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Application of Maleic Acid–Acrylic Acid Copolymer as an Eco-Friendly Depressant for Effective Flotation Separation of Chalcopyrite and Galena

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Abstract: Environmentally achieving the flotation separation of chalcopyrite and galena is always a difficult problem due to the similar floatability of the two minerals. To conquer the problem, maleic acid–acrylic acid copolymer (MA/AA), an eco-friendly reagent, was applied as a potential depressant for flotation separation of chalcopyrite from galena for the first time. Single-mineral flotation tests exhibit that MA/AA has a much better depression ability and selectivity than those of traditional galena depressants (Na_2S and $K_2Cr_2O_7$), which can inhibit the floatability of galena well but barely affects the flotation behavior of chalcopyrite in a wide pH range (7–11). A satisfying flotation separation effect of artificially mixed galena and chalcopyrite was realized by using MA/AA as a depressant. Based on a series of measurements including zeta potential, XPS, and contact angle, it appears that MA/AA was much more inclined to be chemically adsorbed on the surface of galena than that of chalcopyrite, which restrains the further adsorption of collectors on galena. In contrast, for chalcopyrite, the low adsorption of MA/AA hardly affects the further adsorption of collectors. According to these findings, MA/AA is considered to be potentially applicable as an effective and eco-friendly depressant in the industrial flotation separation of chalcopyrite and galena.

Keywords: chalcopyrite; galena; flotation; depressant; mineral separation

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1. Introduction

Copper is an important metal element that can be widely applied in communication technology, military industry, electronic manufacturing, aerospace technology, and other fields [1,2]. In metallurgical industry, chalcopyrite is one of the most important copper-bearing minerals for extraction of Cu metal. In natural ore deposits, chalcopyrite has a closely paragenic relationship with other sulfide minerals, among which galena is a very common example [3,4]. In Cu-Pb sulfide ores, chalcopyrite and galena co-exist as a densely packed mixture [5]. At present, a significant portion of chalcopyrite mineral products are derived from this kind of sulfide ore [6].

As a typical sulfide mineral, froth flotation is the most applied method for the beneficiation of chalcopyrite from ore deposits due to its prominent advantage of high efficiency and economy [7]. In the flotation process, xanthate (e.g., butyl xanthate and ethyl xanthate) is commonly applied as the collector, which can be absorbed on the surface of chalcopyrite to enhance its floatability [8]. However, the separation of chalcopyrite and galena has always been a difficult problem due to the analogical floatability and collector adsorption ability of the two minerals [9,10]. Thus, correspondingly, the separation effect of Cu-Pb is commonly considered one of the most important indexes in the industrial flotation recovery of chalcopyrite [11,12].

In the flotation process, the addition of a depressant is indispensable to realizing the separation of chalcopyrite and galena. For a long time, potassium dichromate ($K_2Cr_2O_7$) was the most widely used depressant to selectively decrease the floatability of galena by forming a lead chromate layer on its surface [13]. However, this depressant is highly poisonous, and its use would result in huge environmental pressure due to the release of chromium ions, which limits its further application at present [1,14]. Sodium sulfide (Na_2S) is extensively applied as a nontoxic depressant for galena via generating a hydrophilic film on its surface. Nevertheless, when using Na_2S as depressant, it is often difficult to obtain a satisfactory separation effect, a problem attributed to the poor selectivity and high dosage of Na_2S. Apart from the two traditional depressants, in recent years, natural polymers depressants, e.g., dextrin, fenugreek gum, and locust bean gum, have also been researched as selective depressants for galena. This kind of depressant is rich in carboxy groups (-COO-), which can be absorbed on the surface of galena through hydrogen bonding. However, natural polymers have the prominent defects of poor solubility, low depression performance, and large consumption, which limits their further application [3,9,15,16]. Even so, it is still noteworthy work to research eco-friendly depressants that contain abundant carboxy groups. Moreover, according to recent literature [17,18], 3-mercaptopropionic acid and sodium 2,3-dihydroxypropyl dithiocarbonate can be synthesized in the laboratory for use as depressants. Nevertheless, the preparation costs of the depressants are too high for industrial applications. Thus, further exploration of comprehensive depressants that have strong depression ability, environmental friendliness, and economic feasibility is necessary to improve the flotation separation of chalcopyrite and galena. In addition, the flotation indexes and prices of several depressants in chalcopyrite and galena flotation systems are listed in Table 1 (indicating that prices will fluctuate).

Table 1. Flotation indexes of several depressants in chalcopyrite and galena flotation systems.

Flotation Method	Depressant (Dosage)	Product	Yield (%)	Cu Grade (%)	Cu Recovery (%)	Price (RMB/ton)
Positive flotation	Maleic acid–acrylic acid copolymer (30 mg/L)	Concentrates Tailings Feed	50.56 49.44 100	29.89 2.83 16.51	91.53 8.47 100.00	7500.00
	Dextrin (2500 g/t) [19]	Concentrates Tailings Feed	13.00 87.00 100.00	12.20 0.34 1.93	84.80 15.20 100.00	28,000.00
	Fenugreek gum (4 mg/L) [20]	Concentrates Tailings Feed	53.89 46.11 100.00	29.95 1.34 16.76	96.32 3.68 100.00	55,000.00
	Locust bean gum (5 mg/L) [5]	Concentrates Tailings Feed	45.37 54.63 100.00	29.68 4.31 15.82	85.12 14.88 100.00	80,000.00
	Sodium 2,3-dihydroxypropyl dithiocarbonate (1.9g/L) [18]	Concentrates Tailings Feed	- - -	29.52 - -	82.15 17.85 100.00	-
Reverse flotation	3-mercaptopropionic acid (5E-4 mol/L) [17]	Concentrates Tailings Feed	56.07 43.93 100.00	6.22 27.47 15.56	22.42 77.58 100.00	62,500.00
	Thioglycolic acid (5E-4 mol/L) [17]	Concentrates Tailings Feed	68.43 31.57 100.00	12.12 22.95 15.54	53.37 46.63 100.00	30,000.00

Maleic acid–acrylic acid copolymer (MA/AA) is an eco-friendly and biodegradable reagent that combines maleic acid and acrylic acid in a certain proportion. The molecular structure of MA/AA is presented in Figure 1. It not only possesses excellent water solubility but also has strong chelating properties for polyvalent metal ions due to its abundant carboxyl functional groups. Owing to these special properties, in industry, MA/AA is commonly applied as a scale inhibitor and remover of heavy metal ions (e.g., Pb^{2+}, and Zn^{2+} ions) in treating wastewater and soil remediation, respectively [21,22]. In the flotation area, MA/AA can also be applied as a depressant for the separation of apatite and dolomite due to its excellent chelation ability toward Ca^{2+}, as reported by Yang et al. [23]. Since MA/AA has strong chelating properties for polyvalent metal ions, MA/AA potentially can be applied as an efficient depressant for the separation of galena and chalcopyrite. However, to date, little research has been done on this.

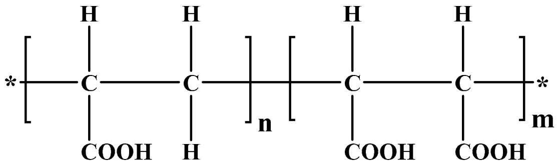

Figure 1. The schematic of molecular structure of MA/AA.

Based on the above summary, for the first time, MA/AA was employed as a depressant to realize the flotation separation of chalcopyrite and galena in this research. As expected, MA/AA was an excellent depressant with high selectivity and depression ability, by which the separation of chalcopyrite and galena can be effectively achieved. Under laboratory conditions, a high-quality product with a Cu grade of 29.89% and recovery of 91.53% was obtained by using MA/AA as a depressant. Furthermore, various measurements including contact angle, zeta potential, and X-ray photoelectron spectroscopy (XPS) were carried out to acquire a detailed comprehension of the interaction between reagents and minerals.

2. Experimental

2.1. Materials and Reagents

Both chalcopyrite and galena mineral samples were commercially acquired from Hunan Province in China. The block mineral samples were successively crushed with corundum, hand-sorted, and ground by a three-head grinder into powders. The particle sizes fraction of $-74+38$ μm was collected to be used for the flotation test. X-ray diffraction analyses were carried out to verify the purity of the as-prepared minerals, and the results are shown in Figure 2. Clearly, it can be concluded from the results that the as-prepared chalcopyrite and galena mineral samples are of high purity.

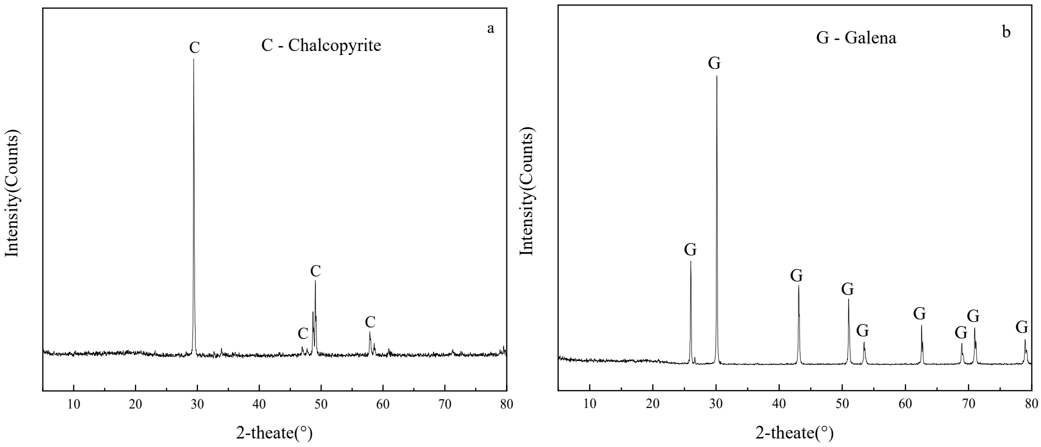

Figure 2. XRD patterns of the as-prepared mineral samples: (**a**) Chalcopyrite; (**b**) Galena.

MA/AA solution (content: 48%, RMB 7500/t) and MIBC (purity: 99%) purchased from Macklin Biochemical Co., Ltd., Shanghai, China, were used as depressant and frother, respectively. $K_2Cr_2O_7$ (analytically pure, RMB 20,000/t) and Na_2S (analytically pure, RMB 6000/t) purchased from Xilong Scientific Co., Ltd., Shantou, China, were used as contrast depressants. Sodium butyl xanthate (SBX, industrially pure) purchased from Xinyuan Chemical Additives Co., Ltd., Qingdao, China, was a collector. Deionized water was used in the entire test and measurements.

2.2. Micro-Flotation Tests

All the micro-flotation tests of pure minerals were performed on a hanging-type flotation machine (XFGII$_5$, Jilin Exploration Machinery Factory) equipped with a cell (volume: 40 mL), whose impeller speed was fixed at 1900 r/min during the whole flotation process. For the micro-flotation of a single mineral, 2 g of mineral sample and 35 mL deionized water were added into the cell to form a uniform pulp. The pH value of the pulp was adjusted to the desired value by the addition of HCl and NaOH solution (0.1 mol/L). After 5 min agitation, the specified dosages of depressant, collector (SBX), and frother (MIBC) were successively added to the pulp at a regular interval of 3 min. After stirring for 1 min, inflated flotation was carried out, and the floated froth product was collected manually for 3 min. The froth product and tailings were successively filtered, dried, and weighed. The recovery rate can be calculated based on the weight distributions between froth products and tailings. For the micro-flotation of mixed binary minerals, chalcopyrite and galena were mixed at a mass ratio of 1:1. The flotation operation was the same as a single-mineral flotation test. At the end of the flotation, the foam product was chemically determined for Cu and Pb. The Cu and Pb recovery of the foam product was calculated by Cu and Pb grade of foam product and feed.

All the flotation tests were repeated 3 times to take the average as a final value, and error bars represent one standard deviation around the average value.

2.3. Contact Angle Measurements

The wettability of the mineral surface was closely related to the floatability of minerals [24]. The contact angles were carried out on Droplet Shape Analyzer-DSA 100 Contact Angle analyzer (Kruess Scientific Instruments Co., Ltd., Shanghai, China). Before measurement, large samples of pure chalcopyrite and galena mineral were selected to be polished with 1000-mesh sandpaper and then cast into a smooth surface in 3μm medium with the Tegramin-25 polishing machine. The above-mentioned polished mineral samples were cleaned with deionized water under ultrasound and then pretreated with SBX and MA/AA. Finally, the sample was dried under nitrogen conditions. The measurements were repeated three times for each condition, and the results reported in this study are averages.

2.4. Zeta Potential Measurements

The ZetaProbe zeta potential analyzer (Colloidal Dynamics LLC, NY, USA) was used to measure the zeta potential of chalcopyrite and galena after treatment with different agents. For the zeta potential measurements, the mineral samples were ground to $-$ 2 μm in an agate mortar. 40 mg of the above mineral samples were taken and dispersed in 40 mL electrolyte solution (1×10^{-3} mol/L KNO_3 solution) and magnetically stirred for 15 min to form a suspension in a beaker. HCl and NaOH solution was then added to adjust the pH value in the suspension. According to the micro-flotation test, MA/AA depressant and SBX collector were added to the suspension. During the measurement process, HCl or NaOH solution (0.1 mol/L) was added in the suspension to maintain the pre-determined pH value. The zeta potential of the sample was measured 3 times, and the average was taken as the result. Error bars represent one standard deviation around the average value.

2.5. XPS Measurements

ESCALAB 250Xi (Thermo Fisher, Waltham, USA) was used to measure and analyze the chemical states of chalcopyrite and galena surface elements before and after MA/AA treatment, using contaminant carbon (C1 at 284.8 eV) to calibrate all elements' binding energies [25–27]. To prepare samples for analysis, 2 g of mineral samples were added into a 40 mL aqueous solution with a MA/AA concentration of 30 mg/L. The pH value of the pulp was adjusted with HCl and NaOH solution to 8.0. After stirring for 20 min, the sample was separated from the liquor by high-speed centrifugation and subsequently rinsed with deionized water. In the end, it was dried in a vacuum oven at 50 °C.

3. Results and Discussion

3.1. Micro-Flotation Results

Micro-flotation tests were carried out to evaluate the effect of MA/AA on the flotation behavior of galena and chalcopyrite. For comparative purposes, traditional depressants, including Na_2S and $K_2Cr_2O_7$, were tested as the contrast depressants for the flotation separation of chalcopyrite and galena in the current research.

Figure 3 presents the effect of different pH values on the flotation recovery of chalcopyrite (a) and galena (b) under different depressant systems (flotation condition: SBX = 5 mg/L, $K_2Cr_2O_7$ = 40mg/L, Na_2S = 250mg/L, MA/AA = 30 mg/L). It can be seen that chalcopyrite and galena have a high flotation recovery rate (above 95%) in the absence of a depressant, confirming excellent floatability. The pH value of the pulp barely affects the flotation behaviors of chalcopyrite and galena, although the pulp chemistry affected the natural hydrophobicity of chalcopyrite, particularly in oxidizing and reducing environments [28]. However, in this experiment, the addition of MA/AA had little effect on the flotation behavior of chalcopyrite within the pH range of 7 to 11. On the contrary, for galena, the flotation recovery decreased from above 95% to less than 3% with the addition of MA/AA. Obviously, the presence of MA/AA depressed the flotation of galena, while it had little effect on the flotation of chalcopyrite. Moreover, as presented in Figure 3, MA/AA depressed galena significantly more than $K_2Cr_2O_7$ and Na_2S, while the two traditional depressants have a greater influence on the flotation of chalcopyrite. Clearly, the selectivity and depression effect of MA/AA were significantly better than those of Na_2S and $K_2Cr_2O_7$.

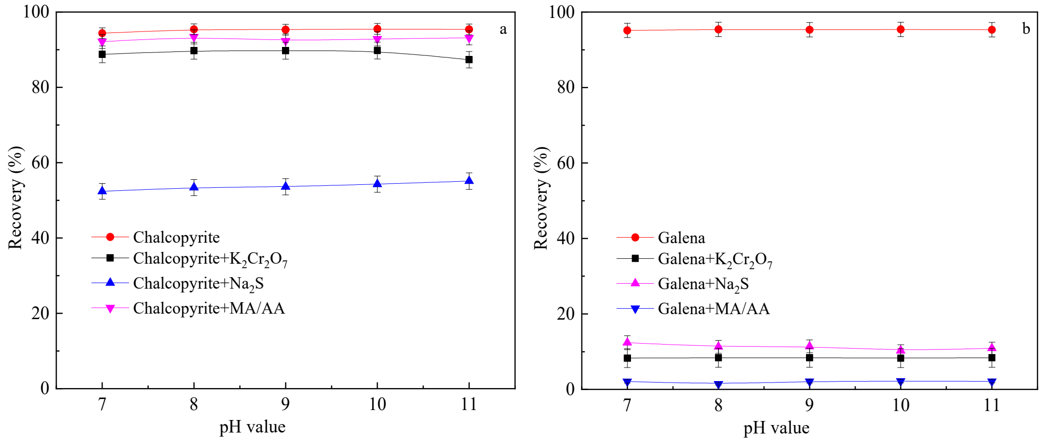

Figure 3. Effect of different pH values on the flotation recovery of chalcopyrite (**a**) and galena (**b**) under different depressant systems.

Figure 4 illustrates the effect of depressant dosage on the flotation recovery of chalcopyrite and galena (SBX = 5mg/L, pH = 8.0). As shown in Figure 4a, the recovery of chalcopyrite basically remained unchanged with the increase in $K_2Cr_2O_7$ and MA/AA concentration, while with the increase in Na_2S concentration, the recovery of chalcopyrite significantly decreased. It can be seen from Figure 4b that the recovery of galena sharply decreased with the increases in these three depressants, while, the recovery of galena barely changed when the dosage exceeded a certain value. Clearly, MA/AA displayed significantly better depression of galena than $K_2Cr_2O_7$ and Na_2S even at much lower dosages. These results confirm MA/AA's excellent selectivity and depression for the flotation separation of chalcopyrite and galena. Moreover, according to the results of laboratory experiments, the optimum dosages of MA/AA, $K_2Cr_2O_7$, and Na_2S should be 30 mg/L, 40 mg/L, and 250 mg/L, respectively.

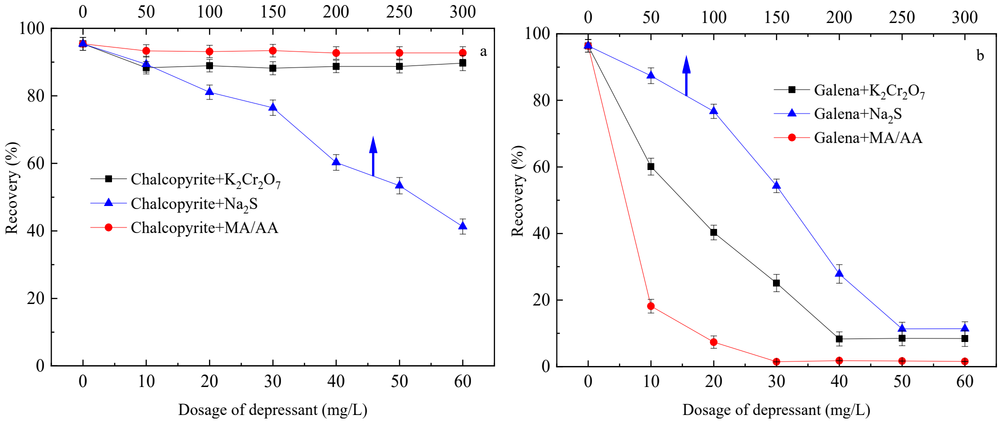

Figure 4. The flotation recovery rate of chalcopyrite (**a**) and galena (**b**) as a function of depressant dosage.

According to the single-mineral flotation results, flotation tests on artificially mixed minerals (chalcopyrite and galena mixed at a 1:1 mass ratio) were conducted to further verify the effect of MA/AA on the separation of chalcopyrite and galena. For comparative purposes, $K_2Cr_2O_7$ and Na_2S were tested as the contrast depressants. The concentrate and tailings indicators under different test conditions are shown in Table 2 (flotation condition: pH = 8.0; SBX = 5 mg/L).

Table 2. Results of flotation of chalcopyrite and galena mixed minerals under different conditions.

Depressant	Product	Yield (%)	Pb Grade (%)	Cu Grade (%)	Pb Recovery (%)	Cu Recovery (%)
Without any depressant	Concentrates	93.58	41.98	16.35	92.63	92.67
	Tailings	6.42	48.68	18.84	7.37	7.33
	Feed	100.00	42.41	16.51	100.00	100.00
MA/AA (30 mg/L)	Concentrates	50.56	5.26	29.89	6.27	91.53
	Tailings	49.44	80.40	2.83	93.73	8.47
	Feed	100.00	42.41	16.51	100.00	100.00
$K_2Cr_2O_7$ (40 mg/L)	Concentrates	50.94	10.1	27.96	12.13	86.27
	Tailings	49.06	75.96	4.62	87.87	13.73
	Feed	100.00	42.41	16.51	100.00	100.00
Na_2S (250 mg/L)	Concentrates	46.35	11.7	20.16	12.79	56.60
	Tailings	53.65	68.94	13.36	87.21	43.40
	Feed	100.00	42.41	16.51	100.00	100.00

As seen, almost all galena was entered into concentrate in the absence of depressant. This confirms that the separation of the two minerals cannot be achieved without the addition of a depressant. When applying MA/AA as a depressant, high-quality concentrates with Cu grade of 29.89% and recovery of 91.53% were obtained. The Pb grade of the concentrates was only 5.26%. From Table 2, it can be seen that this flotation index was much better than the flotation index when using $K_2Cr_2O_7$ and Na_2S as depressants. All in all, the result implies that MA/AA can potentially be used as an efficient depressant in the flotation separation of chalcopyrite and galena.

3.2. Zeta Potential Measurement

Zeta potential measurements were performed to elucidate the adsorption behavior of the reagent with galena and chalcopyrite in the flotation process. The results are shown in Figure 5 (conditions: SBX = 5mg/L, MA/AA = 30 mg/L).

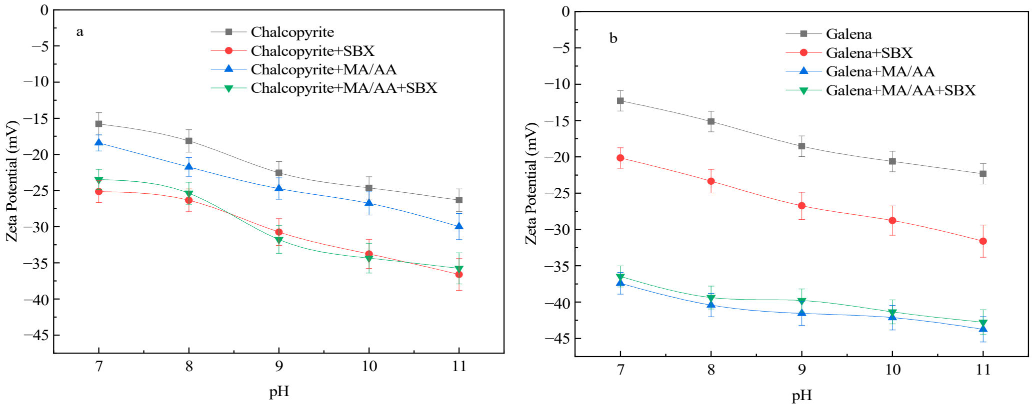

Figure 5. Zeta potentials of chalcopyrite (**a**) and galena (**b**) as functions of pH under different reagent conditions.

As seen in Figure 5, the zeta potential of the original chalcopyrite and galena gradually decreased as the pH value increased due to the adsorption of the carboxyl group on the surface, which basically corresponds to previous research works [29,30]. Figure 5a shows the zeta potential of chalcopyrite decreases with the addition of MA/AA. This indicates the adsorption of MA/AA took place on the surface of chalcopyrite. After the addition of SBX to the MA/AA–chalcopyrite system, the variation trend of zeta potential was almost in accordance with the single SBX system. Clearly, MA/AA has little influence on the interaction between SBX and the surface of chalcopyrite. In contrast, as presented in Figure 5b, the zeta potential of galena greatly decreased with the presence of MA/AA. This implies that a large amount of MA/AA was absorbed on the surface of galena [3,29]. Moreover, the zeta potential of galena was little changed, as was the presence of SBX in the MA/AA–chalcopyrite system. Obviously, the adsorption of MA/AA depressed the further adsorption of SBX.

3.3. Contact Angle Measurement

Contact angle measurements were carried out to investigate the wettability changes in chalcopyrite and galena before and after being treated with different reagents. The results are shown in Figure 6 (conditions: SBX = 5 mg/L, MA/AA = 30 mg/L).

The contact angles of bare chalcopyrite and galena were 92° and 93.5°, respectively, implying their high natural hydrophily. After being treated with MA/AA, the contact angles of chalcopyrite and galena reduced to 39.1° and 83.7°, respectively. This indirectly indicates that much more MA/AA was absorbed in galena than in chalcopyrite. The contact angle of galena increases to 43.6° after being further treated with SBX, while, for chalcopyrite, it increases to 103.1°. Obviously, the adsorption of MA/AA on galena significantly depressed the further adsorption of SBX. On the contrary, it barely affects the adsorption of SBX on chalcopyrite due to the much lower adsorption of MA/AA. These results are consistent with the flotation results.

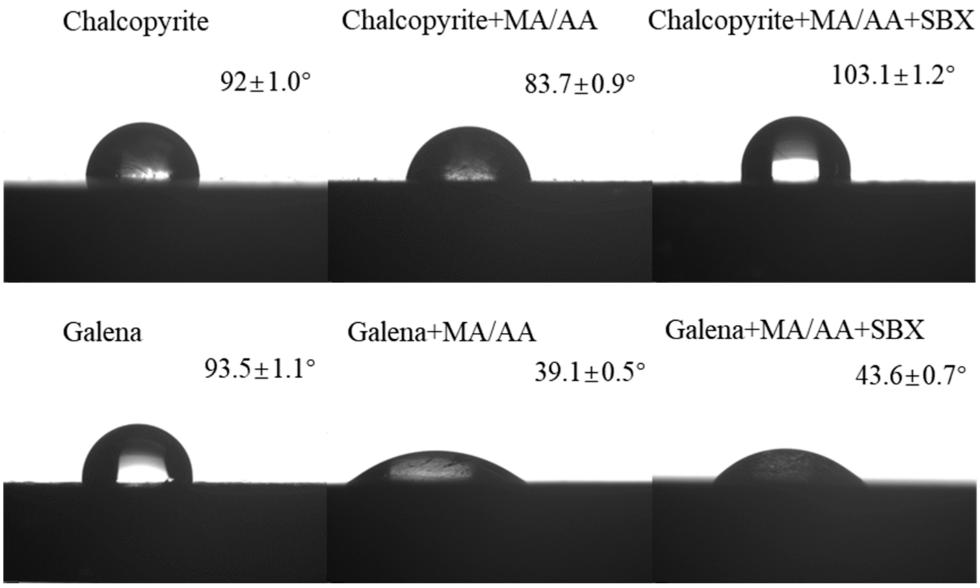

Figure 6. Contact angles of chalcopyrite and galena before and after being treated with different reagents.

3.4. XPS Analysis Results

XPS analysis was carried out to examine the variation in chemical state on the surface of chalcopyrite and galena before and after treatment with MA/AA. The results are shown in Figures 7 and 8.

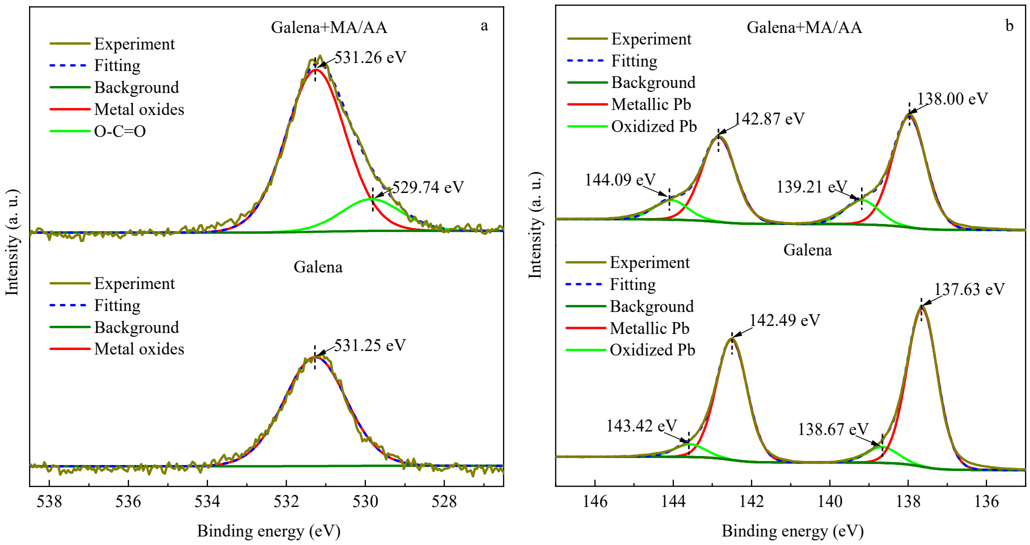

Figure 7. The high-resolution XPS spectra of galena before and after MA/AA treatment: (**a**) O 1s; (**b**) Pb 4f.

Figure 7 presents the high-resolution spectra of O 1s and Pb 4f of galena before and after being treated with MA/AA. As can be seen in Figure 7a, for initial galena, the peak binding energy at 531.25 eV can be attributed to lead oxide [10,31]. After being treated with MA/AA, a new separation peak appears at 529.74 eV, which can be attributed to O–C=O in the molecule structure of MA/AA [23]. It can be seen in Figure 7b that the peak of Pb $4f_{7/2}$ appears at 137.63 eV and 138.67 eV, and the peak of Pb $4f_{5/2}$ appears at 142.49 eV and 143.42 eV, which was consistent with the previous reports [32,33]. After being treated with MA/AA, the intensity of these peaks was significantly decreased, which can be attributed to the adsorption of MA/AA on the surface of galena. Moreover, the binding energy of Pb 4f was significantly shifted (from 137.63 eV, 138.67 eV, 142.49 eV, 143.42 eV to 138.00 eV, 139.21 eV, 142.87 eV, 144.09 eV). This can be attributed to the chelation reaction between MA/AA and Pb^{2+} sites on the surface of galena.

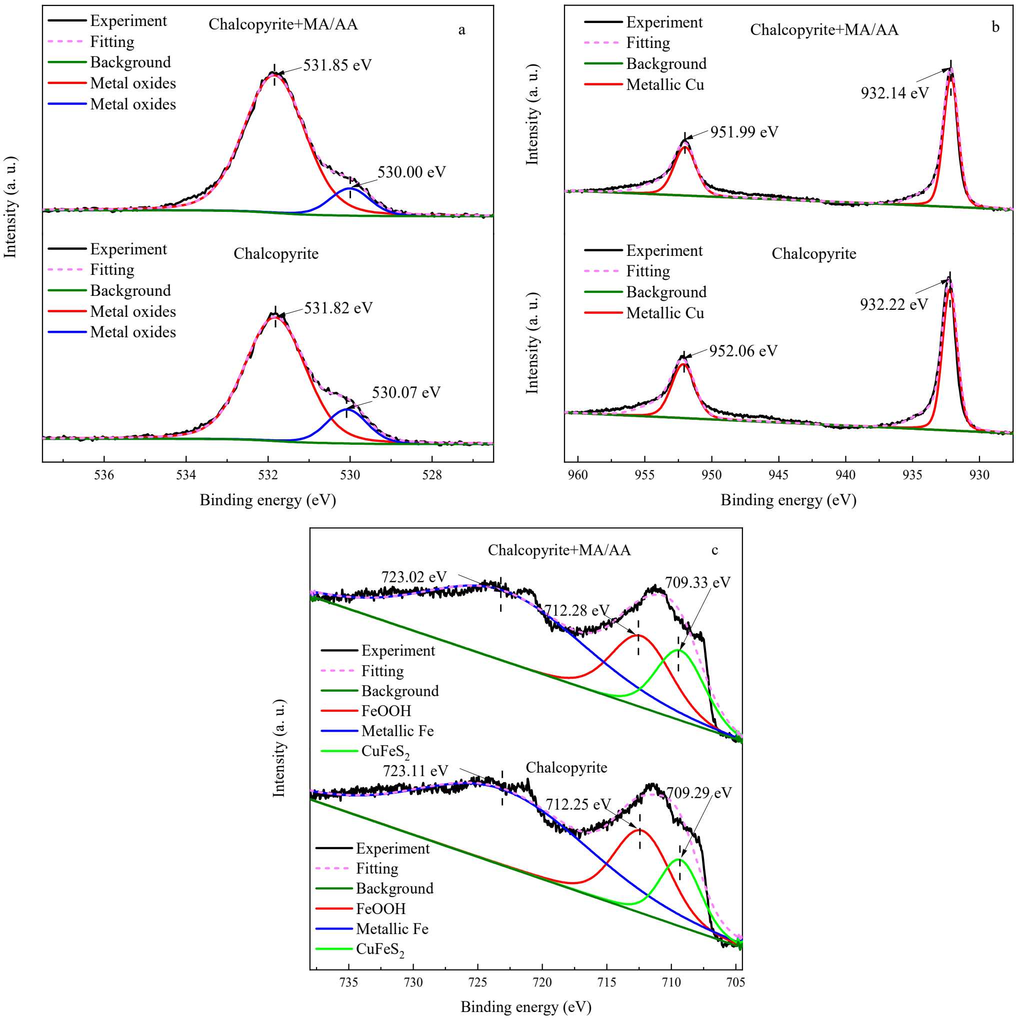

Figure 8. The high-resolution XPS spectra of chalcopyrite before and after MA/AA treatment: (**a**) O 1s; (**b**) Cu 2p; (**c**) Fe 2p.

Figure 8 presents the high-resolution spectra of O 1s, Cu 2p and Fe 2p of chalcopyrite before and after being treated with MA/AA. It can be seen in Figure 8a that binding energy peaks at 531.82 eV and 530.07 eV were attributed to sulfate and CuO [34]. This can be attributed to the light oxidization of chalcopyrite in the process of crushing and sample preparation [3]. It can be seen in Figure 8b that peaks at 932.22 eV and 952.06 eV corresponded to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively [11]. Figure 8c shows the peaks at 709.29 eV, 712.25 eV, and 723.11 eV can be assigned to the $CuFeS_2$, FeOOH, and $FeSO_4$ content on the surface of chalcopyrite, respectively [27,35]. After being treated with MA/AA, the intensity and binding energy of all peaks were little changed. This confirms minor adsorption of MA/AA on the chalcopyrite surface, which barely affected the surface properties of chalcopyrite.

3.5. Depression Mechanism of MA/AA

According to the above flotation test and surface detection analysis, the possible interaction model of MA/AA on the surface of chalcopyrite and galena can be simply illustrated in Figure 9. The adsorption capacity of MA/AA was derived from the existence of many free carboxyl groups (-COO-) in MA/AA molecules with an alkaline solution [21]. These free carboxyl groups could chelate in solution with metal ions on the mineral surface, which makes the initially hydrophobic surface hydrophilic, leading to its depression. Thus, the available metal sites exposed to the mineral surface were a key factor. Some studies suggest that [5,35] S^{2-} may be the dominant ion due to the small ionic radius of Cu^{2+} and Fe^{2+} on the chalcopyrite surface. In this case, the anion S^{2-} on the chalcopyrite surface can prevent MA/AA from adsorbing to Fe^{2+}/Cu^{2+} through electrostatic repulsion and steric hindrance. Differently, Pb^{2+} on the galena surface has a larger ionic radius than Fe^{2+}/Cu^{2+} and can effectively chelate with the carboxyl functional groups in MA/AA, which would increase the hydrophilicity of the galena surface.

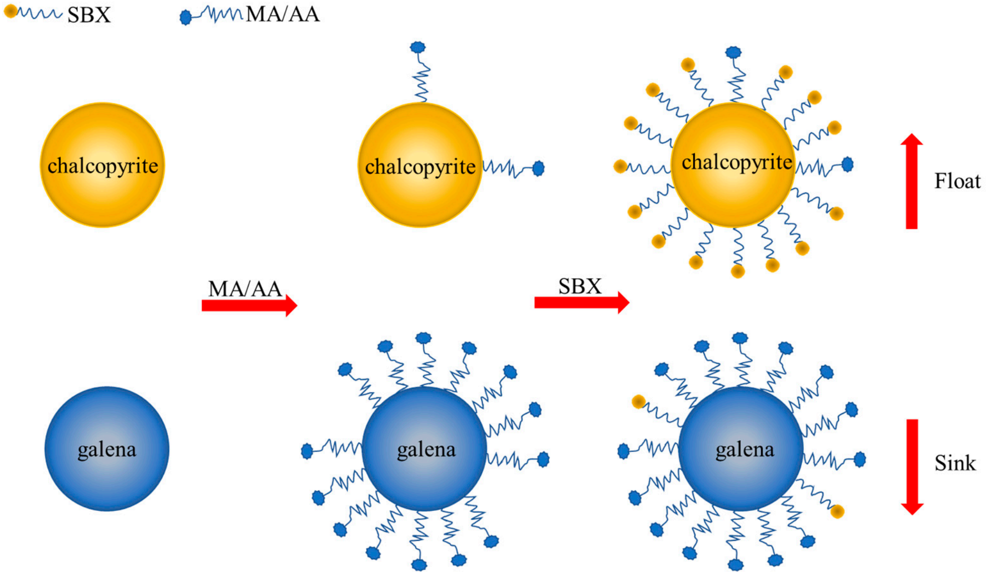

Figure 9. Conceivable mechanism of MA/AA for separation of chalcopyrite and galena.

4. Conclusions

The flotation separation of chalcopyrite and galena by applying MA/AA, an eco-friendly reagent, was carried out in the current research. It was found that MA/AA can depress the flotation of galena well but barely affects the recovery of chalcopyrite, exhibiting the excellent depression ability and selectivity of MA/AA. Based on applying MA/AA (dosage: 30 mg/L) as a depressant, the flotation separation of artificially mixed chalcopyrite and galena can be effectively achieved at pH 8.0 using 5 mg/L SBX. XPS, zeta potential, and contact angle analysis indicates that significant adsorption of MA/AA took place on the surface of galena, which on one hand improves the hydrophily and on the other hand hinders the further adsorption of SBX, thus greatly depressing the flotation of galena. In contrast, under the same condition, minor MA/AA was absorbed on the surface of chalcopyrite and barely affected its floatability.

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