

## Article

# New Insights into the Role of Thiol Collectors in Malachite Flotation

Congren Yang <sup>1</sup>, Siying Chen <sup>1</sup>, Haodong Li <sup>2</sup> and Wenqing Qin <sup>1,\*</sup><sup>1</sup> School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China<sup>2</sup> Zijin Mining Group Co., Ltd., Xiamen 361000, China

\* Correspondence: qinwenqing369@126.com

**Abstract:** Malachite is one of the most important copper-bearing oxide minerals; however, it shows poor floatability prior to sulfidization under the thiol collector system. This study investigated the reasons for the low recovery of malachite flotation without sulfidization. The results of adsorption capacity and contact angle test indicated that the malachite surface could adsorb a sufficient amount of the collector, obviously increasing the hydrophobicity of the malachite surface under static conditions. By measuring the amount of inorganic carbon in the flotation solution, it was found that the amount of inorganic carbon in the solution increased significantly when the thiol collectors were added into pulp, which could be attributed to the induced dissolution of the malachite surface by thiol collectors. Solubility tests further demonstrated that the copper ions released from the natural dissolution of malachite proved difficult in regard to reactions with thiol collector to form precipitates; however, the thiol collector induced the dissolution of malachite surface, and so the hydrophobic complexes' copper-collector could not firmly adsorb on the mineral surface. Fourier transform infrared (FTIR) analysis revealed that thiol collectors do not adsorb stably on malachite surfaces. This was considered to be a substantial reason for the poor performance of malachite flotation without sulfidization.

**Keywords:** malachite; induced dissolution; thiol collector; flotation without sulfidization



**Citation:** Yang, C.; Chen, S.; Li, H.; Qin, W. New Insights into the Role of Thiol Collectors in Malachite Flotation. *Minerals* **2024**, *14*, 483. <https://doi.org/10.3390/min14050483>

Academic Editor: Dave Deglon

Received: 28 March 2024

Revised: 24 April 2024

Accepted: 29 April 2024

Published: 30 April 2024



**Copyright:** © 2024 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/>).

## 1. Introduction

Copper is widely used in power transmission, air conditioning refrigeration, transportation, electronics, construction and other industries, and it has also proven to be an indispensable base metal in the national industrial system [1–4]. By 2025, global copper demand will rise to around 29 million tonnes, of which 83.5% will be used in renewable energy industries such as wind power and energy storage [5,6]. Therefore, the stable supply of copper resources has aroused widespread concerns [6–9]. Copper sulfide minerals and copper oxide minerals are two major copper-bearing resources in natural deposits [10,11]. Generally speaking, copper sulfide minerals exhibit good floatability with thiol collector, as their inherent surface properties allow them to easily interact with thiol collectors, forming hydrophobic complexes on mineral surfaces [12,13]. However, copper oxide minerals, unlike copper sulfide minerals, are generally characterized by non-conductivity, so they do not respond efficiently to thiol collectors in flotation [14–17]. Malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) is one of the most common copper oxide minerals, and numerous investigations have indicated that it was difficult to achieve efficient recovery of malachite by flotation without sulfidization using thiol collectors [18,19], but such a procedure, featuring the sulfidization of malachite before flotation, was feasible to remarkably promote the flotation recovery of malachite with thiol collectors [20–23]. It was reported that there were various reasons accounting for the drawback of malachite flotation without sulfidization: (1) the adsorption layer of thiol collectors on the malachite surface is unstable [24,25], which some researchers believe is because the stability index of the thiol collector's adsorption layer on the surface of malachite is too low [26,27]; (2) malachite is prone to metal ion dissolution, meaning that

the collector will react with the metal ions in solution, resulting in a high collector dosage requirement [26,28,29]; (3) the portion of ionic bonding in the crystal lattice of malachite is high, leading to the establishment of a stronger hydrated shell [30]; (4) copper oxide minerals often exhibit a metal-deficient surface in pulp due to their high solubility, which is detrimental to xanthate adsorption [31,32].

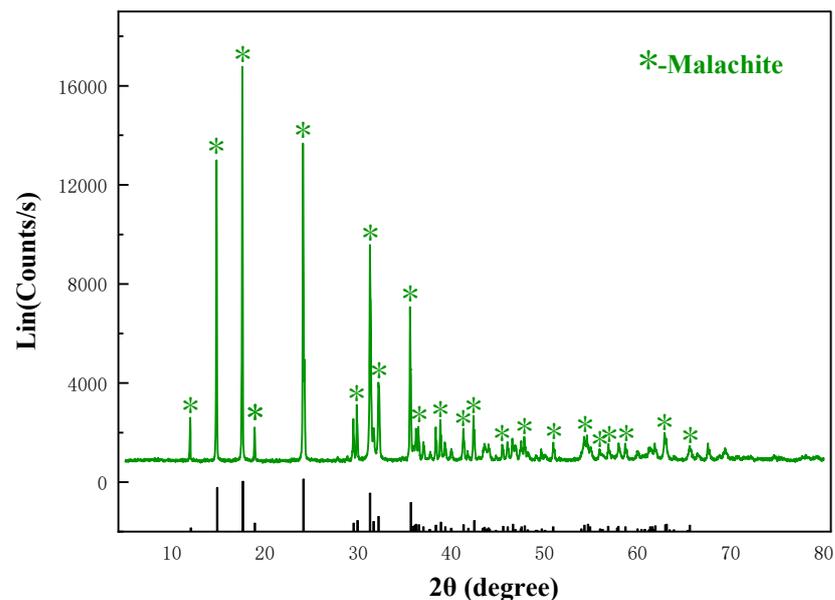
For the efficient flotation of malachite, some new mechanisms have now been proposed. Qiming Zhuo et al. [33] observed sulfide product evolution on malachite surfaces treated with sodium sulfide. The results revealed the direct growth process of the sulfide film on malachite, the presence of Cu(I) in sulfide products, and the sulfide film's role in promoting the formation of butyl xanthate layers and enhancing interfacial interactions between malachite and bubbles. The development of new chelating collectors is also of great significance for the efficient flotation of malachite. Jun Liu et al. [34] found that TMATT exhibits superior hydrophobicity and flotation performance for malachite. The adsorption mechanism of TMATT was revealed and involves the reduction of Cu(II) to Cu(I) and the formation of TMATT-Cu(I) complexes, which enhances its flotation response to malachite over calcite. Zhang Xingrong et al. [35] investigated the flotation separation of malachite from calcite using a new chelating collector, CMDTP. CMDTP exhibited a superior performance compared to other collectors. Successful separation was achieved at pH 9.0 with Na<sub>2</sub>S as a regulator. Its affinity for a malachite surface was stronger than for calcite, with CMDTP reacting easily with Cu<sup>2+</sup> sites on malachite.

Many of the above-mentioned reasons could be found to explain the importance and necessity of sulfidization during malachite flotation in the available literature; however, few studies have tried to systematically explain the reason for the poor floatability of malachite flotation without sulfidization using thiol collectors. There is no doubt that a comprehensive understanding of the reason for the poor floatability of malachite is crucial in identifying the root cause of inefficiency of flotation without sulfidization. Such an understanding will also help to modify malachite flotation for an improved recovery and efficiency while allowing us to better understand the interaction between malachite and thiol collectors. In this study, the effect of the surface dissolution behavior of malachite on its flotation was studied under a thiol collector system. This was accomplished through the use of a series of experiments and analytical techniques, including micro-flotation tests, adsorption capacity tests and organic carbon content determinations. The findings presented in this study provided new evidence for the poor floatability of malachite without sulfidization and could inspire scholars in related fields to formulate corresponding countermeasures to optimize or maximize the utilization efficiency of malachite.

## 2. Materials and Methods

### 2.1. Materials and Reagents

The malachite samples used in this study were obtained from the Yunnan province, China, and the results of chemical analysis indicated the malachite contained 56.58% Cu, similar to its theoretical copper mass fraction at 57.57%. The characteristic diffraction peak at  $2\theta$  of 14.800°, 17.567°, 24.090°, 31.275° and 35.574° is in good accordance with the reported data (PDF# 41-1390), and any other impurity diffraction peaks can be observed in the X-ray diffraction pattern, indicating that the purity of the malachite sample exceeds 95%. Malachite samples were crushed, followed by being ground using agate mortar, and they were then sieved to obtain powder particles with two size fractions. The malachite particles with a size of  $-75 + 38 \mu\text{m}$  were used for micro-flotation, adsorption amount determination and inorganic carbon (IC) measurement, and those with a size of  $-38 \mu\text{m}$  were further ground to less than 5  $\mu\text{m}$  to be used for chemical analysis, X-ray diffraction (XRD) analysis and solubility testing. Bulk malachite samples were used in the contact angle test. The X-ray diffraction analysis results of malachite samples are shown in Figure 1.



**Figure 1.** The XRD analysis results of malachite.

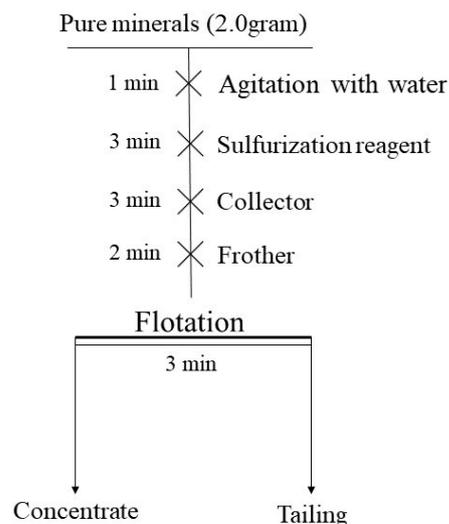
Thiol collectors are characterized by having one minerophilic thiol group (-SH) at the polar end and one or two hydrophobic alkyl groups (-RH) at the nonpolar end of their molecule structures. The main types of thiol collectors include xanthates, dithiophosphates and dithiocarbamates, and five specific types (ethyl xanthate (EX), butyl xanthate (BX), pentyl xanthate (PX), sodium diethyldithiocarbamate (DDTC) and ammonium dibutyl dithiophosphate (DDTP)) were used in this study. The purity of the thiol collectors was more than 95%. Analytical-grade  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and methyl isobutyl carbinol (MIBC) were employed as the sulfidizing agent and foaming agent, respectively. The deionized (DI) water was used in all tests.

## 2.2. Micro-Flotation Experiments

All micro-flotation experiments were carried out using an XFG series laboratory flotation machine (Jilin Exploration Equipment, Changchun, China) with a flotation cell (effective volume 40 mL). The spindle speed of the flotation machine was set at 1690 rpm. The micro-flotation procedure proceeded as follows: First, prior to each test, pure mineral particles (2 g) and distilled water (35 mL) were sequentially added into 40 mL plexiglass cells and stirred for one minute to prepare the slurry. In sulfidization flotation,  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  was added as a sulfidizing agent and conditioned for 3 min. Next, one of the five thiol collectors and methyl isobutylcarbinol (MIBC) as a frother were added into the slurry in sequence, then conditioned for 3 min and 2 min, respectively. The time for froth collection was 3 min. The flowsheet of microflotation was presented in Figure 2. Finally, the concentrates and tailings were separately collected, dried and then weighted, and the malachite recovery was calculated using Equation (1). Each experiment was repeated three times and averaged.

$$\varepsilon = \frac{m_1}{m_1 + m_2} \times 100\% \quad (1)$$

where  $\varepsilon$  represents flotation recovery (%);  $m_1$  and  $m_2$  represent masses (g) of concentrates and tailings, respectively.



**Figure 2.** Flowsheet of micro-flotation experiment.

### 2.3. Adsorption Amount Determinations

A TOC-LCPH analyser (Shimadzu, Kyoto, Japan) was used to determine the amount of each thiol collector adsorbed on the malachite surface by measuring the residual concentration of total organic carbon in the supernatant. The adsorption test protocol was carried out as follows: First, 2.0 g of malachite sample ( $-75 + 38 \mu\text{m}$ ) was dispersed in 35 mL of DI water. The malachite-DI-water mixture was then agitated at 1690 rpm for 3 min to produce a suspension. Each collector was then added to the suspension and stirred at 1690 rpm for a further 3 min. The resulting suspension was centrifuged at 9000 rpm for 20 min to separate the solids from the liquid. The supernatant was then collected for further analysis. The amount of flotation reagents adsorbed on the mineral surface was calculated using the residual concentration method.

$$\Gamma = \frac{(C_0 - C)V}{M} \quad (2)$$

where  $C_0$  and  $C$  are the initial and final concentrations (mg/L) of the flotation reagents, respectively;  $V$  is the volume (mL) of the flotation slurry; and  $M$  is the weight (g) of the mineral samples.

### 2.4. Inorganic Carbon Measurement

TOC-LCPH Analyzer (Shimadzu, Kyoto, Japan) was used to quantitatively determine the concentration of inorganic carbon in the supernatant after centrifugation. There are four potential sources of IC in supernatant, i.e., blank DI water, thiol collectors added, natural dissolution of malachite, and malachite dissolution induced by thiol collectors, and the testing procedure for inorganic carbon (IC) measurement was performed as follows: (1) The inorganic carbon content in DI water was determined and denoted  $C_1$ , which was set up as a blank control group. (2) A 2.0 g malachite sample ( $-75 + 38 \mu\text{m}$ ) was dispersed into 35 mL DI water and stirred at 1690 r/min for 3 min. Then, the suspension was filtered and centrifuged to separate the malachite from the slurry, followed by the determination of IC content in the supernatant, which was denoted as  $C_2$ , and the result of  $C_2 - C_1$  was responsible for the natural dissolution of malachite in the aqueous environment, releasing the inorganic anions, such as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , into the solution. (3) Each solution of the five thiol collectors was diluted to the desired concentration used in micro-flotation, and the corresponding IC content in each collector solution was determined separately and denoted as  $C_3$ . The result of  $C_3 - C_1$  was the amount of inorganic carbon released into the solution by the dissolution of each collector. (4) Malachite samples were added to the flotation cell, and then each thiol collector, at different concentrations, was added to interact with the malachite. The stirring time (3 min) and spindle speed (1690 r/min) were consistent

with that of the micro-flotation experiment. The suspension was filtered and centrifuged to separate the malachite from the slurry, followed by the determination of IC content in the supernatant, which was denoted as  $C_4$ . The result of  $(C_4 - C_1) - (C_2 - C_1) - (C_3 - C_1)$  was identified as the amount of IC released into the solution after the action of malachite with the thiol collector, which could be attributed to the malachite dissolution induced by thiol collectors. To determine the amount of inorganic carbon released into the slurry by the sulfidized malachite, only the step of sulfidization was added to Steps (2) and (4). The conditions for sulfidization remained the same as for the micro-flotation experiment.

### 2.5. Contact Angle Test

Using the JY-82C Automatic Video Contact Angle Meter (Ding-sheng Tester, Chengde, China), contact angle measurements were conducted through the sessile drop method. Initially, ore samples of  $2.0 \times 2.0 \times 1.0 \text{ cm}^3$  were prepared by cutting mineral samples with surfaces identical to those used in the micro-flotation experiments. These block ore samples were then sequentially polished using Wuxi brand sandpaper of various mesh sizes (200, 600, 1000, 2000 and 3000 mesh). Prior to testing, the polished samples were immersed in a beaker containing 35 mL of DI water. The samples were then treated with the required amount of flotation reagents, rinsed repeatedly with DI water and dried with nitrogen. A drop of DI water was deposited on the surface of the treated sample and a series of microscopic images were taken. The most stable image was selected for analysis to determine the contact angle. Following the measurement, the tested sample surface was cleaned with soap and a soft toothbrush, dried, re-polished with 3000 mesh sandpaper, rinsed with DI water and prepared for the next round of tests.

### 2.6. Solubility Test

A solubility test was designed to clarify the reason for the large consumption of thiol collector. The testing procedure for solubility of malachite was performed as follows: (1) The solution of thiol collector with a curtailed concentration (e.g., 150 mg/L) was prepared and denoted as solution A. (2) A 2.0 g sample of malachite powder ( $-38 \mu\text{m}$ ) was dispersed into 35 mL DI water and stirred at 1690 r/min for 3 min, and then the suspension was filtered to obtain the supernatant, which was denoted as solution B. (3) An amount of 2.0 g of solution A was added to 10 mL of solution B, obtaining solution C, which was then shook well in order for the changes to be observed. (4) An amount of 2.0 g of solution B was added to 10 mL of solution A, obtaining solution D, which was then shook well so the changes could be observed. (5) A 0.57 g sample of malachite powder ( $-38 \mu\text{m}$ ) was added to 10 mL of solution A, obtaining solution E, which was then shook well so the changes could be observed.

ICP-OES (PlasmaQuant PQ9000, Jena, Germany) was used to detect the total Cu concentration in the slurry. Malachite samples ( $-75 + 38 \mu\text{m}$ ) of 2.0 g were dispersed into 35 mL DI water, and each of the five thiol collectors was stirred at 1690 r/min for 3 min. Then, the suspension was filtered and centrifuged to separate the malachite from the slurry, followed by the determination of Cu content in the supernatant.

### 2.7. FTIR Spectra

FTIR was used to determine the presence of the adsorption collector. The massive malachite ( $\Phi 20 \text{ mm}$ ) was divided into two groups, with one group being treated with sulfidizing agent under conditions consistent with the sulfidization flotation tests while the other group was left untreated. The resulting massive malachite samples were fixed to the impeller of the flotation machine with synthetic fibers, as shown in Figure 3. The concentration of collector in the flotation cell was fixed at 150 mg/L, and the stirring time was kept the same as that of the micro-flotation test. The external force on the surface of the malachite was varied by changing the spindle speed of the flotation machine and by adding quartz to the flotation tanks; the FTIR spectra of the massive malachite samples were determined separately. The effect of external forces on the stability of the adsorption

of the thiol collector on the malachite surface was determined by comparing the FTIR spectra of the individual massive malachite samples.

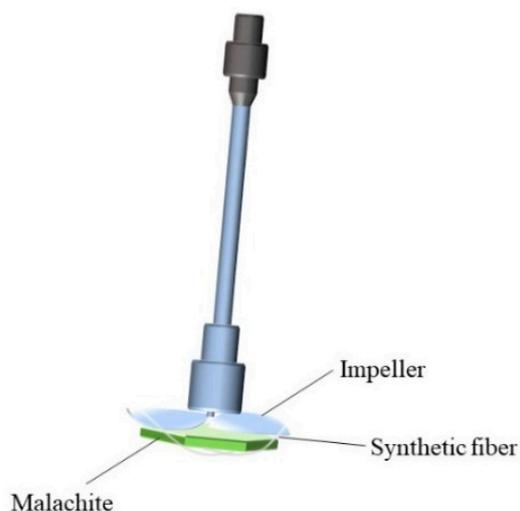


Figure 3. Flotation machine stirring section.

### 3. Results and Discussion

#### 3.1. Micro-Flotation Experiments

As shown in Figure 4, the results indicate that sulfidization can significantly improve the recovery of malachite. Although the recovery rate of malachite flotation without sulfidization presented an obvious upward trend with the increase in collector concentration, it was not satisfactory. The best results were observed in the flotation group using sodium diethyl dithiocarbamate (DDTC) as the collector at a dosage of 200 mg/L, but the recovery rate of the malachite only reached 25%. Additionally, the lowest flotation recovery of sulfidized malachite was 40%. From above results, it was confirmed that, in the absence of sulfurization, the flotation effect of the thiol collector on malachite was poor even if the concentration of the collector was increased to a high level, which was consistent with the literature reports.

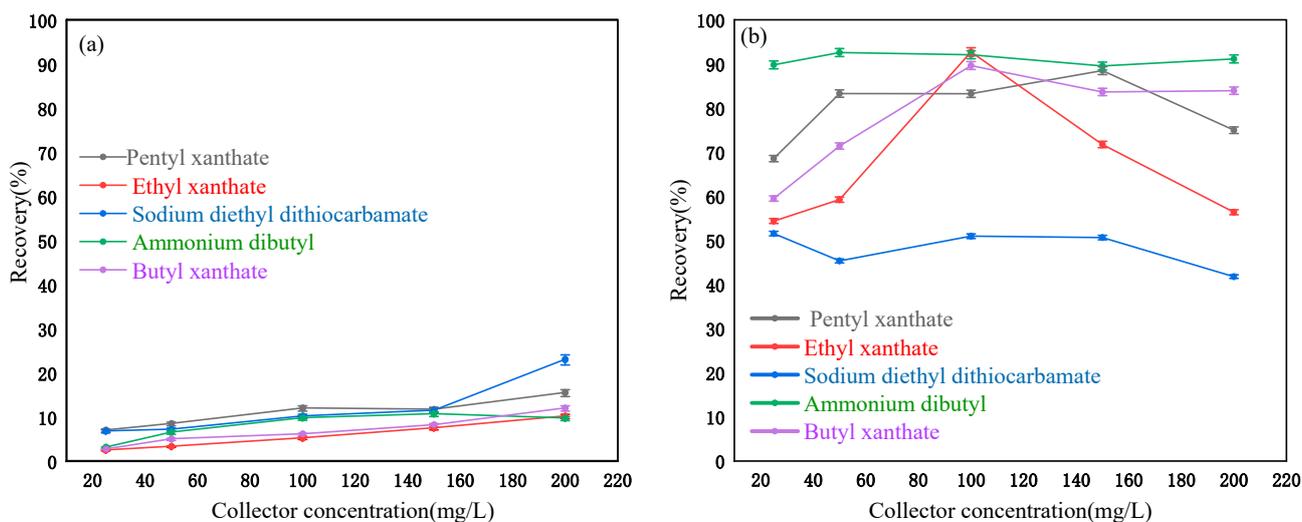
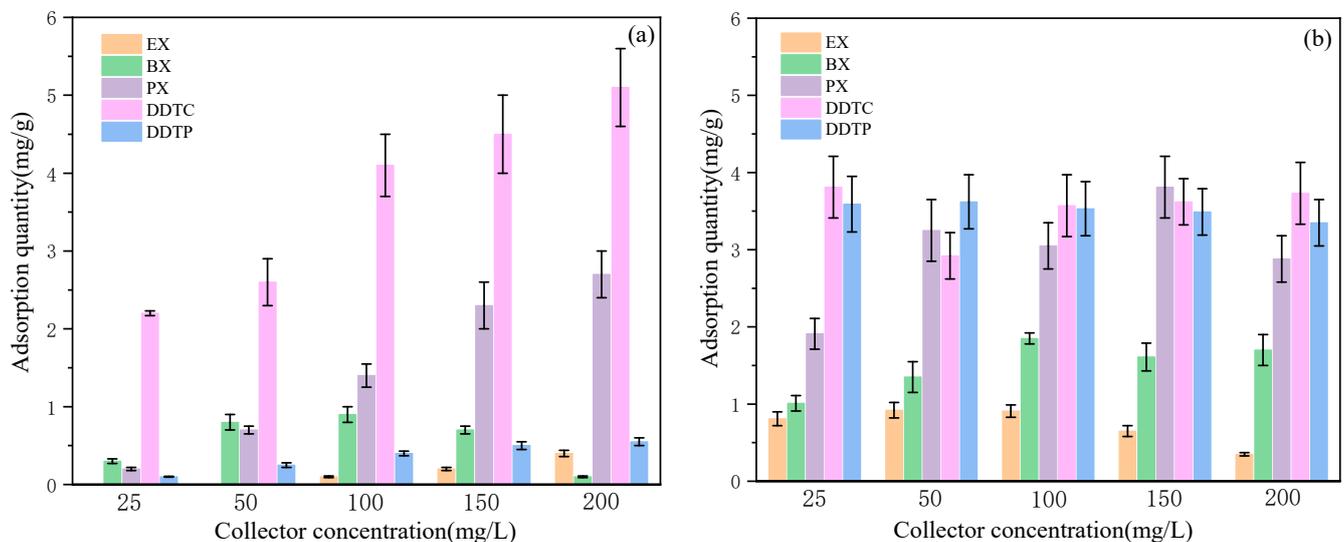


Figure 4. The flotation recovery with different thiol collectors of: (a) Malachite flotation without sulfidization, (b) Sulfidized malachite.

### 3.2. Adsorption Amount Measurements

In general, there is a direct relationship between the floatability of a mineral and the amount of collector adsorbed on its surface during the flotation. In order to find out the relationship between the recovery rate of malachite and the adsorption amount of collector on its surface, the residual concentration method was used in this section to determinate the adsorption amount of collector on malachite surface at different concentrations. As illustrated in Figure 5a, it could be seen that the adsorption amount increased with the increase in collector concentration. However, as illustrated in Figure 4a, although there was an obvious increase in the adsorption amount of collector on the malachite surface, it did not result in a satisfactory recovery of malachite all the time. This is consistent with what other researchers have observed [26,29]. Figure 5b demonstrates the adsorption of sulfidized malachite to different concentrations of collectors. From the figure, it can be seen that the adsorption of sulfidized malachite to the collectors does not increase with the increase in the concentration of the collectors, indicating that it can be effectively floated as long as it adsorbs a certain amount of the collectors. It was reported that the adsorption amount of thiol collector (i.e., xanthate) on the sulfurized malachite surface was similar to that of the untreated malachite surface, but the recovery of sulfurized malachite by xanthate collector was greatly improved and satisfactory [17,36]. Therefore, it could be found that, during the un-sulfurized malachite flotation with thiol collectors, the adsorption amount of collector on mineral surface was not low and should not be the main cause of low flotation recovery of un-sulfurized malachite in this study. The low flotation recovery of untreated malachite may be due to the unstable adsorption of thiol collectors on the surface of malachite. The adsorption amount of different thiol collectors on malachite surface as a function of collector concentration were shown in Figure 5.

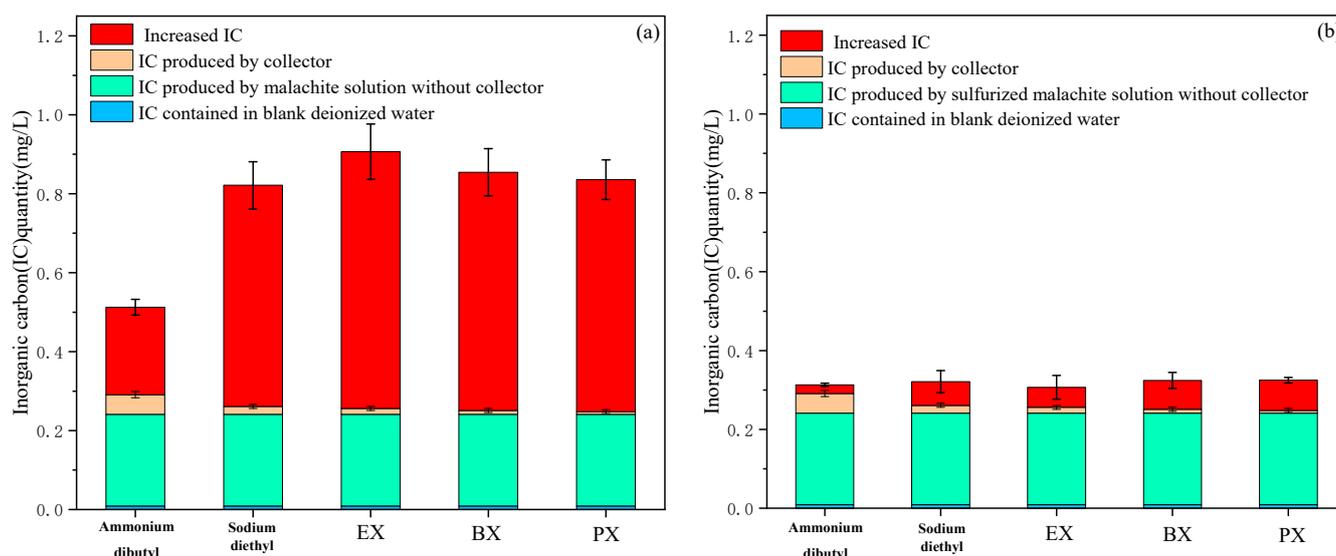


**Figure 5.** Adsorption amount of different thiol collectors on: (a) Malachite without sulfidization, (b) Sulfidized malachite.

### 3.3. Inorganic Carbon Measurement

As illustrated in Figure 6a, after the interaction of malachite with five thiol collectors, the detected amount of inorganic carbon released into the solution was obviously higher than the total amount of inorganic carbon sourced from the DI water itself, the natural dissolution of malachite in the pure water environment, and the thiol collectors added to the flotation system. In other words, there was a macroscopic increase in the inorganic carbon in the solution after the reaction of malachite with the collector. The reason for this result might be that the presence of thiol collectors could induce the dissolution of malachite, leading to the acceleration of surface dissolution of malachite and the release of extra amounts of inorganic carbon, such as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , into the solution. This was

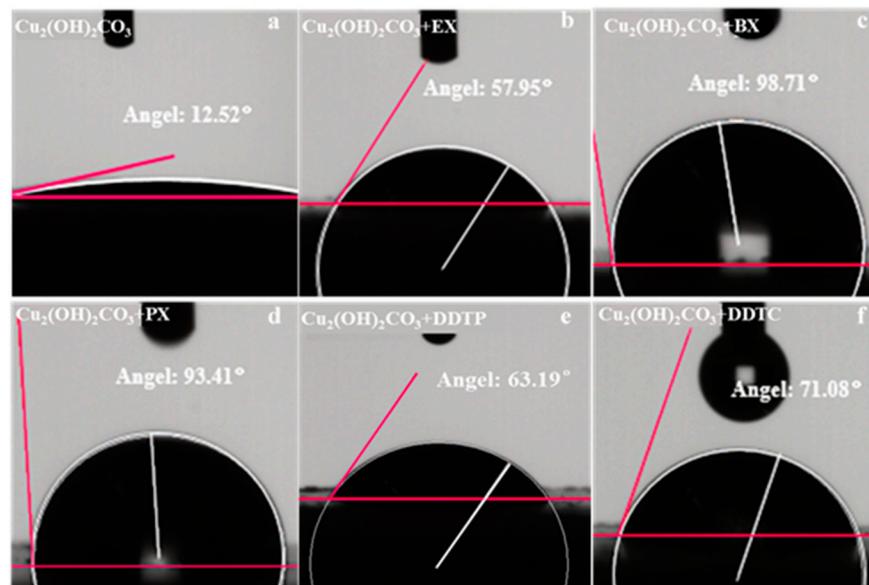
considered to be an important aspect that could account for the poor flotation of malachite with thiol collectors in this study, i.e., the presence of thiol collector accelerated the surface dissolution of malachite, which made it difficult for the collectors to stably adsorb on the mineral surfaces or caused the adsorbed collectors to fall off from the mineral surfaces. In contrast, as shown in Figure 6b, the amount of inorganic carbon released into the solution was found to be much less than that of malachite without sulfidization when sulfidized malachite was treated with the thiol collectors. This suggests that sulfidization is capable of potentially inhibiting the induced dissolution of thiol collectors on the surface of malachite.



**Figure 6.** Amount of inorganic carbon in solution during flotation of malachite with (a) Malachite without sulfidization, (b) Sulfidized malachite.

### 3.4. Contact Angle Test

As shown in Figure 7a, the contact angle of malachite without flotation agent treatment was only  $12.52^\circ$ , indicating a strong hydrophilicity. As shown in Figure 7b–f, after reacting with five thiol collectors, the contact angle on the surface of malachite all increased significantly, indicating that the collector improved the hydrophobicity of malachite. This evidence supported the previous results of the adsorption amount measurements (i.e., the high contact angle of surface justified the sufficient adsorption amount of collectors). However, although the malachite surface tended to be hydrophobic under the action of thiol collectors, the flotation recovery was unsatisfactory (i.e., enough hydrophobicity did not return to a high recovery). The reason for the low recovery of flotation malachite might be that the surface dissolution of malachite induced by collectors resulted in the detachment of the collector adsorption layers, which led to the loss of hydrophobicity during the flotation. The effect of thiol collectors on the hydrophobicity and hydrophilicity of malachite is shown in Figure 7.

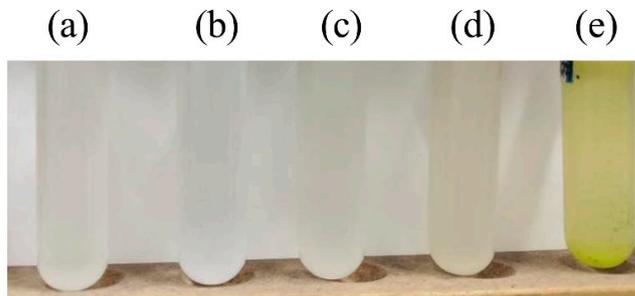


**Figure 7.** Contact angle of (a) Raw malachite ore, malachite treated with, (b) Ethyl xanthate, (c) Butyl xanthate, (d) Pentyl xanthate, (e) Ammonium dibutyl dithiophosphate (DDTP), (f) Sodium diethyl dithiocarbamate (DDTC).

### 3.5. Solubility Test

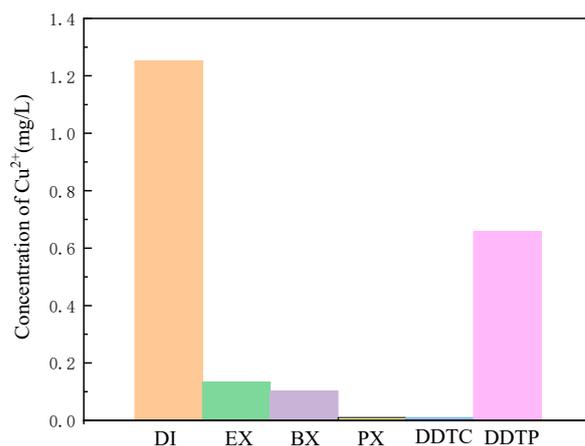
Some researchers believed that the reason for the poor flotation behavior of non-sulfurized malachite with thiol collector was that a large amount of collector was consumed by the dissolved copper ions from the soluble malachite surface [28,29]. To uncover the real reason for the poor flotation behavior of non-sulfurized malachite by thiol collectors, the solubility test was carried out in this section. As shown in Figure 8, solution A was the BX solution with a concentration of 150 mg/L, while solution B was the filtrate of malachite after stirring. BX solution was dropped into the filtrate of malachite, and no significant change in the color of the solution C was observed, as it remained clear even after shaking; conversely, there was also no significant change in the color of the solution when the filtrate of malachite was dropped into the BX solution, and solution D also remained clear. The above two facts indicated that the copper ions released by natural dissolution of malachite in aqueous system were too limited to react with the xanthate ( $X^-$ ) and form copper-xanthate precipitate; therefore, they could not have consumed a large amount of the thiol collector. Note that the solubility product ( $K_{sp}$ ) of copper-xanthate precipitate was about  $10^{-20}$ , which was so small that trace copper ions could be captured in solution and, consequently, a macroscopic phenomenon (i.e., yellow precipitate) could be observed. However, when a small amount of malachite powder was added to BX solution, a significant change in the color of the solution was observed after shaking the solution E well. The added malachite powder gradually reacted with the BX solution, forming the yellow precipitates, and the initial clear solution transformed into a yellow color. It thus could be found that, when malachite was exposed to the aqueous flotation system with thiol collector, its surface dissolution would be greatly accelerated because of the inducement of xanthate collector. As a result, a large amount of the copper ions and inorganic anions (e.g.,  $CO_3^{2-}$ ,  $HCO_3^-$ ) were released from the malachite surface. The copper sites on the mineral surface easily reacted directly with the collector, forming the copper-xanthate precipitates that were responsible for the hydrophobic surface of the malachite; however, a considerable number of precipitates fell off the malachite surface and entered the aqueous flotation system because of the accelerated dissolution of the malachite surface induced by thiol collector. The free copper-xanthate detached from malachite surface easily adhered to the flotation bubbles and was floated out. That was why the adsorption amount of collector detected on the malachite surface was not low, the inorganic carbon content in the solution

increased significantly after reaction, and the hydrophobic surface did not deliver a desired flotation recovery. The induced dissolution of the malachite surface by thiol collector might be one of the real reasons why malachite was difficult to float out with thiol collectors prior to sulfidization. The procedure of the solubility test is shown in Figure 8.



**Figure 8.** The procedure of solubility test: (a) Butyl xanthate, (b) Filtrate of malachite after stirring (c) Add butyl xanthate to the filtrate of malachite (d) Add the filtrate of malachite to butyl xanthate (e) Add malachite powder to butyl xanthate.

Above, the inorganic carbon measurement and solubility test were used to analyze the dissolution of the malachite surface. It is known that malachite surface dissolution can release copper ions. Therefore, this section focuses on the amount of copper ions released by malachite stirred in DI water and the aqueous flotation system with thiol collector. The concentration of copper ions in the stirred supernatant of malachite with DI water and thiol collectors was determined by ICP-OES analysis. As shown in Figure 9, the highest concentration of copper ions released from malachite after stirring in pure water was only 1.2 mg/L, which was not enough to consume a large amount of collector. The concentration of copper ions released from malachite in the collectors solution was lower than those released in DI water due to the reaction of copper ions with the collector to form a precipitate. The smaller the solubility product (Ksp) of copper-xanthate precipitate, the easier the precipitation, i.e., the smaller the concentration of copper ions in the supernatant. The solubility product (Ksp) of copper-xanthate precipitate is shown in Table 1.



**Figure 9.** Concentration of copper ions in the supernatant after malachite stirred with DI water and thiol collectors.

**Table 1.** The Ksp(PL<sub>MeX2</sub>) of copper-xanthate precipitate.

Thiol Collector	EX	BX	PX	DDTC	DDTP
Ksp(PL <sub>MeX2</sub> )	24.20	26.20	27.00	30.85	16.00

### 3.6. FTIR Spectra

In order to further investigate the stability of the adsorption of the thiol collector on the malachite surface, a FTIR analysis was carried out, and the results are shown in Figures 10 and 11. In the Infrared spectrogram of butyl xanthate shown in Figure 10, the asymmetric stretching vibration of C–O–C is observed at  $1310\text{ cm}^{-1}$ . The methylene group has a deformation vibrational absorption peak at  $1431\text{ cm}^{-1}$ . The vibrational absorption peak of C–O=S is at  $1631\text{ cm}^{-1}$ .

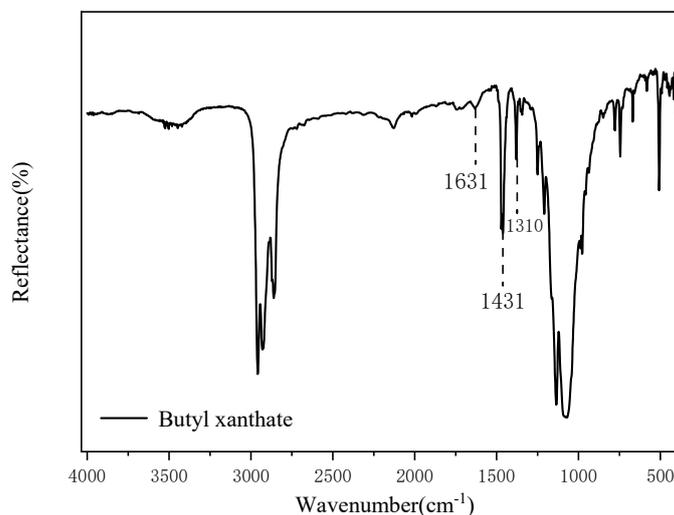


Figure 10. Infrared spectra of butyl xanthate used in this study.

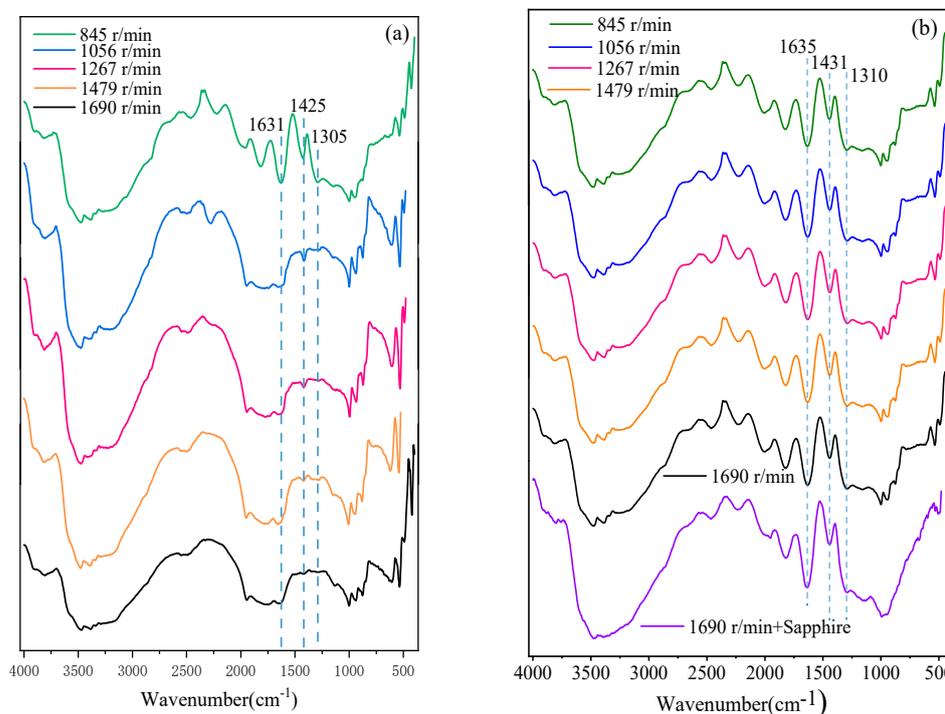
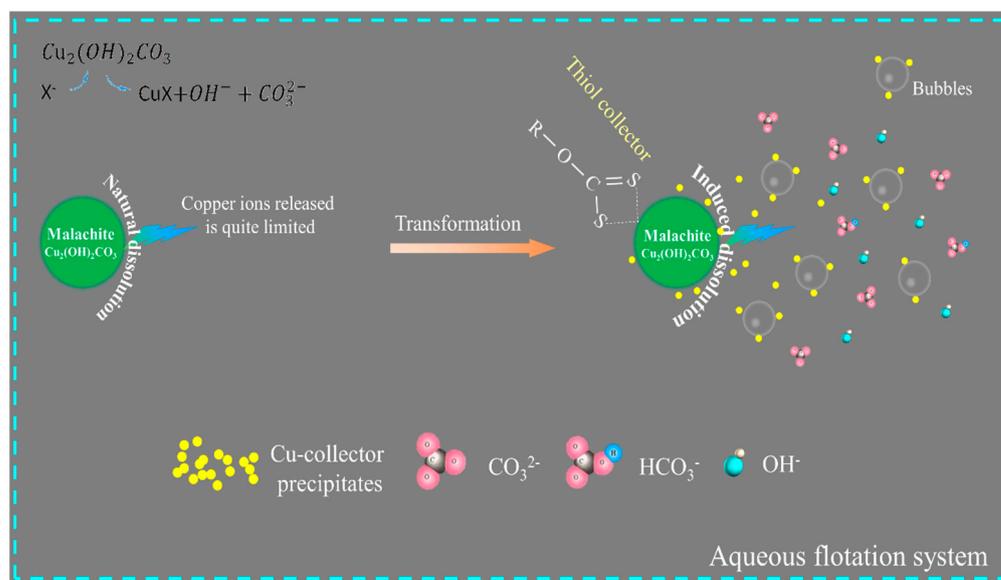


Figure 11. Infrared spectra of: (a) Massive malachite without sulfidization, (b) Sulfidized massive malachite.

Figure 11a shows the FTIR spectra of massive malachite after interaction with butyl xanthate at different spindle speeds of the flotation machine. From the figure, it can be established that the infrared spectra of the massive malachite samples showed absorption peaks at  $1304\text{ cm}^{-1}$ ,  $1425\text{ cm}^{-1}$  and  $1631\text{ cm}^{-1}$  when the spindle speed of the flotation

machine spindle was 845 r/min, indicating that butyl xanthate was adsorbed on the surface of the malachite. When the spindle speed of the flotation machine was increased to 1056 r/min, the absorption peaks at  $1031\text{ cm}^{-1}$  and  $1035\text{ cm}^{-1}$  had disappeared, and the absorption peak at  $1425\text{ cm}^{-1}$  was still present, although its intensity had diminished. With the gradual increase in the spindle speed, the intensity of the absorption peak at  $1425\text{ cm}^{-1}$  became weaker and weaker. When the spindle speed reached 1690 r/min, the characteristic peaks of butyl xanthate were hardly observed on the surface of the massive malachite. This result indicates that the xanthate collector is able to adsorb on the surface of malachite, but the adsorption is not stable, and the adsorbed layer of the collector falls off when there is an external force (for example, in an agitated fluid environment). The contradiction between the results of the previous contact angle test and the micro-flotation test is also well explained by this result. In the contact angle test, since the external force on malachite is small, the collector can still be adsorbed more firmly on the surface of the mineral, resulting in a large contact angle. However, during the micro-flotation test, the spindle speed of the flotation machine was too fast, and the fluid force on the malachite surface was sufficient to dislodge the poorly adsorbed collector, resulting in low flotation recoveries of malachite despite a large amount of collector being consumed.

Figure 11b shows the FTIR spectra of sulfidized malachite after interaction with butyl xanthate at different spindle speeds of the flotation machine. As can be seen from the figure, three infrared absorption peaks of butyl xanthate were always observed on the surface of the massive malachite even when the spindle speed was increased from 845 r/min to 1690 r/min. In order to increase the friction force on the surface of the malachite, 2.0 g of quartz particles with a size of  $-75 + 38\ \mu\text{m}$  were added to the flotation tank, the spindle speed was kept at 1690 r/min, and the infrared spectra of the surface of the massive malachite were tested. It was found that, even at the highest spindle speed and in the presence of friction from the quartz particles, three characteristic absorption peaks of the xanthate could be observed on the surface of the sulfidized malachite. This implies that sulfidization significantly improves the stability of the adsorption of the xanthate collector on the surface of malachite, explaining the previous results of micro-flotation as well as inorganic carbon measurement. The schematic model of the induced dissolution of the malachite surface by thiol collector is shown in Figure 12.



**Figure 12.** The schematic model of malachite dissolution induced by thiol collectors, taking xanthate as an example.

#### 4. Conclusions

The experimental findings reveal that, under static conditions, malachite surfaces without sulfidization exhibit a strong capacity to adsorb thiol collectors, resulting in a significant enhancement of their hydrophobicity. This property augmentation is particularly noteworthy given the potential for improved flotation efficiency. However, despite this positive adsorption behavior, a surprisingly low flotation recovery rate is observed, with the maximum only reaching 25% even when using high concentrations of DDTC. This discrepancy is attributed to the unstable adsorption of thiol collectors on the malachite surfaces during the flotation process. A significant increase in inorganic carbon levels in the solution upon the addition of thiol collectors is observed. This increase is attributed to the induced dissolution of malachite surfaces, a previously unrecognized phenomenon that adds a new dimension to the flotation mechanism. Furthermore, solubility tests demonstrate that, while copper ions released from natural malachite dissolution do not readily react with thiol collectors to form precipitates, the collectors themselves play a pivotal role in inducing surface dissolution.

**Author Contributions:** Conceptualization, C.Y.; investigation, S.C. and H.L.; writing—original draft preparation, S.C.; writing—review and editing, C.Y.; supervision, C.Y. and W.Q.; funding acquisition, C.Y. and W.Q. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China (Grant No. 51904339 and No. 51974364); Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources (Grant No. 2018TP1002); Co-Innovation Centre for Clean and Efficient Utilization of Strategic Metal Mineral Resources.

**Data Availability Statement:** Dataset available on request from the authors.

**Conflicts of Interest:** Haodong Li is employees of Zijin Mining Group Co., Ltd., the paper reflects the views of the scientists and not the company.

#### References

1. Liu, S.; Liu, W.; Tan, Q.Y.; Li, J.H.; Qin, W.Q.; Yang, C.R. The impact of China's import ban on global copper scrap flow network and the domestic copper sustainability. *Resour. Conserv. Recycl.* **2021**, *169*, 105525. [[CrossRef](#)]
2. Eheliyagoda, D.; Wei, F.; Shan, G.J.; Albalghiti, E.; Zeng, X.L.; Li, J.H. Examining the Temporal Demand and Sustainability of Copper in China. *Environ. Sci. Technol.* **2019**, *53*, 13812–13821. [[CrossRef](#)] [[PubMed](#)]
3. Hayes, R.; Price, D.; Ralston, J.; Smith, R. Collectorless flotation of sulphide minerals. *Miner. Process. Extr. Metall. Rev.* **1987**, *2*, 203–234. [[CrossRef](#)]
4. Cheng, X.; Iwasaki, I. Pulp potential and its implications to sulfide flotation. *Miner. Process. Extr. Metall. Rev.* **1992**, *11*, 187–210. [[CrossRef](#)]
5. Prior, T.; Giurco, D.; Mudd, G.; Mason, L.; Behrisch, J. Resource depletion, peak minerals and the implications for sustainable resource management. *Glob. Environ. Chang.-Hum. Policy Dimens.* **2012**, *22*, 577–587. [[CrossRef](#)]
6. Elshkaki, A.; Graedel, T.E.; Ciacci, L.; Reck, B.K. Copper demand, supply, and associated energy use to 2050. *Glob. Environ. Chang.-Hum. Policy Dimens.* **2016**, *39*, 305–315. [[CrossRef](#)]
7. Singer, D.A. Future copper resources. *Ore Geol. Rev.* **2017**, *86*, 271–279. [[CrossRef](#)]
8. Zhang, L.; Cai, Z.J.; Yang, J.M.; Yuan, Z.W.; Chen, Y. The future of copper in China—A perspective based on analysis of copper flows and stocks. *Sci. Total Environ.* **2015**, *536*, 142–149. [[CrossRef](#)]
9. 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](#)]
10. Ying, L.J.; Chen, Y.C.; Wang, D.H.; Tang, J.X.; Chen, Z.H.; Wang, C.H. A Preliminary Review of Metallogenic Regularity of Copper Deposits in China. *Acta Geol. Sin.-Engl. Ed.* **2015**, *89*, 251–269.
11. 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. Fuerstenau, M.C.; Jameson, G.J.; Yoon, R.-H. *Froth Flotation: A Century of Innovation*; Society for Mining, Metallurgy, and Exploration: Littleton, CO, USA, 2007; pp. 425–464.
13. Nagaraj, D.; Farinato, R. Evolution of flotation chemistry and chemicals: A century of innovations and the lingering challenges. *Miner. Eng.* **2016**, *96*, 2–14. [[CrossRef](#)]
14. Feng, Q.C.; Yang, W.H.; Wen, S.M.; Wang, H.; Zhao, W.J.; Han, G. Flotation of copper oxide minerals: A review. *Int. J. Min. Sci. Technol.* **2022**, *32*, 1351–1364. [[CrossRef](#)]

15. Lee, K.; Archibald, D.; McLean, J.; Reuter, M.A. Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors. *Miner. Eng.* **2009**, *22*, 395–401. [[CrossRef](#)]
16. Rao, S.; Finch, J. Base metal oxide flotation using long chain xanthates. *Int. J. Miner. Process.* **2003**, *69*, 251–258. [[CrossRef](#)]
17. 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](#)]
18. Lenormand, J.; Salman, T.; Yoon, R. Hydroxamate flotation of malachite. *Can. Metall. Q.* **1979**, *18*, 125–129. [[CrossRef](#)]
19. Li, Z.; Rao, F.; García, R.E.; Li, H.; Song, S. Partial replacement of sodium oleate using alcohols with different chain structures in malachite flotation. *Miner. Eng.* **2018**, *127*, 185–190. [[CrossRef](#)]
20. Soto, H.; Laskowski, J. Redox conditions in the flotation of malachite with sulphidizing agent. *Trans. Inst. Min. Metall. C Miner. Process. Extract. Metall.* **1973**, *82*, C153–C157.
21. Jones, M.; Woodcock, J. Optimization and control of laboratory sulphidization of oxidized copper ores with an ion selective electrode. *Proc. Australas. Inst. Min. Metall.* **1978**, *266*, 11–19.
22. Liu, S.; Zhong, H.; Liu, G.; Xu, Z. Cu(I)/Cu(II) mixed-valence surface complexes of S-[(2-hydroxyamino)-2-oxoethyl]-N, N-dibutylthiocarbamate: Hydrophobic mechanism to malachite flotation. *J. Colloid Interface Sci.* **2018**, *512*, 701–712. [[CrossRef](#)]
23. Castro, S.; Goldfarb, J.; Laskowski, J. Sulphidizing reactions in the flotation of oxidized copper minerals, I. Chemical factors in the sulphidization of copper oxide. *Int. J. Miner. Process.* **1974**, *1*, 141–149. [[CrossRef](#)]
24. Ren, Y.; Xiong, K. Research on the Adsorption and Desorption Characteristics of Xanthate on Malachite Surface. *Metal Mine* **2014**, *12*, 112–115.
25. Wen, S.M. Research test on stability of xanthate layer absorbed onto surface of malachite. *Chin. Min. Mag.* **2001**, *10*, 58–60.
26. Wen, S.M.; Zhang, W.B.; Li, B.R. *Effect of Vulcanization on Xanthate Adsorption Activity on Copper Oxide Surface and Stability of Adsorption Layer*; Nonferrous Metals (Mineral Processing Section): Beijing, China, 1997; pp. 17–20.
27. Du, P. Study on Parameterization and Surface Adsorption of Malachite. Master's Thesis, Guangxi University, Nanning, China, 2020.
28. Castro, S.; Gaytan, H.; Goldfarb, J. The stabilizing effect of Na<sub>2</sub>S on the collector coating of chrysocolla. *Int. J. Miner. Process.* **1976**, *3*, 71–82. [[CrossRef](#)]
29. Sun, Q.Y. Research on Crystal Chemical Gene Characteristics and Flotation Mechanism of Copper Minerals. Ph.D. Thesis, Northeastern University, Shenyang, China, 2019.
30. Deng, T.; Chen, J. Treatment of oxidized copper ores with emphasis on refractory ores. *Miner. Process. Extr. Metall. Rev.* **1991**, *7*, 175–207. [[CrossRef](#)]
31. Lee, J.; Nagaraj, D.; Coe, J. Practical aspects of oxide copper recovery with alkyl hydroxamates. *Miner. Eng.* **1998**, *11*, 929–939. [[CrossRef](#)]
32. Liu, D.; Wang, D.; Xian, Y.; Tian, X.; Wen, S. Enhancement of xanthate adsorption on chrysocolla surface via sodium diethyldithiocarbamate (DDTC) modification. *Physicochem. Probl. Miner. Process.* **2022**, *58*, 152599. [[CrossRef](#)]
33. Zhuo, Q.M.; Wang, P.P.; Shen, P.L.; Wang, P.H.; Tian, Y.Q.; Chen, D.C.; Deng, J.S.; Liu, W.L. Microscale exploration of the sulfidization flotation theory in malachite. *Appl. Surf. Sci.* **2024**, *642*, 158631. [[CrossRef](#)]
34. Liu, J.; Hu, Z.; Liu, G.Y.; Huang, Y.G.; Zhang, Z.Y. Selective Flotation of Copper Oxide Minerals with A Novel Amino-Triazole-Thione Surfactant: A Comparison to Hydroxamic Acid Collector. *Miner. Process. Extr. Metall. Rev.* **2020**, *41*, 96–106. [[CrossRef](#)]
35. Zhang, X.R.; Lu, L.; Li, Y.H.; Zhu, Y.G.; Han, L.; Li, C.B. Flotation separation performance of malachite from calcite with new chelating collector and its adsorption mechanism. *Sep. Purif. Technol.* **2021**, *255*, 117732. [[CrossRef](#)]
36. Feng, Q.; Zhao, W.; Wen, S. Ammonia modification for enhancing adsorption of sulfide species onto malachite surfaces and implications for flotation. *J. Alloys Compd.* **2018**, *744*, 301–309. [[CrossRef](#)]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.