



# Article Evaluation of L-arginine as an Eco-friendly Activator for Malachite Sulfidization Flotation

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**Abstract:** Sulfidization xanthate flotation remains the most promising method for the beneficiation of malachite. In this study, L-arginine (LA) was first used to modify the malachite surface and improve the efficiency of sulfidization flotation. The performance of LA was evaluated by the flotation experiments. The mechanism of interaction between LA and the malachite surface was investigated by adsorption experiments, zeta potential measurements, scanning electron microscopy (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) analysis. Flotation experiments showed that LA had a significantly promoting effect on malachite sulfidization flotation. Adsorption experiments and SEM-EDS results indicated that LA improved the adsorption of S (II) species into the malachite surface and promoted the formation of sulfides. This finding was further confirmed by the XPS analysis. The XPS measurements results determined that S (II) species reacted with Cu (II) on the malachite surface and form polysulfides, adding LA promoted the reaction. The zeta potential measurements showed that LA increased the positive electrical properties of the mineral surface, which was conducive to S (II) species adsorption and the sulfidization reaction. This work sheds new light on the development of sulfidization activation.

Keywords: malachite; surface; flotation; sulfidization; activation

# 1. Introduction

Copper metal has a wide range of applications in electrical, electronic, military, machinery manufacturing, and transportation industries [1,2]. Copper sulfide mineral (Cu<sub>2</sub>S) is the common mineral of copper. With the increasing demand for copper, copper sulfide resources cannot meet the needs. The exploitation and utilization of other copper resources is the key to solving the crisis. For example, Kasongo et al. used a  $2^4$ -factor design experiment to explore the influencing factors of flotation in order to recover copper metal as much as possible [3]. The utilization of copper oxide also attracts more and more attention. Oxidized copper reserves deposits are relatively abundant in the world, and oxidized mineral belts are also found above most sulfide deposits [4]. Copper oxide minerals include malachite (Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>), cuprite (Cu<sub>2</sub>O), chrysocolla (Cu,Al)<sub>2</sub>H<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>·nH<sub>2</sub>O), azurite (Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>), tenorite (CuO), and atacamite (Cu<sub>2</sub>Cl(OH)<sub>3</sub>) [5–7]. Malachite is a representative copper oxide mineral, which has received increasing attention [8]. Copper oxide minerals has strong hydrophilicity and poor floatability, which makes it difficult to recover [5]. The efficient recovery of copper oxide minerals is a major problem.

Flotation is an economical method for malachite beneficiation [9]. Some studies have shown that the surface tension of flotation solution can be changed by adding a



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). collector, and the change of surface tension of the solution will affect the wettability of mineral particles in the solution [10]. For malachite, the surface can strongly interact with water molecules to form a hydration layer, which makes the surface hydrophilic and the collector molecules cannot effectively adsorb [11]. Direct flotation cannot effectively recover malachite. Sulfidization-xanthate flotation is an effective strategy for malachite beneficiation, and it has been extensively used in industrial applications [12–14]. The basic idea of sulfidization-xanthate flotation is as follows: first, sulfur ions reach the hydration layer of the surface of malachite, adsorb onto the surface, and react with the surface to form a sulfide layer, which provides suitable conditions for the absorption of the collector; second, xanthate is used as a collector to achieve the beneficiation of sulfation malachite [15]. Compared with direct flotation, sulfidization flotation has the advantages of better selectivity and high recovery. However, controlling sulfidization is not a simple task [16]. In the presence of excessive sulfide, colloidal copper sulfide species are formed in the solution, which will depress malachite flotation [17,18]. Surface sulfidization is the key stage of sulfidization flotation [19]. In improving the efficiency of sulfidization flotation, many scholars have focused on finding an activator to improve the efficiency of sulfidization flotation. Ammonium sulfate [20], ethylenediamine phosphate [8], and 8-hydroxyquinoline [21] have been used to promote the sulfidization flotation of malachite. Among them, ammonium sulfate and ethylenediamine phosphate are the most common activators. Liu et al. [22] investigated the activation mechanism of ammonium sulfate and proposed that the addition of ammonium sulfate can reduce the inhibitory effect caused by excess S ions and accelerate the speed of sulfidization. Liu et al. [20] and Shen et al. [7] further confirmed that ammonium sulfate can eliminate the inhibitory effect of excess S ions. Furthermore, Liu et al. [23] inferred that ammonium ions may mediate the nucleation and growth of a sulfidization product during malachite sulfidization. Feng et al. [8] found that an ethanediamine-modified mineral surface adsorbed with more sulfide ion species and enhanced the reactivity of the sulfidization products.

Although organic activators can significantly promote the sulfidization of malachite, these options have their shortcomings. Most of these compounds have relatively high levels of toxicity. Once discharged into the environment, they cause serious pollution of water bodies. Finding new, highly efficient, and non-toxic reagents is important.

As a natural amino acid, L-arginine (LA) is abundantly present in meat protein, which possesses the advantages of being inexpensive and environmentally friendly. The molecular model of LA is shown in Figure 1. LA with a molecular formula of  $C_6H_{14}N_4O_2$  and a molecular weight of 174.2 is easily soluble in water and slightly soluble in ethanol, can be used as a non-toxic, easily biodegradable [24], and widespread activator. In this study, LA was first introduced as a sulfidization activator to enhance the sulfidization flotation of malachite. The effectiveness of LA as the activator was determined by the flotation experiments. In addition, the activation mechanism was explored by adsorption experiments, zeta potential measurements and scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) analyses.



Figure 1. Molecular structure of L-arginine.

## 2. Materials and Methods

# 2.1. Materials

The malachite sample (the purity is about 96%) used in this study was collected from Yunnan Province, China. After manual cleaning, the malachite ore was ground in a porcelain ball mill to obtain a mineral of -0.074 mm size fraction. Then, the ground malachite sample was collected in a jar, and used for the flotation experiments and characterization studies. Based on X-ray diffraction (XRD) (shown in Figure 2) results, the sample was of high purity.



Figure 2. XRD pattern of malachite simple.

Analytical-grade LA, ammonium sulfate  $((NH_4)SO_4)$ , and sodium sulfide  $(Na_2S\cdot9H_2O)$  were used as the activators and sulfidization agent, respectively. Industrial-grade amyl xanthate (AX) and butyl xanthate (BX) (the purity is around 86%) were used as the collector. Moreover, industrial-grade terpineol (the purity is around 80%) was used as a frother. Analytically pure hydrochloric acid (HCl) (38% concentration) and analytically pure sodium hydroxide (NaOH) were used as pH regulators, and deionized (DI) water was used in all the tests.

## 2.2. Methods

#### 2.2.1. Flotation Experiments

The flotation experiments were performed using an XFG-type flotation machine (Shun Ze Mining Metallurgy Machinery Manufacturing Co., Ltd., Changsha, China) at a spindle speed of 2000 rpm. For each test, 6.0 g of malachite was placed in a 150 mL flotation cell and mixed with 140 mL DI water (the solid-liquid ratio was about 4.3%), stirred for 1 min. Next, the activator solution was added to the suspension and stirred for 1 min. Subsequently, the prepared Na<sub>2</sub>S solution was added to sulfurize the malachite surface for 2 min. The pH of the pulp was adjusted to 9.6 (or a specified value) using HCl and NaOH, as necessary. Next, the collector was freshly added, and the mixture was conditioned for 1 min. Finally, terpineol was added as the frother, and the mixture was floated for 4 min. The floating particles were collected, dried, and assayed to measure the recovery. All the tests were repeated three times under the same conditions.

#### 2.2.2. Adsorption Experiments

An inductively coupled plasma (ICP) atomic emission spectrometer (Spectro Blue II, Speck Instruments, Roth, Germany) was used to measure the residual S species in the solution. The UV spectrophotometer (UV2600, Shimadzu Corporation, Kyoto, Japan) at a wavelength ( $\lambda$ ) of 300.5 nm was used to determine the residual xanthate in the solution. The adsorption amount of the xanthate was calculated using Equation (1).

$$\Gamma = \frac{(C_i - C_r) \times V}{m} \tag{1}$$

where  $\Gamma$  is the adsorption amount (mg/g);  $C_i$  and  $C_r$  are the initial concentration (mg/L) and residual concentration in solution (mg/L), respectively. *V* is the pulp volume (L), and *m* is the weight of the mineral sample (g). The samples were prepared as follows: 1.0 g of malachite was placed into the beaker and 30 mL of DI water was added. Then, the activator was added (if necessary), and the mixture was conditioned for 1 min. Subsequently, the Na<sub>2</sub>S solutions were added, and then the pH was adjusted to 9, and stirred for 2 min. Finally, BX (if necessary) was added. After the adsorption experiments, the solution was collected and filtered by syringe and filter. The final clear solution was used to measure the concentration of S or BX in the solution.

## 2.2.3. SEM-EDS Analysis

Scanning electron microscopy (SEM, TESCAN MIRA3 LMU, TESCAN, Brno, Czechia) coupled with energy-dispersive spectroscopy (EDS; Oxford X-Max20, Oxford Instruments, Abingdon, UK) was used to observe the surface topography of malachite. The mineral samples were prepared as follows: 1 g of malachite was added to 30 mL of an aqueous solution. Then, the activator was added to the slurry (if necessary) and stirred for 1 min. Next, Na<sub>2</sub>S solution was added (if necessary) to modify the mineral surface and adjust the pH to 9, and stirred for 2 min. After the reaction, the solid particles were collected and dried in a vacuum drying oven at 40 °C. Then, a dry sample was used for SEM-EDS analysis.

#### 2.2.4. XPS Analysis

A PHI 5000 VersaProbe II system (ESCALAB250Xi, ThermoFisher-VG Scientific, Waltham, MA, USA) with a monochromatic Al K X-ray source was used for XPS measurements. Casa software (CasaXPS Version 2.3.25, CASA SOFTWARE LIMITED, Devon, UK) was used for analysis. The samples were prepared using the method described in Section 2.2.3.

#### 2.2.5. Zeta Potential Measurements

The zeta potential measurements were carried out using a Zetasizer Nano Zs90 potential analyzer (Malvern Panalytical, Malvern, UK). Before the measurement, the mineral sample was ground to a particle size of 2  $\mu$ m. Then, 1.0 g of the sample was added to a 100 cm<sup>3</sup> beaker filled with 50 mL of DI water containing 1  $\times$  10<sup>-3</sup> mol/L KNO<sub>3</sub> as a background solution and then stirred with a magnetic stirrer for 2 min. The pH was adjusted using HCl or NaOH. At the pH of the slurry, the flotation reagent was added and stirred for 1 min. The suspension was allowed to stand for the coarse particles settle down for 4 min, and the supernatant was collected for testing. Each sample was measured three times.

#### 3. Result and Discussion

#### 3.1. Flotation Experiments

The flotation recovery of malachite as a function of Na<sub>2</sub>S concentration is shown in Figure 3a. The flotation results showed that the malachite flotation recovery varied for both collectors; it initially increased and then decreased with the increase of Na<sub>2</sub>S dosage. The recovery reached its peak when the Na<sub>2</sub>S concentration was  $3-5 \times 10^{-3}$  mol/L. Afterwards, the flotation recovery of malachite decreased with the increase of Na<sub>2</sub>S concentration. This phenomenon was attributed to the inhibitory effect of excessive Na<sub>2</sub>S on the malachite surface [7,12,25]. When BX was used as the collector, the maximum flotation recovery of malachite reached with  $3.0 \times 10^{-3}$  mol/L of Na<sub>2</sub>S. Therefore, the Na<sub>2</sub>S dosage of  $3.0 \times 10^{-3}$  mol/L was selected as an optimum dosage to study the activation behavior of LA.



**Figure 3.** Flotation recovery of malachite as a function of (**a**) Na<sub>2</sub>S dosage (c(collector) = 1.0 × 10<sup>-3</sup> mol/L; pH = 9.5) and (**b**) BX dosage in the absence and presence of Na<sub>2</sub>S (c(Na<sub>2</sub>S) = 3.0 × 10<sup>-3</sup> mol/L; pH = 9.6).

At pH 9.6, the flotation recovery of malachite in the absence and presence of Na<sub>2</sub>S as a function of the collector (BX) concentration is shown in Figure 3b. The flotation recovery showed a positive correlation with the collector concentration. In the absence of Na<sub>2</sub>S, the recovery of malachite was low. This result can be attributed to the malachite surface forming a hydration film, making it difficult for the collector xanthate to adsorb [26]. When  $3.0 \times 10^{-3}$  mol/L of Na<sub>2</sub>S was added to modify the mineral surface, the flotation recovery of malachite sharply increased from 51.30% to 70.50% as BX dosage increased to  $1.0 \times 10^{-4}$  mol/L. The recovery then remained nearly constant with the increase of BX. After sulfidization, the malachite surface could easily interact with xanthate, which improved the hydrophobicity of the mineral surface [27]. This result indicated that the sulfidization could promote the flotation of malachite.

In the previous experiment, the optimal dosage of BX was determined to be  $1.0 \times 10^{-4}$  mol/L. Under this condition, the effect of the activator concentration on the malachite flotation was studied at pH 9.6, and the corresponding flotation results are shown in Figure 4.

Figure 4 shows that the flotation recovery of malachite increased with the increase of LA dosage, and a maximum flotation recovery of 87% was achieved with  $6.0 \times 10^{-5}$  mol/L of LA. Furthermore, the flotation recovery of malachite decreased when the dosage of LA was further increased. It was hypothesized that in the presence of an excessive amount of LA, the covering effect of LA makes it difficult for S species to contact the mineral surface, thereby hindering surface sulfidization. This results in a decrease in the hydrophobicity of the mineral surface. After adding ammonium sulfate, the flotation recovery of 82% was achieved with  $4.0 \times 10^{-4}$  mol/L of ammonium sulfate. Compared with ammonium sulfate, LA as the activator showed a better promoting effect at low concentrations.

The flotation behavior of malachite as a function of pH is shown in Figure 5. The recovery of malachite without Na<sub>2</sub>S increased as pH increased from 3 to 9, and after that the recovery slightly decreased as the pH increased from 9 to 11. This result indicates that malachite does not respond well to traditional copper sulfide collectors. When  $3 \times 10^{-3}$  mol/L of Na<sub>2</sub>S was added, the flotation recovery initially decreased and then increased, whereas at pH 9, it reached a maximum of 75%. At this pH, the main S species in the solution was HS<sup>-</sup>, and the presence of a large amount of HS<sup>-</sup> is conducive to the sulfidization of the malachite surface [28]. These results were similar to those in the previously reported literature. Notably, adding  $6.0 \times 10^{-5}$  mol/L of LA in sulfide, the flotation recovery of malachite significantly improved in the whole pH range. At pH 3, the recovery rate exceeded 75%. This phenomenon can be explained as surface sulfidization involves ion-exchange

reaction, surface adsorption, and redox reaction [14,29,30], although the content of  $HS^-$  in the solution is little under acidic conditions, leading to a decrease in the ionic adsorption of  $HS^-$  on the mineral surface,  $H_2S$  still undergoes redox reactions with mineral surfaces. The addition of LA can promote the redox reaction and promote the formation of sulfide, which can improve the sulfide flotation of malachite. Furthermore, the recovery was highest at pH 7. This result indicates that LA has a positive effect on the sulfidization-xanthate flotation of malachite in the pH range of the experiment.



**Figure 4.** Flotation recovery of malachite as a function of LA and  $(NH_4)_2SO_4$  dosage  $(c(BX) = 1.0 \times 10^{-4} \text{ mol/L}; c(Na_2S) = 3.0 \times 10^{-3} \text{ mol/L}; pH = 9.6).$ 



**Figure 5.** Flotation recovery of malachite as a function of pH ( $c(BX) = 1.0 \times 10^{-4} \text{ mol/L}$ ).

#### 3.2. Adsorption Experiments

3.2.1. Adsorption Behavior of S Species onto Malachite Surfaces in the Presence and Absence of LA

During the sulfidization flotation, a large amount of S species was transferred onto the mineral surface. Figure 6 shows the adsorption behavior of S species on the malachite surface as a function of Na<sub>2</sub>S dosage in the absence and presence of  $6 \times 10^{-5}$  mol/L of LA. As shown in Figure 6, the adsorption amount increased as the dosage of Na<sub>2</sub>S increased. Furthermore, after adding LA, the adsorption amount of S species on the surface of malachite was larger than that without LA. This phenomenon could be attributed to LA increasing the adsorption of S species on the surface of minerals.



**Figure 6.** The adsorption amount of S in the solution as a function of Na<sub>2</sub>S dosage in the absence and presence of LA ( $c(LA) = 6.0 \times 10^{-5} \text{ mol}/\text{L}$ ; pH = 9).

3.2.2. Adsorption Behavior of S Species onto Malachite Surfaces as a Function of LA Dosage

When adding  $3 \times 10^{-3}$  mol/L Na<sub>2</sub>S, the adsorption behavior of BX as a function of BX dosage is shown in Figure 7. Without LA, the adsorption capacity of BX increased rapidly at first, and then the growth rate tends to be gentle. In the presence of LA, the adsorption of BX on the malachite surface is greater than that in the absence of LA. This was owing to the fact that the LA increases the sulfidization on the malachite surface and thus increases the adsorption of BX on the surface. However, when the concentration of the collector is too large, LA inhibits the adsorption of xanthate. This phenomenon is consistent with the flotation results.



**Figure 7.** The adsorption amount of BX in the solution as a function of BX dosage in the absence and presence of LA ( $c(LA) = 6.0 \times 10^{-5} \text{ mol/L}$ ;  $c(Na_2S) = 3.0 \times 10^{-3} \text{ mol/L}$ ; pH = 9).

# 3.3. SEM-EDS Measurements

The surface microtopography (SEM) of malachite particles before and after treatment is shown in Figure 8. The EDS results are presented in Table 1. The SEM images show that the surface of raw malachite particles was smooth and flat, and a small number of grains were found on malachite surfaces. The EDS results indicate the absence of an S element on the surface of raw malachite. The weight and atom percentages (wt% and at%) of Cu on the surface of raw malachite were only 46.62% and 16.89%, respectively. After the treatment with Na<sub>2</sub>S, the surface of malachite developed a layer of adhering material, particularly at the faults, which made the edges and corners blunt. Based on the EDS results, it was found that the S element appeared on the surface of malachite, indicating that sulfides were attached to the surface of malachite. Moreover, adding LA and Na<sub>2</sub>S, more attachments were found on the surface of malachite, and the edges and corners of the fracture layers were less apparent. The atom percentage of S increased from 0.29% to 0.39%, indicating that the addition of LA promoted the formation of surface sulfides.



**Figure 8.** SEM images: (**a**,**b**) raw malachite; (**c**,**d**) malachite treated with Na<sub>2</sub>S; (**e**,**f**) malachite treated with LA + Na<sub>2</sub>S (*c*(LA) =  $6.0 \times 10^{-5}$  mol/L; *c*(Na<sub>2</sub>S) =  $3.0 \times 10^{-3}$  mol/L; pH = 9.6).

Table 1. Results of EDS analyses (%).

Element	Malachite		Malachite + Na <sub>2</sub> S		Malachite + LA + $Na_2S$	
Liement	Weight(%)	Atomic(%)	Weight(%)	Atomic(%)	Weight(%)	Atomic(%)
СК	13.49	25.85	12.47	22.9	14.49	25.49
O K	39.69	57.12	45.2	61.31	46.44	61.33
SK	0.2	0.15	0.28	0.29	0.59	0.39
Cu K	46.62	16.89	42.05	14.6	38.48	12.8

## 3.4. XPS Analysis

The activation mechanism of LA was investigated by XPS analyses. The XPS full-range spectra of treated or untreated malachite are shown in Figure 9, in which the surface of malachite comprised C, O, S, and Cu; their corresponding atomic surface concentrations are summarized in Table 2.



**Figure 9.** XPS spectra of malachite before or after treatment ( $c(LA) = 6.0 \times 10^{-5} \text{ mol/L}$ ;  $c(Na_2S) = 3.0 \times 10^{-3} \text{ mol/L}$ ; pH = 9.6).

Simula		Atomic Concent	ration (Atomic %)	
Simple –	C 1s	O 1s	Cu 2p	S 2p
Malachite	33.90	47.51	18.21	0.38
Malachite + $Na_2S$	35.92	43.93	15.89	4.26
Malachite + LA + $Na_2S$	36.75	42.3	15.89	5.07
Malachite + LA	33.88	47.65	18.09	0.39

Table 2. Relative contents of representative elemental constituents of malachite surface.

In the spectra, N was not detected, which demonstrated that LA did not stably adsorb or form compounds on the surface of malachite. LA adsorbed on the malachite surface through hydrogen bonding. After the treatment with Na<sub>2</sub>S, peaks representing S 2s or S 2p were observed. Table 2 shows that with the addition of LA, the atomic concentration of S on the malachite surface was increased. This finding suggests that LA promotes the sulfidization efficiency of the malachite surface, which is consistent with the SEM-EDS results.

Cu and S peak fitting were conducted to reveal the chemical state of each element on the malachite surface, and the results are shown in Figures 10 and 11. The Cu 2p spectra of malachite samples before and after treatment show that the Cu 2p spectra consisted of peaks representing Cu 2p3/2 and Cu 2p1/2 [21,31,32]. In the same chemical state, the Cu 2p3/2 peak was consistent with the Cu 2p1/2 peak. In this study, the Cu 2p3/2 peak was used to explore changes in the chemical state of the malachite surface. For the untreated malachite, the peak assigned to Cu (II) (cupric) appeared at 935.23 eV [11,33]. After treatment with  $3 \times 10^{-3}$  mol/L of Na<sub>2</sub>S, the peak representing Cu (I) (cuprous) [34–37] appeared in the



spectrum, which indicated that a reduction reaction occurred on the surface of malachite. S(II) species will interact with the malachite surface through redox reaction.

**Figure 10.** Cu 2p XPS spectra of (**a**) raw malachite, (**b**) malachite treated with Na<sub>2</sub>S, (**c**) malachite treated with LA and Na<sub>2</sub>S, (**d**) malachite treated with LA ( $c(LA) = 6.0 \times 10^{-5} \text{ mol/L}$ ;  $c(Na_2S) = 3.0 \times 10^{-3} \text{ mol/L}$ ; pH = 9.6).



**Figure 11.** S 2p XPS spectra of (**a**) malachite treated with Na<sub>2</sub>S, (**b**) malachite treated with LA and Na<sub>2</sub>S (c(LA) = 6.0 × 10<sup>-5</sup> mol/L; c(Na<sub>2</sub>S) = 3.0 × 10<sup>-3</sup> mol/L; pH = 9.6).

Notably, the addition of LA changed the intensity of the peak representing Cu (I). Table 3 shows that after adding LA, the percentage of Cu (I) in the Cu species increased from 9.59% to 19.53%. LA promoted the chemical reaction of S (II) species and Cu (II) on the mineral surface. However, if only LA was added, the chemical state of Cu in the malachite remained unchanged. LA did not react with copper on the malachite surface, which confirmed our conjecture.

Sample	Species	Cu 2p3/2 Binding Energy (eV)	Relative Content of Cu Species (%)	Percentage in Total Cu (%)
Malachita + Na-S	Cu (I)	932.12	9.59	1.52
1 $1$ $1$ $1$ $1$ $1$ $1$ $1$ $1$ $1$	Cu (II)	934.73	90.41	14.37
Malashita + I A + NI- C	Cu (I)	932.18	19.53	3.10
Malachile + LA + $Na_25$	Cu (II)	934.5	80.48	12.79

Table 3. Contents and percentages of different Cu species in total Cu on the malachite surface.

The S 2p spectrum was further analyzed to elucidate the effect of LA on the sulfidization products, and the results are shown in Figure 11. The S 2p spectrum of malachite treated with Na<sub>2</sub>S was divided into four pairs of spin-orbit peaks, which were attributed to the S 2p3/2 and S 2p1/2 doublet [38]. The S 2p peaks with binding energies ranging from 161.2 to 162.3 eV represent divalent sulfide ions (S<sup>2–</sup>) [39,40]; peaks with high binding energies (162.4–164.3 eV) [25,41] represent polysulfide ions (Sn<sup>2–</sup>, n  $\geq$  2), and peaks with binding energies ranging from 164.5 to 167.1 eV correspond to SO<sub>3</sub><sup>2–</sup> ions [33,34]. Furthermore, the peaks with binding energies of 167.8 and 169.9 eV correspond to the sulfate ion (SO<sub>4</sub><sup>2–</sup>) [42–44]. After adding LA, the peak intensities were altered.

Table 4 shows that the percentage of  $S^{2-}$  decreased and that of  $Sn^{2-}$  increased, indicating that more low-valent states of S species were oxidized. These results indicate that LA promotes the redox efficiency of the malachite surface, thereby increasing the proportion of polysulfide species on the malachite surface.

Table 4. Contents and percentages of different S species in total S on the malachite surface.

Samples Species		Cu2p3/2 Binding Energy (eV)	Relative Content of Cu Species (%)	Percentage in Total Cu (%)
	S <sup>2-</sup>	161.68	37.37	1.59
Malashita + Na C	$Sn^{2-}/S^{0}$	162.97	32.44	1.38
$Malacline + 1Na_23$	$SO_{3}^{2-}$	165.08	12.8	0.55
	$SO_4^{2-}$	168.45	17.39	0.74
	S <sup>2-</sup>	161.66	31.65	1.60
Malachita + I A + Na-S	$Sn^{2-}/S^{0}$	162.82	39.71	2.01
$Malaclifte + LA + Ma_23$	$SO_{3}^{2-}$	164.78	9.18	0.47
	$SO_4^{2-}$	168.41	19.46	0.99

#### 3.5. Zeta Potential Measurements

The zeta potential measurements were carried out to estimate the surface electrical property of the particle in suspension. The adsorption of ions onto the malachite surface significantly affected the zeta potential. As shown in Figure 12, the zeta potential of malachite decreased with the increase of pH values. As a typical copper oxide mineral, malachite has certain hydrophilicity, and it can easily adsorb hydroxide ions in the solution, thereby forming a surface hydration film. This phenomenon leads to a decrease in the zeta potential. After adding LA, the zeta potential of malachite became more positive in the absence of LA, and the IEP value also increased [45,46]. With the addition of Na<sub>2</sub>S, the zeta potential of malachite was significantly and negatively charged. This result indicated that S(II) species in the pulp solution were adsorbed onto the mineral surface. Moreover, the addition of LA and Na<sub>2</sub>S modified the malachite surface, and the zeta potential became more negative than that treated with Na<sub>2</sub>S. This means that more S(II) species is adsorbed on the surface of malachite.



**Figure 12.** Zeta potential of malachite as a function of pH in the absence or presence of flotation reagent ( $c(LA) = 6.0 \times 10^{-5} \text{ mol/L}$ ;  $c(Na_2S) = 3.0 \times 10^{-3} \text{ mol/L}$ ).

Based on the previous results, it was hypothesized that LA produces a hydrogen bond with OH<sup>-</sup> adsorbed on a malachite surface through its N atom, resulting in a decrease of hydroxide ion in the surface and an increase of surface potential. The positive electrical properties of the mineral surface are conducive to the adsorption of S(II) species, which thereby increases the contact of S(II) species with the mineral surface, promotes the reaction of S with the mineral surface, and improves surface sulfidation efficiency. The activation mechanism of LA is shown in Figure 13.



Figure 13. Proposed model of LA to promote malachite sulfidization flotation.

The activation effects and mechanism of LA on malachite sulfidization flotation were investigated by flotation, adsorption experiments, SEM-EDS and XPS analyses and the zeta potential measurements. The main findings of this study are as follows:

- (1) The flotation experiments demonstrated that using LA as the activator can significantly improve the recovery of malachite sulfidization flotation. Furthermore, LA showed a higher promoting effects and lower reagent consumption in comparison with ammonium sulfate.
- (2) Based on the adsorption experiments and SEM-EDS results, it was concluded that LA promoted the adsorption of sulfur ions on the surface of malachite and improved the sulfidization efficiency of the malachite surface.
- (3) The zeta potential measurements that indicated that LA enhanced the positive charge on the malachite surface. More positive surface was conducive to the adsorption of S(II) species and facilitation of the contact of S(II) species with the mineral surface, thereby promoting the reaction of S with the malachite surface, and improving the surface sulfidation efficiency. XPS analysis further confirmed this phenomenon.

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# References

- David Grande-Tovar, C.; Vallejo, W.; Zuluaga, F. Equilibrium and Kinetic Study of Lead and Copper Ion Adsorption on Chitosan-Grafted-Polyacrylic Acid Synthesized by Surface Initiated Atomic Transfer Polymerization. *Molecules* 2018, 23, 2218. [CrossRef] [PubMed]
- Qu, W.; Yuan, D.; Zhao, L.; Zong, W.; Liu, R. Exploring the binding interaction between copper ions and Candida rugosa lipase. *Toxicol. Res.* 2018, *6*, 1100–1107. [CrossRef] [PubMed]
- Brest, K.K.; Henock, M.M.; Guellord, N.; Kimpiab, M.; Kapiamba, K.F. Statistical investigation of flotation parameters for copper recovery from sulfide flotation tailing. *Results Eng.* 2021, 9, 100207. [CrossRef]
- 4. Wu, D.; Ma, W.; Mao, Y.; Deng, J.; Wen, S. Enhanced sulfidation xanthate flotation of malachite using ammonium ions as activator. *Sci. Rep.* 2017, 7, 2086. [CrossRef]
- Corin, K.C.; Kalichini, M.; O'Connor, C.T.; Simukanga, S. The recovery of oxide copper minerals from a complex copper ore by sulphidisation. *Miner. Eng.* 2017, 102, 15–17. [CrossRef]
- 6. Frost, R.L.; Xi, Y.; Wood, B.J. Thermogravimetric analysis, PXRD, EDX and XPS study of chrysocolla (Cu,Al)2H2Si2O5(OH)4·nH2O: Structural implications. *Thermochim. Acta* 2012, 545, 157–162. [CrossRef]
- Shen, P.; Liu, D.; Zhang, X.; Jia, X.; Song, K.; Liu, D. Effect of (NH4)2SO4 on eliminating the depression of excess sulfide ions in the sulfidization flotation of malachite. *Miner. Eng.* 2019, 137, 43–52. [CrossRef]
- 8. Feng, Q.; Zhao, W.; Wen, S. Surface modification of malachite with ethanediamine and its effect on sulfidization flotation. *Appl. Surf. Sci.* 2018, 436, 823–831. [CrossRef]
- 9. Yin, W.; Sun, Q.; Li, D.; Tian, Y.; Fu, Y.; Yao, J. Mechanism and application on sulphidizing flotation of copper oxide with combined collectors. *Trans. Nonferrous Met. Soc. China* **2019**, *29*, 178–185. [CrossRef]
- Kapiamba, K.F.; Kimpiab, M. The effects of partially replacing amine collectors by a commercial frother in a reverse cationic hematite flotation. *Heliyon* 2021, 7, e06559. [CrossRef]

- Liu, G.; Huang, Y.; Qu, X.; Xiao, J.; Yang, X.; Xu, Z. Understanding the hydrophobic mechanism of 3-hexyl-4-amino-1, 2,4-triazole-5-thione to malachite by ToF-SIMS, XPS, FTIR, contact angle, zeta potential and micro-flotation. *Colloids Surf. A-Physicochem. Eng. Asp.* 2016, 503, 34–42. [CrossRef]
- 12. Castro, S.; Soto, H.; Goldfarb, J.; Laskowski, J. Sulphidizing reactions in the flotation of oxidized copper minerals, II. Role of the adsorption and oxidation of sodium sulphide in the flotation of chrysocolla and malachite. *Int. J. Miner. Process.* **1974**, *1*, 151–161. [CrossRef]
- 13. Shengo, L.M.; Gaydardzhiev, S.; Kalenga, N.M. Assessment of water quality effects on flotation of copper-cobalt oxide ore. *Miner. Eng.* **2014**, *65*, 145–148. [CrossRef]
- 14. Zhou, R.; Chander, S. Kinetics of sulfidization of malachite in hydrosulfide and tetrasulfide solutions. *Int. J. Miner. Process.* **1993**, 37, 257–272. [CrossRef]
- 15. Feng, Q.; Wen, S.; Deng, J.; Zhao, W. Combined DFT and XPS investigation of enhanced adsorption of sulfide species onto cerussite by surface modification with chloride. *Appl. Surf. Sci.* **2017**, *425*, 8–15. [CrossRef]
- Smith, J.A.; Mulhall, R.; Goodman, S.; Fleming, G.; Allison, H.; Raval, R.; Hasell, T. Investigating the Antibacterial Properties of Inverse Vulcanized Sulfur Polymers. ACS Omega 2020, 5, 5229–5234. [CrossRef]
- 17. Raghavan, S.; Adamec, E.; Lee, L. Sulfidization and flotation of chrysocolla and brochantite. *Int. J. Miner. Process.* **1984**, *12*, 173–191. [CrossRef]
- 18. Soto, H.; Laskowski, J. Redox conditions in the flotation of malachite with a sulphidizing agent. *Trans. Inst. Min. Metall. C Miner. Process. Extract. Metall.* **1973**, *82*, c153–c157.
- Yin, W.Z.; Sheng, Q.Y.; Ma, Y.Q.; Sun, H.R.; Yang, B.; Tang, Y. Effects of copper ions on malachite sulfidization flotation. *Physicochem. Probl. Miner. Process.* 2020, 56, 300–312. [CrossRef]
- 20. Liu, C.; Feng, Q.; Zhang, G. Effect of ammonium sulfate on the sulfidation flotation of malachite. *Arch. Min. Sci.* **2018**, *63*, 139–148. [CrossRef]
- Li, F.; Zhong, H.; Xu, H.; Jia, H.; Liu, G. Flotation behavior and adsorption mechanism of α-hydroxyoctyl phosphinic acid to malachite. *Miner. Eng.* 2015, 71, 188–193. [CrossRef]
- 22. Liu, D.; Fang, J.; Zhang, X.; Wen, S.; Wei, Z.; Bai, S.; Xu, B.; Zhang, W. Sulfidisation Promotion Effect of Ammonium Sulfate on Flotation of Copper Oxide Ore. *Adv. Mater. Res.* **2012**, *524*, 1109–1114. [CrossRef]
- 23. Liu, R.; Liu, Z.; Li, J.; Ao, S.; Pei, B.; Liu, D.; Li, J. Reexamining the Role of Ammonium Ions in the Sulfidization, Xanthate-Flotation of Malachite. *Minerals* 2020, *10*, 537. [CrossRef]
- Banjarnahor, S.; Rodionov, R.N.; Konig, J.; Maas, R. Transport of L-Arginine Related Cardiovascular Risk Markers. J. Clin. Med. 2020, 9, 3975. [CrossRef] [PubMed]
- 25. Feng, Q.; Zhao, W.; Wen, S.; Cao, Q. Copper sulfide species formed on malachite surfaces in relation to flotation. *J. Ind. Eng. Chem.* **2017**, *48*, 125–132. [CrossRef]
- Ejtemaei, M.; Gharabaghi, M.; Irannajad, M. A review of zinc oxide mineral beneficiation using flotation method. *Adv. Colloid Interface Sci.* 2014, 206, 68–78. [CrossRef]
- Chen, D.X.; Liu, M.F.; Hu, B.; Dong, Y.H.; Xue, W.; He, P.; Chen, F.; Zhu, J.Y.; Zhang, C.Y. New insights into the promotion mechanism of (NH4)<sub>2</sub>SO<sub>4</sub> in sulfidization flotation: A combined experimental and computational study. *Physicochem. Probl. Miner. Process.* 2021, 57, 57–70. [CrossRef]
- 28. Hu, Y.; Qiu, G.; Cheng, Y.; Wang, D. Solution chemistry studies on flotation of malachite and smithsonite. *Nonferrous Met.* **1996**, *48*, 40–44.
- 29. Bessière, J.; Housni, A.E. Dielectric study of activation and deactivation of malachite by sulfide ions. *Int. J. Miner. Process.* **1991**, 33, 165–183. [CrossRef]
- Park, K.; Park, S.; Choi, J.; Kim, G.; Tong, M.; Kim, H. Influence of excess sulfide ions on the malachite-bubble interaction in the presence of thiol-collector. *Sep. Purif. Technol.* 2016, 168, 1–7. [CrossRef]
- 31. Kartio, I.J.; Basilio, C.I.; Yoon, R.H. An XPS study of sphalerite activation by copper. Langmuir 1998, 14, 5274–5278. [CrossRef]
- 32. Lotter, N.O.; Bradshaw, D.J.; Barnes, A.R. Classification of the Major Copper Sulphides into semiconductor types, and associated flotation characteristics. *Miner. Eng.* 2016, 96–97, 177–184. [CrossRef]
- 33. Chen, X.; Peng, Y.; Bradshaw, D. The separation of chalcopyrite and chalcocite from pyrite in cleaner flotation after regrinding. *Miner. Eng.* **2014**, *58*, 64–72. [CrossRef]
- Fairthorne, G.; Fornasiero, D.; Ralston, J. Effect of oxidation on the collectorless flotation of chalcopyrite. *Int. J. Miner. Process.* 1997, 49, 31–48. [CrossRef]
- He, Z.; Liu, G.; Yang, X.; Liu, W. A novel surfactant, N, N-diethyl-N'-cyclohexylthiourea: Synthesis, flotation and adsorption on chalcopyrite. J. Ind. Eng. Chem. 2016, 37, 107–114. [CrossRef]
- 36. Gan, Y.; Deng, R.; Liu, Q. Surface characteristics, collector adsorption, and flotation response of covellite in oxidizing environment. *Trans. Nonferrous Met. Soc. China* 2022, 32, 657–667. [CrossRef]
- 37. Li, F.; Zhou, X.; Lin, R. Flotation performance and adsorption mechanism of novel 1-(2-hydroxyphenyl)hex-2-en-1-one oxime flotation collector to malachite. *Trans. Nonferrous Met. Soc. China* **2020**, *30*, 2792–2801. [CrossRef]
- De Giudici, G.; Rossi, A.; Fanfani, L.; Lattanzi, P. Mechanisms of galena dissolution in oxygen-saturated solutions: Evaluation of pH effect on apparent activation energies and mineral-water interface. *Geochim. Cosmochim. Acta* 2005, 69, 2321–2331. [CrossRef]

- 39. Ikumapayi, F.; Makitalo, M.; Johansson, B.; Rao, K.H. Recycling of process water in sulphide flotation: Effect of calcium and sulphate ions on flotation of galena. *Miner. Eng.* **2012**, *39*, 77–88. [CrossRef]
- 40. 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. [CrossRef]
- Smart, R.S.; Skinner, W.M.; Gerson, A.R. XPS of sulphide mineral surfaces: Metal-deficient, polysulphides, defects and elemental sulphur. Surf. Interface Anal. 1999, 28, 101–105. [CrossRef]
- 42. Siriwardane, R.V.; Cook, J.M. Interactions of NO and SO<sub>2</sub> with iron deposited on silica. *J. Colloid Interface Sci.* **1985**, *104*, 250–257. [CrossRef]
- 43. Turner, N.H. Summary Abstract: Quantitative determination of the surface composition of sulfur-bearing anion mixtures by Auger electron spectroscopy. J. Vac. Sci. Technol. A Vac. Surf. Film. 1980, 17, 84–92. [CrossRef]
- 44. Liu, M.; Zhang, C.; Hu, B.; Sun, Z.; Chen, D. Enhancing flotation separation of chalcopyrite and galena by the surface synergism between sodium sulfite and sodium lignosulfonate. *Appl. Surf. Sci.* **2020**, *507*, 145042. [CrossRef]
- 45. Yu, X.; Zhang, R.; Zeng, Y.; Cheng, C.; Huang, Z.; Wang, J.; He, G.; Wang, H. The effect and mechanism of cinnamic hydroxamic acid as a collector in flotation separation of malachite and calcite. *Miner. Eng.* **2021**, *164*, 106847. [CrossRef]
- Li, Z.; Rao, F.; Song, S.; Uribe, S.A.; Lopez, V.A. Effects of common ions on adsorption and flotation of malachite with salicylaldoxime. *Colloids Surf. A-Physicochem. Eng. Asp.* 2019, 577, 421–428. [CrossRef]