8 and Tables 4–7.

In Fig. 4, the binding-energy bands of Pb at 137.78 eV and 142.57 eV are the Pb $4f_{7/2}$ and Pb $4f_{5/2}$ bands, which are associated with PbS. Previous studies indicate that PbO may also be present because the $4f_{7/2}$ binding energy of PbO is very similar to that of PbS [26]. No shift in the Pb 4f spectrum was observed after the FCLS treatment. These results indicate that FCLS did not affect the chemical composition of the Pb of galena. Shchukarev *et al.* [27] and Laajalehto *et al.* [28] confirmed this concept. If the chemical state of lead is changed, the binding energy of the Pb 4f peak will be higher by approximately 0.6 eV than that of Pb 4f in galena.

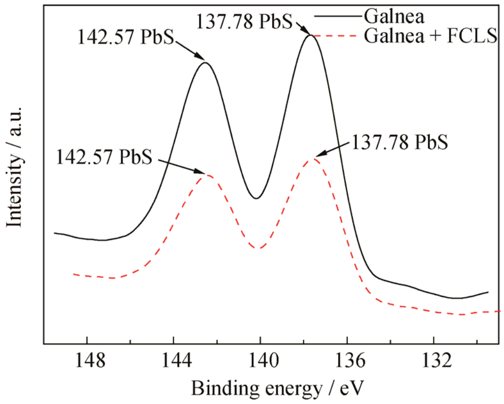

Fig. 4. Pb 4f spectrum of galena with and without FCLS treatment (FCLS dose: 100 mg·L^{-1}).

In this study, in the S 2p spectrum (Fig. 5), each component consists of two Gaussian–Lorentzian bands separated by 1.18 eV, where the intensity of the lower-binding-energy band (S $2p_{3/2}$) is twice that of the band at higher binding energy (S $2p_{1/2}$). A strange peak was observed at approximately 158.5 eV in the S 2p spectra of untreated galena [29]. These peaks were ignored during the analysis of the S 2p spectra. The S 2p spectra of untreated galena were divided into three components. The S 2p peaks at 160.70 eV and 161.88 eV were assigned to the S 2p levels of the PbS substrate (S^{2-}) [26,30]. The peaks at 163.29 eV and 164.47 eV were attributed to the formation of elemental sulfur (S^0) or polysulfide (S_n^{2-}, n > 2) [16,30–32]. The peaks at 167.10 eV and 168.28 eV were consistent with the presence of SO_3^{2-}, which indicated that the galena surface was oxidized [33–34]. After FCLS treatment, two new peaks at 168.40 eV and 169.58 eV were observed; these peaks were derived from the sulfonate ($-SO_3^-$) groups of FCLS [35–36]. These results indicate that FCLS could be adsorbed onto the galena surface.

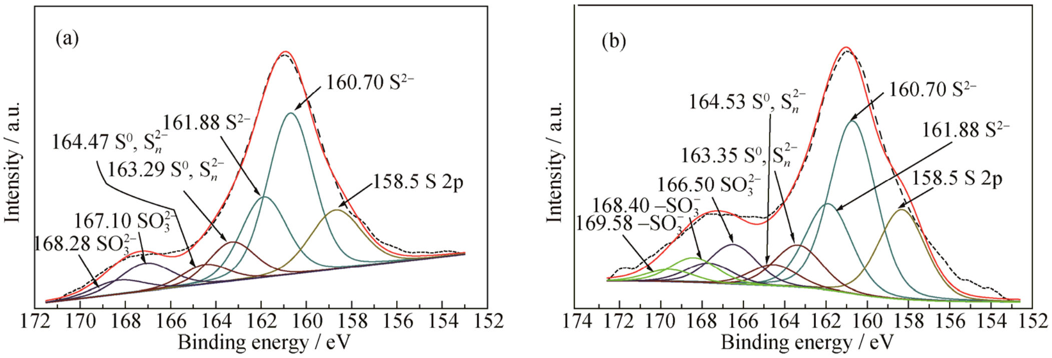

Fig. 5. S 2p spectra of untreated galena (a) and galena treated with 100 mg·L^{-1} FCLS (b).

Tables 4 and 5 show that, compared with the untreated galena, the contents of S^{2-} and S^0/S_n^{2-} with FCLS treatment decreased from 69.59% to 61.39% and from 16.94% to 15.28%, respectively, while the content of SO_3^{2-} increased from 13.47% to 14.37%, and the content of $-SO_3^-$ was 8.96%. These results indicate that FCLS was adsorbed onto the surface of galena and promoted the oxidation of galena, leading to the deterioration of the floatability of this ore.

Table 4. S 2p XPS results of untreated galena

Binding energy / eV	Species	Content / at%	Ref.
160.70/161.88[a]	S^{2-}	69.59	[26,30]
163.29/164.47[a]	S_0, S_n^{2-} ($n > 2$)	16.94	[16,30–32]
167.10/168.28[a]	SO_3^{2-}	13.47	[33–34]

Note: [a]$(S\ 2p_{3/2})/(S\ 2p_{1/2})$.

Table 5. S 2p XPS results for galena treated with 100 mg·L^{-1} FCLS

Binding energy / eV	Species	Content / at%	Ref.
160.70/161.88[a]	S^{2-}	61.39	[26,30]
163.35/164.53[a]	S_0, S_n^{2-} ($n > 2$)	15.28	[16,30–32]
166.50/167.68[a]	SO_3^{2-}	14.37	[36]
168.40/169.58[a]	$-SO_3^-$	8.96	[35–36]

Note: [a]$(S\ 2p_{3/2})/(S\ 2p_{1/2})$.

The Cu 2p spectra are shown in Fig. 6. The peaks at 932.30 eV and 932.10 eV corresponded to chalcopyrite [31–32]. No shift in the binding energy of the Cu 2p spectrum was observed after the addition of FCLS. This phenomenon indicates that the chemical form of Cu was invariable after FCLS was added. The Fe 2p spectra are shown in Fig. 7. The peak at 711.80 eV indicates that the main chemical form of Fe on the chalcopyrite surface without FCLS was Fe^{3+}, such as in $Fe_2(SO_4)_3$, $Fe(OH)_3$, FeOOH, and Fe_2O_3 [37–38]. In the presence of FCLS, the peak at 711.10 eV was attributed to Fe^{2+} in $FeSO_4$ [39]. As shown in Fig. 8, in the absence of FCLS, element S existed in three chemical forms on the surface of untreated chalcopyrite. The peaks at 161.44 eV and 162.62 eV were due to chalcopyrite (S^{2-}). The peaks at 163.35 eV and 164.53 eV were attributed to the formation of S^0 or S_n^{2-} ($n > 2$), whereas those at 168.88 eV and 170.06 eV indicated the presence of sulfate (SO_4^{2-}) [39–43]. After the samples were treated with FCLS, peaks at 168.16 eV and 169.34 eV appeared in the spectra of the chalcopyrite surface; these peaks were due to the sulfonate ($-SO_3^-$) of FCLS and the sulfate (SO_4^{2-}), and the peaks of the two species were coincident [36,44]. After FCLS was added, the content of S^{2-} increased from 49.95% to 56.63%, whereas the content of S^0/S_n^{2-} decreased slightly, from 35.93% to 33.76%. Prior to the FCLS treatment, the SO_4^{2-} content was 14.12%; the contents of SO_4^{2-} and $-SO_3^-$ groups decreased to less than 9.61% after FCLS treatment (Tables 6 and 7).

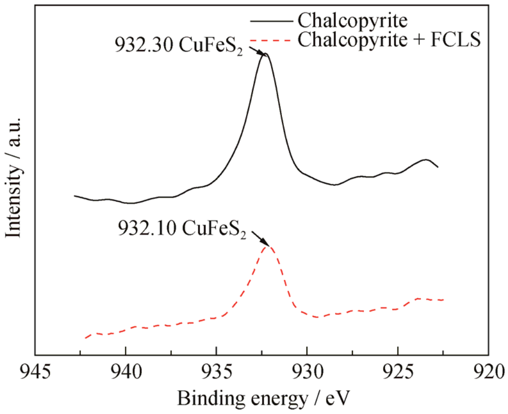

Fig. 6. Cu 2p XPS spectra of chalcopyrite (untreated sample at the top, sample treated in 100 mg·L^{-1} FCLS solution at natural pH value at the bottom).

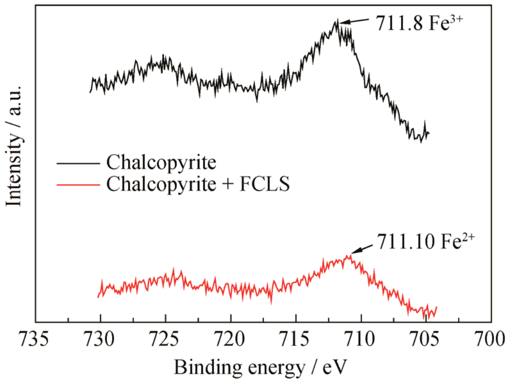

Fig. 7. Fe 2p XPS spectra of chalcopyrite (untreated sample at the top, sample treated in 100 mg·L^{-1} FCLS solution at natural pH at the bottom).

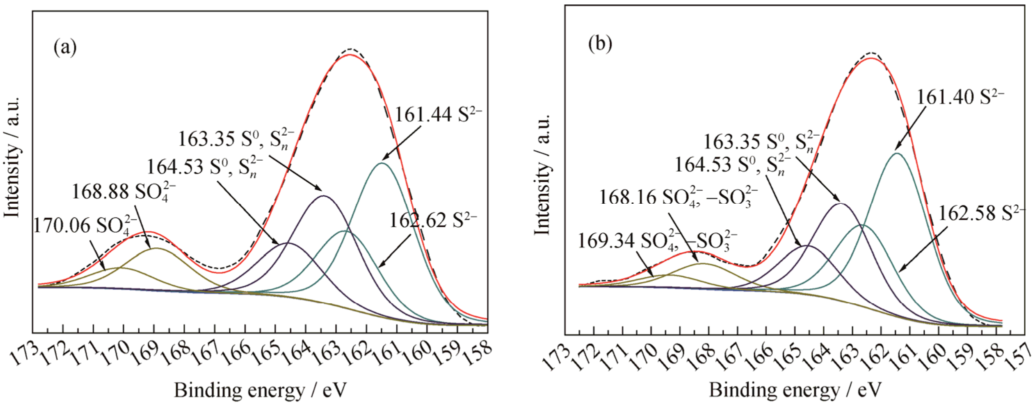

Fig. 8. S 2p XPS spectra of untreated chalcopyrite (a) and treated chalcopyrite with 100 mg·L^{-1} FCLS (b).

Table 6. S 2p XPS results of untreated chalcopyrite

Binding energy / eV	Species	Content / at%	Ref.
161.44/162.62^a	S^{2-}	49.95	[39–41]
163.35/164.53^a	S_0, S_n^{2-} ($n > 2$)	35.93	[16,30–32]
168.88/170.06^a	SO_4^{2-}	14.12	[42–43]

Note: ^{a}(S $2p_{3/2}$)/(S $2p_{1/2}$).

Table 7. S 2p XPS results of chalcopyrite treated with 100 mg·L^{-1} FCLS

Binding energy / eV	Species	Content / at%	Ref.
161.40/162.58^a	S^{2-}	56.63	[39–41]
163.35/164.53^a	S_0, S_n^{2-} ($n > 2$)	33.76	[16,30–32]
168.16/169.34^a	SO_4^{2-}, $-SO_3^-$	9.61	[36,44]

Note: ^{a}(S $2p_{3/2}$)/(S $2p_{1/2}$).

The changes in the S 2p and Fe 2p spectra imply that FCLS could be adsorbed onto the chalcopyrite surface and the oxidation rate of chalcopyrite decreased because of the coverage with FCLS. Thus, the adsorption of FCLS prevented the surface oxidation of chalcopyrite but did not prevent the oxidation of galena. Consequently, the presence of FCLS had a limited effect on the adsorption between xanthate and chalcopyrite and the FCLS slightly influenced the chalcopyrite flotation.

4. Conclusion

In this study, FCLS, which is a waste product from the paper and pulp industry, was tested as a potential selective depressant to separate chalcopyrite and galena. Flotation performances and interaction mechanisms of FCLS with chalcopyrite and galena were investigated by flotation, zeta-potential measurement, and XPS. The results of single and mixed-mineral flotation experiments indicated that FCLS was superior to $K_2Cr_2O_4$ in inhibiting galena and could effectively separate chalcopyrite and galena by flotation under weak acid and alkaline conditions. The batch flotation results indicate the feasibility of using FCLS as a selective depressant in Cu–Pb separation. The recovery of Pb in Cu concentrate decreased from 10.71% to 4.73%. The chalcopyrite/galena selectivity index using FCLS as the depressant was better than that with $K_2Cr_2O_4$ as the depressant. Zeta-potential measurements show that FCLS was more efficiently adsorbed onto the galena surface than onto the chalcopyrite surface. FCLS could not completely prevent BX from being adsorbed onto the mineral surface. XPS results further confirmed that the adsorption of FCLS strongly influenced the surface characteristics of the mineral. Thus, the adsorption of FCLS promoted the surface oxidation of galena but prevented the surface oxidation of chalcopyrite.

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