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The Auxiliary Effect of Copper Ions on the Depressant Effect of Sodium Thioglycolate in Chalcopyrite Flotation

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Abstract: Sodium thioglycolate is a chalcopyrite depressant, but its depressant effect is weak. The paper investigated the effect of CuSO₄ on the depressant performance of sodium thioglycolate towards chalcopyrite through flotation tests, Zeta potential measurements, X-ray photoelectron spectroscopy (XPS) analyses and Fourier-transform infrared (FTIR) spectra measurements. It was found that copper ions could improve the depressant effect of sodium thioglycolate on chalcopyrite. The results showed that copper ions could adsorb on the surface of chalcopyrite and form mixed copper sulfide and cupric oxides/hydroxides adsorption layers. As a result, the mineral composition on the chalcopyrite surface was changed. With sodium thioglycolate treatment, the Zeta potential and the adsorption sites of chalcopyrite surface were both increased, and the hydrophobic substance Sn²⁺/S⁰ concentration was decreased. The electrostatic repulsion of chalcopyrite surface with sodium thioglycolate was also decreased, which made the sodium thioglycolate interact with chalcopyrite more easily. The more active sites could adsorb more sodium thioglycolate, which improved the hydrophilia of chalcopyrite. At the same time, the decrease of Sn²⁺/S⁰ concentration could further improve the hydrophilia of chalcopyrite. The results show that the copper ions could exhibit auxiliary effect with sodium thioglycolate and could further enhance the depressant effect of sodium thioglycolate on the chalcopyrite flotation. This paper provides new insights into the depression of chalcopyrite flotation by sodium thioglycolate.

Keywords: flotation; chalcopyrite; sodium thioglycolate; copper ions; depressant

1. Introduction

Chalcopyrite (CuFeS₂) is the most widely distributed copper mineral in the nature, accounting for about 70% of the Earth's whole copper resources [1]. Chalcopyrite often coexists and is associated with other nonferrous metal sulfide, which brings difficulties to its utilization. The recovery of chalcopyrite is mainly realized by the flotation method. In the flotation separation operations, the main depressants of chalcopyrite used are cyanide [2], sodium sulfides [3], and thioglycolic acids [4]. The effect of cyanide depressed chalcopyrite is the best, but it is highly toxic. In addition, with the improvement of environmental protection awareness in China, cyanide will be gradually eliminated. Sodium sulfide could easily oxidize, and its concentration or dosage in flotation is too high. The depressant effect of thioglycolic acids is worse than that of the former two, but it has the advantages of less pollution, easy control, and high selectivity, giving it certain application in some flotation plants.

Thioglycolic acids, including thioglycolic acid (TGA) and sodium thioglycolate (STG), are organic depressants. The mercapto group ($-SH$) of TGA or STG reacts with copper, and then TGA or STG adsorbs onto the mineral surface [4]. The carboxyl group ($-COOH$) is hydrophilic and could form hydrophilic membrane layer, which could enhance hydrophilic property of the mineral and prevent collector adsorption on the mineral surface. It is generally accepted that the effect of flotation reagent can be changed by metal ions [5–11]. Copper sulphate, as an activator, has been used in industrial flotation for a long time, and is mainly used for the flotation of nonferrous sulfide [5]. It has been proved that adding $CuSO_4$ can significantly improve the recovery of valuable minerals, especially sphalerite. Inactivated sphalerite interacts weakly with xanthate collectors. When copper sulfate activates sphalerite, the Cu ion is exchanged with the Zn ion of sphalerite, which forms the surface of copper sulfide and enhances the adsorption of collector [6]. Unlike sphalerite, inactivated pyrite responds well to xanthate collector, and the copper sulphate activation of pyrite follows a different mechanism from that of sphalerite. The mechanism is not an ion exchange activation mechanism, but the adsorption of copper on the active sulfur site on only the surface [7]. Sodium sulfide is used as a depressant, and the addition of Cu^{2+} can obviously promote the effect of depressing chalcopyrite. $CuOH^+$ and $Cu(OH)_2$ are adsorbed on the mineral surface after the hydrolysis of Cu^{2+} and provide more reactive sites for the depressant [8]. Also, the interaction between butyl xanthate and the surface of unactivated stibnite is weak, and the flotation effect is poor. Pb^{2+} can be adsorbed on the stibnite surface, and the lead atoms on the surface of stibnite can interact with butyl xanthate further. The adsorption energy of butyl xanthate on the surface of lead activation is much lower than that on the surface of nonactivation [9]. This indicates that metal ions, especially copper ions, can change the surface properties of sulphide minerals, and then affect the amounts of active adsorption sites with flotation reagents and the flotation effect. However, there is little research showing that copper ions can enhance the depressant effect of sodium thioglycolate on chalcopyrite.

In this study, the mechanism of copper ions strengthening the sodium thioglycolate's depressing chalcopyrite effect was studied by micro-flotation tests, Zeta potential measurements, X-ray photoelectron spectroscopy (XPS) measurements, and Fourier transform infrared (FTIR) spectra measurements.

2. Materials and Methods

2.1. Mineral Samples and Reagents

The chalcopyrite sample was obtained from Guangxi, China. The pure chalcopyrite sample was handpicked and further crushed and dry-sieved to -2 mm through a jaw crusher and a laboratory roll crusher in turn. The -2 -mm-size fractions were stored for subsequent grinding, flotation, Zeta potential measurements, XPS measurements, and FTIR study. The purity of the chalcopyrite sample was 96.15% according to its X-ray diffraction results (see Figure 1) and chemical analysis (see Table 1).

The butyl xanthate (BX) and pine oil used in this research were purchased from Zhuzhou Flotation Reagents Factory, Zhuzhou, China and were both industrial grade. They were used as the collector and frother, respectively. Copper sulfate ($CuSO_4$) was bought from Tianjing Kermil Chemical Reagents Development Centre, Tianjin, China, and was analytical reagent (AR) grade. $CuSO_4$ was used as flotation modifier. Sodium thioglycolate (STG), sulphuric acid (H_2SO_4), and sodium hydroxide (NaOH) were all obtained from Aladdin Industrial Corporation, Shanghai, China, and were all AR grade. Sodium thioglycolate is a kind of white powder. It easily dissolves in water and is used as depressant. Sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) were used as pH regulators.

Table 1. Chemical composition of the chalcopyrite sample used in this research.

Chemical Composition	Cu	Fe	S	Other
Content (%)	33.23	29.34	33.58	3.85

Figure 1. XRD spectra of the chalcopyrite sample.

2.2. Micro-Flotation Tests

Before micro-flotation tests, the stored -2 -mm-size chalcopyrite sample were ground to $-74\ \mu\text{m}$ for each micro-flotation tests using an agate planetary ball mill (XDQM-2L, Lianyungang Chunlong Experimental Instrument Co., Ltd., Lianyungang, China).

Micro-flotation tests of chalcopyrite sample were carried out in a plexiglass flotation cell with a volume of 50 mL in air conditioning by an inflatable hanging slot flotation machine (XFGCII 5–35 g, Jilin Prospecting Machinery Factory, Changchun, China). First, 2 g of the chalcopyrite sample was mixed with 45 mL of distilled water in the flotation cell. The pH regulator, copper sulfate (if needed), depressant (if needed), collector, and frother were added into the flotation cell in sequence and conditioned for 3 min for each reagent. Then, the flotation began, and the flotation time was 3 min. After flotation, the flotation concentrates and tailings were filtered, dried, and weighted, and recoveries were calculated.

2.3. Zeta Potential Measurements

Before each measurement, the stored -2 -mm-size chalcopyrite sample were ground to $-2\ \mu\text{m}$ for each Zeta potential measurement using an agate planetary ball mill.

The Zeta potentials of chalcopyrite samples were measured using a Zeta Potential Analyzer (Delsa 440sx, Beckman Coulter, Inc., Fullerton, CA, USA). For each Zeta potential measurement, 0.03 g of the chalcopyrite sample was mixed with 30 mL of 1-mmol KNO_3 solution in a 50-mL beaker and, the desired concentrations of the flotation reagents were added. The concentration of copper sulfate was 1×10^{-3} mol/L and sodium thioglycolate was 1.5×10^{-3} mol/L, respectively. The pH of mineral suspension was adjusted by adding of either 10 M of NaOH or H_2SO_4 , and the pH range was 8–12 in the studies. After stirring for 15 min using a magnetic stirrer and standing of 10 min, the fine mineral particles were sucked into electrophoresis cell for measurement from the top of the resultant suspension. Each sample was conducted at least three times measurement independently, with a typical variation of ± 5 mV. The average value was taken as the final result.

2.4. XPS Measurements

Before each measurement, the stored -2 -mm-size chalcopyrite sample were ground to $-74\ \mu\text{m}$ for each XPS measurement using an agate planetary ball mill.

For each XPS measurement, 2 g of the chalcopyrite sample was mixed with 45 mL of distilled water in a 50-mL beaker, and desired concentrations of the flotation reagents were added. The concentration of copper sulfate was 1×10^{-3} mol/L and sodium thioglycolate was 1.5×10^{-3} mol/L, respectively.

The pH of mineral suspension was adjusted by adding of either 10 M of NaOH or H₂SO₄. After stirring for 15 min using a magnetic stirrer, the pulp was filtrated and stored for XPS analysis.

The XPS spectra analysis of chalcopyrite before and after treatment with flotation reagents were recorded on a Perkin-Elmer Physical Electronics Division (PHI) 5100 spectrometer (Thermo Scientific ESCALAB, Thermo Fisher Scientific, Waltham, MA, USA) using K α X-ray source at 200 W and pass energy of 75 eV. The samples were first measured in survey mode, and then the high-resolution of C 1s, Cu 2p, and S 2p were scanned. The XPS spectra were analyzed and fitted by the Thermo Advantage software. The C 1s binding energy at 284.8 eV were selected as a standard to calibrate the binding energy.

2.5. FTIR Spectra Measurements

Before each measurement, the stored –2-mm-size chalcopyrite sample was ground to –74 μ m for each FTIR spectrum measurement using an agate planetary ball mill.

For each FTIR spectrum measurement, 2 g of the chalcopyrite sample was mixed with 45 mL of distilled water in a 50-mL beaker, and desired concentrations of the flotation reagents were added. The concentration of copper sulfate was 1×10^{-3} mol/L and sodium thioglycolate was 1.5×10^{-3} mol/L, respectively. The pH of mineral suspension was adjusted by adding of either 10 M of NaOH or H₂SO₄. After stirring for 15 min using a magnetic stirrer, the pulp was filtrated and rinsed two or three times using the corresponding pH stock solutions. The samples were stored in a vacuum desiccator at room temperature for FTIR spectra analysis.

The FTIR spectra analysis of chalcopyrite before and after treatment with flotation reagents were recorded on an Fourier Transform Infrared Spectrometer (IRAffinity-1, shimadzu, Kyoto, Japan) by potassium bromide (KBr) reflection method. The spectra were recorded at a 2 cm^{–1} resolution in the 4000–400 cm^{–1} region.

3. Results

3.1. Micro-Flotation Results

The effect of STG on the chalcopyrite flotation was studied, and then the auxiliary actions of the copper ions on the depressant effect of STG on the chalcopyrite flotation were investigated. The results are shown in Figures 2–4, respectively.

Figure 2. The flotation recovery of chalcopyrite under different sodium thioglycolate (STG) concentrations; $c(\text{BX}) = 1 \times 10^{-3}$ mol/L, pH = 10.

As shown in Figure 2, the floatability of chalcopyrite decreased as the STG dosage increased. When the STG dosage increased from 0 mol/L to 2.0×10^{-3} mol/L, the chalcopyrite recovery decreased from 92% to around 45%. The decreased recovery indicates that the STG exhibited some depressant effect on the chalcopyrite flotation. However, the inhibition of chalcopyrite using STG alone was not efficient, as shown by the stable existed recovery value ($>40\%$) when STG concentration continued to rise.

Figure 3. The flotation recovery of chalcopyrite under different Cu^{2+} concentrations; $c(\text{STG}) = 1.5 \times 10^{-3}$ mol/L, $c(\text{BX}) = 1 \times 10^{-3}$ mol/L, $\text{pH} = 10$.

Figure 3 shows the depressant effect of copper ions on the chalcopyrite flotation in the presence and absence of STG. In the absence of STG, the chalcopyrite flotation was merely influenced as copper ions dosage increased, indicating that the copper ions had no effect on the chalcopyrite flotation. In the presence of STG, the chalcopyrite recovery witnessed a big decrease (from 44% to around 22%) when the copper ions dosage increased from 0 mol/L to 1.4×10^{-3} mol/L. The decreased recovery indicates that the copper ions exhibited an auxiliary depressant effect on the chalcopyrite flotation with STG and that the inhibition was quite efficient.

Figure 4. The flotation recovery of chalcopyrite under different pH values; $c(\text{Cu}^{2+}) = 1 \times 10^{-3}$ mol/L, $c(\text{STG}) = 1.5 \times 10^{-3}$ mol/L, $c(\text{BX}) = 1 \times 10^{-3}$ mol/L.

Figure 4 shows the flotation performance of chalcopyrite under different reagent schemes. It was first noted that chalcopyrite was well floated using collector BX (or using BX and a copper ions scheme)

in the whole pH range tested. The flotation recovery with both reagent schemes remained nearly unchanged and above 90%. With treatment of 1.5×10^{-3} mol/L STG + 1×10^{-3} mol/L BX scheme, the chalcopyrite recovery was decreased to 40–50% in the pH range of 8–12. However, with the treatment of 1×10^{-3} mol/L Cu^{2+} + 1.5×10^{-3} mol/L STG + 1×10^{-3} mol/L BX scheme, the chalcopyrite flotation was well depressed in the pH range of 8–10, indicating that the Cu^{2+} exhibited auxiliary effect on the depressant effect of STG on the chalcopyrite flotation.

To define the auxiliary depressant effect of Cu^{2+} and STG on chalcopyrite flotation, the surface property analysis including surface potential, XPS, and FTIR of chalcopyrite particles with similar flotation reagent scheme treatment was conducted.

3.2. Zeta Potential Measurement Results

In this study, the Zeta potentials of chalcopyrite with different reagent treatment were used to evaluate the relative adsorption strength of certain reagents. The Zeta potentials of chalcopyrite particles under corresponding flotation conditions as studied in Section 3.1 were measured, and the results are shown in Figure 5.

For bare chalcopyrite, the Zeta potential was negatively charged in the whole pH range studied. As pH increased, the Zeta potential of chalcopyrite decreased from -14.65 mV (pH 8.0) to -34.63 mV (pH 12.0). With copper ion treatment, the Zeta potential of chalcopyrite increased in the whole pH range studied. The rise of the Zeta potential showed that copper ions adsorbed on the chalcopyrite surface and changed character of chalcopyrite surface. Meanwhile, the electrostatic repulsion of chalcopyrite surface with STG was decreased, which made the STG interact with chalcopyrite easier.

With the STG treatment, the Zeta potential of chalcopyrite decreased in the whole pH range studied. The fall of the Zeta potential shows that STG can chemically adsorb on the chalcopyrite surface. Compared with the copper ion treatment, with the copper ion and STG treatment, the Zeta potential of chalcopyrite decreased again. Compared with the Zeta potential of chalcopyrite in the presence and absence of STG, the Zeta potential decreased by around 4.0 mV (pH 8.0), 4.0 mV (pH 9.0), 3.0 mV (pH 10.0), 1.3 mV (pH 11.0), and -1.6 mV (pH 12.0). Compared with the Zeta potential of copper-treated chalcopyrite in the presence and absence of STG, the Zeta potential decreased by around 5.5 mV (pH 8.0), 7.3 mV (pH 9.0), 6.5 mV (pH 10.0), 5.0 mV (pH 11.0), and 0.5 mV (pH 12.0). The decrease of Zeta potential was further expanded with copper ions treatment and became smaller as the pH increased over 10, indicating that copper-treated chalcopyrite surface adsorbed more STG and improved the depressant effect at pH 8–10.

Figure 5. The Zeta potential of chalcopyrite under different pH values; $c(\text{Cu}^{2+}) = 1 \times 10^{-3}$ mol/L, $c(\text{STG}) = 1.5 \times 10^{-3}$ mol/L, $c(\text{BX}) = 1 \times 10^{-3}$ mol/L.

3.3. X-Ray Photoelectron Spectroscopy (XPS) Results

In order to explain the phenomenon that copper ions could enhance the depressant effect of STG on chalcopyrite, the X-ray photoelectron spectroscopy of chalcopyrite samples with and without the treatment of corresponding flotation reagents schemes was measured. The results are shown in Tables 2 and 3 and Figures 6 and 7, respectively.

Figure 6 shows the S 2p spectra of the chalcopyrite with treatment of different flotation reagents. The XPS bands at 161.2–161.4 eV were attributed to surface monosulfide S^{2-} [6,12–15]. The XPS bands at 162.4–162.8 eV were attributed to the disulfide species S_2^{2-} by the oxidation process of S^{2-} on the chalcopyrite surface [6,12–15], and the XPS bands at 163.3–164.0 eV were the results of the polysulfide and elemental sulfur S_n^{2-}/S^0 that were formed in the oxidation operations [6,12–15]. With the copper ion treatment (see Figure 6b), it can be seen that a new S 2p3/2 peak appeared at 168.83 eV, which is mostly attributed to the adsorption of the SO_4^{2-} on the chalcopyrite surface [14,16]. The S_n^{2-}/S^0 concentration decreased largely from 22.08% to 11.96%, indicating that the added $CuSO_4$ had successfully prevented the formation of S_n^{2-}/S^0 . At the same time, the S^{2-} concentration also decreased from 63.52% to 47.68%, showing that the hydrophobicity of the chalcopyrite was also largely influenced. The above decreases strongly prove that the mineral composition on the surface of chalcopyrite changed with the $CuSO_4$ treatment. Figure 6c shows the XPS band of the chalcopyrite with the treatment of STG. It can be seen that a new band appeared at 162.03 eV [17], suggesting that the STG adsorbed on the particle surface, mainly through the C–SCu bond. However, with the $CuSO_4$ and STG treatment, the concentrations of the sulfur species and C–SCu bond concentration significantly increased from 18.49% to 39.36%, as shown in Figure 6d. The results indicate that the added copper ions exhibited an auxiliary effect with STG on the chalcopyrite flotation.

Figure 6. S 2p XPS spectra of chalcopyrite (a), chalcopyrite + $CuSO_4$ (b), chalcopyrite + STG (c) and chalcopyrite + $CuSO_4$ + STG (d); $c(CuSO_4) = 1 \times 10^{-3}$ mol/L, $c(STG) = 1.5 \times 10^{-3}$ mol/L.

Table 2. The parameters and assignment of high-resolution S 2p XPS spectra.

Species	Binding Energy/eV	FWHM/eV	Percentage/%	Assignment
Chalcopyrite	161.27/162.37	0.88	63.52	S ²⁻
	162.75/163.85	1.1	14.39	S ₂ ²⁻
	163.34/164.44	1.68	22.08	S _n ²⁻ /S ⁰
Chalcopyrite + Cu	161.35/162.45	0.98	47.68	S ²⁻
	162.58/163.68	1.46	33.00	S ₂ ²⁻
	163.92/165.22	1.25	11.98	S _n ²⁻ /S ⁰
	168.83/169.93	1.65	7.36	SO ₄ ²⁻
Chalcopyrite + STG	161.21/162.49	0.86	55.63	S ²⁻
	162.03/163.13	0.82	18.49	C-SCu
	162.40/163.70	1.17	9.27	S ₂ ²⁻
	163.69/164.79	1.07	16.62	S _n ²⁻ /S ⁰
Chalcopyrite + Cu + STG	161.24/162.34	0.83	30.70	S ²⁻
	161.88/162.98	1.25	39.36	C-SCu
	162.64/163.91	1.41	17.14	S ₂ ²⁻
	163.32/164.62	0.90	5.35	S _n ²⁻ /S ⁰
	168.44/169.74	1.51	4.47	SO ₄ ²⁻

It should be noted that with the CuSO₄ and STG treatment, the band of the C–SCu bond also witnessed a significant shift from 162.03 eV to 161.88 eV, implying that the CuSO₄ could interact with the STG on the chalcopyrite surface. Under this reagent condition, the SO₄²⁻ concentration on the chalcopyrite decreased from 7.36% to 4.47%, which agrees well with the above auxiliary effect. The addition of the CuSO₄ induced a certain drop in the S_n²⁻/S⁰ concentration (from 16.62% to 5.94%) on the chalcopyrite surface and resulted in the auxiliary depressant effect of the STG [15].

Figure 7 shows the Cu 2p_{3/2} XPS spectra of the chalcopyrite with treatment of different flotation reagents. The XPS bands at 932.05 eV was attributed to cuprous [15,16,18]. The XPS bands at 933.26 eV were attributed to copper sulfide Cu-S [15,16,18] by the oxidation process of cuprous on the chalcopyrite surface. It can be seen that the copper species included chalcopyrite and copper sulfide on the chalcopyrite surface, and the copper on the chalcopyrite surface only was monovalent.

With copper ion treatment (see Figure 7b), copper species and their proportion on the chalcopyrite sample surface were changed. It can be seen that a new Cu 2p_{3/2} peak appeared at 934.40 eV due to the cupric oxides/hydroxides [19,20]. The copper concentration in chalcopyrite decreased largely from 65.30% to 3.36%, indicating that a large quantity of copper ions were adsorbed on the chalcopyrite sample surface. At the same time, the copper concentration in copper sulfide increased largely from 34.70% to 51.66% on the chalcopyrite sample surface, indicating that the added CuSO₄ successfully changed allocation proportion of copper species. In the pulp, iron first dissolved on the chalcopyrite surface [21–23], which is consistent with previous reports. Therefore, some surface defects were formed on the surface of chalcopyrite. After adding CuSO₄, a part of copper ions could fill these surface defects and finally form copper sulfide or cupric oxides/hydroxides.

Figure 7c shows the XPS band of the chalcopyrite with the treatment of STG. It can be seen that a new Cu 2p_{3/2} peak appeared at 932.49 eV, suggesting that the STG had chemically adsorbed on the chalcopyrite sample surface, mainly through the Cu-STG complex [24,25]. The copper concentration in chalcopyrite decreased from 65.30% to 52.04%, while the copper concentration in copper sulfide decreased largely from 34.70% to 16.62% on the chalcopyrite sample surface, indicating that STG was more easily adsorbed on copper sulfide. However, with the CuSO₄ + STG treatment (see Figure 7d), the Cu-STG complex concentration significantly increased from 31.34% to 68.15%, indicating that the addition of copper ions could contribute to the adsorption of STG. and the depression of chalcopyrite was realized by the hydrophilic group (–COO⁻) in the STG. At the same time, the Cu²⁺-O/OH concentration decreased from 44.98% to 15.26%. The above results strongly prove that the addition of copper ions increased the reaction sites on the surface of chalcopyrite and exhibited an auxiliary effect with STG on the chalcopyrite inhibition.

Figure 7. Cu 2p XPS spectra of chalcopyrite (a), chalcopyrite + CuSO₄ (b), chalcopyrite + STG (c) and chalcopyrite + CuSO₄ + STG (d); (c(CuSO₄) = 1 × 10^{−3} mol/L, c(STG) = 1.5 × 10^{−3} mol/L).

Table 3. The parameters and assignment of high-resolution Cu 2p_{3/2} XPS spectra.

Species	Binding Energy/eV	FWHM/eV	Percentage/%	Assignment
Chalcopyrite	932.05	1.27	65.30	CuFeS ₂
	933.26	3.17	34.70	CuS,
Chalcopyrite + Cu	932.06	0.79	3.36	CuFeS ₂
	933.24	1.23	51.66	CuS,
	934.40	2.16	44.98	Cu ²⁺ -O/OH
Chalcopyrite + STG	931.94	1.05	52.04	CuFeS ₂
	932.49	1.28	31.34	Cu-STG
	933.78	2.10	16.62	CuS
Chalcopyrite + Cu + STG	932.44	1.21	68.15	Cu-STG
	933.30	1.10	16.60	CuS,
	934.22	1.37	15.26	Cu ²⁺ -O/OH

3.4. FTIR Studies

The FTIR spectra of chalcopyrite with and without CuSO₄ and STG treatment were presented in Figure 8. The functional groups of STG are shown in Figure 8e. The two bands with peaks at around 1593 cm^{−1} and 1416 cm^{−1} represent the antisymmetric ($\nu_{as}(\text{COO}^-)$) [4,26,27] and symmetric ($\nu_s(\text{COO}^-)$) [4,26,27] stretching bands of carboxyl groups of STG, respectively. The bands at around 658 cm^{−1} [28] and 2554 cm^{−1} [29] were due to the C–S and S–H stretching vibration, respectively.

With the STG and CuSO₄ + STG treatment, several peaks appeared on the surface of chalcopyrite, as shown in Figure 8f, e. The band at around 668 cm^{−1} was due to the C–S stretching vibration.

The bands at around 1635 cm^{-1} and 1385 cm^{-1} represent the antisymmetric ($\nu_{\text{as}}(\text{COO}^-)$) and symmetric ($\nu_{\text{s}}(\text{COO}^-)$) stretching bands, respectively. Meanwhile, the S–H stretching vibration peak vanished, while C–S stretching vibration peak was still presented. These changes in the FTIR spectra indicate that STG was successfully chemical adsorbed on chalcopyrite surfaces.

Figure 8d shows the FTIR difference spectrum of Figure 8f,e. The characteristic peaks of C–S and COO^- were both still presented, indicating the adsorption quantity of STG increased after the CuSO_4 treatment. Therefore, more hydrophilic groups covered the chalcopyrite surface and increased the depressant effect on the chalcopyrite flotation with STG.

The results described above show that it is obvious that copper ions can be adsorbed on the chalcopyrite surface, which resulted in significant changes in the type and proportion of copper and increased the reaction sites of the chalcopyrite surface. With copper ion treatment, the copper concentration in chalcopyrite decreased largely, while the copper concentration in copper sulfide increased largely on the chalcopyrite sample surface. In addition, the adsorption capacity of STG on copper sulfide was stronger than that on chalcopyrite which caused more STG to adsorb on the chalcopyrite sample surface. At the same time, the decrease of $\text{Sn}^{2-}/\text{S}^0$ concentration further improved the hydrophilia of chalcopyrite, and the increase of the Zeta potential made the electrostatic repulsion of chalcopyrite surface with STG decrease, which made STG interact with chalcopyrite easier.

Figure 8. The FTIR spectra of chalcopyrite (a), chalcopyrite + CuSO_4 (b), STG (c), difference spectrum (d), chalcopyrite + STG (e), and chalcopyrite + CuSO_4 + STG (f); $c(\text{CuSO}_4) = 1 \times 10^{-3}\text{ mol/L}$, $c(\text{STG}) = 1.5 \times 10^{-3}\text{ mol/L}$.

4. Conclusions

In this paper, STG was introduced as a depressant on chalcopyrite flotation. The copper ions were proved to exhibit an auxiliary effect on the depressant effect of STG when xanthate was used as a collector. Copper ions can adsorb on the surface of chalcopyrite and increase the reaction sites on the surface of chalcopyrite. These increased active sites could allow the absorption of more sodium thiolglycolate on the particle surface and could result in the enhancement of chalcopyrite depression.

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