

## Enhancement of xanthate adsorption on chrysocolla surface via sodium diethyldithiocarbamate (DDTC) modification

Dan Liu <sup>1,2</sup>, Daqian Wang <sup>1,2</sup>, Yongjun Xian <sup>1,2</sup>, Xiaosong Tian <sup>3</sup>, Shuming Wen <sup>1,2</sup>

<sup>1</sup> Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, China

<sup>2</sup> State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming 650093, Yunnan, China

<sup>3</sup> Yunnan Diqing Nonferrous Metals Co., Ltd, Diqing Tibetan Autonomous Prefecture 674400, Yunnan, China

Corresponding authors: yjxian@kust.edu.cn (Yongjun Xian); txsongcm@163.com (Xiaosong Tian)

**Abstract:** Chrysocolla is a kind of copper oxide mineral which was difficult to float. In this study, Diethyldithiocarbamate (DDTC) was employed to modify the surface of chrysocolla to improve its xanthate adsorption and floatability. Flotation experiments showed that the DDTC exhibited ability to activate rather than acting as a collector for chrysocolla flotation. After DDTC activation, chrysocolla can be effectively recovered by xanthate. The activation mechanism of DDTC was investigated via Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). During the activation, DDTC bonded to the surface copper atoms of chrysocolla, and more Cu(II) species on the mineral surface were reduced to Cu(I) species, which caused the formation of larger amounts of Cu active sites as -N-C(=S)S-Cu(II)- and Cu(I) species. The results of the adsorption tests and zeta potential measurements revealed that the DDTC-modified mineral surface reinforced adsorption of xanthate ions, thereby improving the chrysocolla floatability. Therefore, the Cu ions double interaction of DDTC and xanthate on the chrysocolla surfaces enhanced the strength and stability of the hydrophobic layer, resulting in an enhanced hydrophobization of the chrysocolla for its flotation.

**Keywords:** chrysocolla, flotation, diethyldithiocarbamate, modification, activation

### 1. Introduction

Oxide copper minerals, such as malachite ( $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ), cuprite ( $\text{Cu}_2\text{O}$ ), azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ), and chrysocolla ( $(\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH}) \cdot n\text{H}_2\text{O}$ ), are often found in variable proportions in the weathered surface layer of copper deposits (Lee et al., 1998; Li et al., 2015). Along with the consumption of simply handled sulfide ore, oxide copper ore is more attractive to mine operators. Copper in oxide ore can be directly leached via acid if it contains a small amount of carbonate gangue. However, the colloidal siliceous matter formed from silicate minerals not only causes solid-liquid separation problems but is also detrimental to the subsequent copper extraction. Ammonia has been explored for copper oxide leaching (Chen et al., 2021); however, it is less effective for copper silicate dissolution because of slow leaching rates. These are the main reasons leading to difficulties in the industrial hydrometallurgy application of oxide copper ore (Shi et al., 2020).

Currently, froth flotation is viewed as one effective and economic method to enrich copper oxide minerals. Malachite, cuprite, and azurite can be effectively enriched using conventional flotation methods, whereas chrysocolla flotation remains challenging. In the flotation practice, chrysocolla is often identified as an unrecoverable mineral, which affects the complete copper recovery of concentration plants (Aplan and Fuerstenau, 1984; Barbaro et al., 1997; Corin et al., 2017; Feng et al., 2018; Heyes and Trahar, 1979; Lee et al., 2009; Li et al., 2015; Samsonova et al., 1974). In the past decades, various collectors have been used to evaluate flotation performance of chrysocolla, including long-chain carboxylic acid, amines and sulfoacid (Deng and Chen, 1991; Lee et al., 2009). Moreover, chelating collectors have been employed to float chrysocolla (Carrillo and Carrillo, 1939; Fuerstenau et al., 2000; Hope et al., 2012a; Hope et al., 2012b; Hope et al., 2010). Hope et al. (Hope et

al., 2012a; Hope et al., 2012b) confirmed that n-octanohydroxamate is an effective collector for chrysocolla due to the formation of multiple layers of copper hydroxamate on mineral surface. All these collectors exhibit a superior affinity for copper oxide minerals but exorbitant cost of production and poor selectivity for carbonate gangue minerals, such as calcite and dolomite, thereby has restricted their practical application (Deng and Chen, 1991; Lee et al., 1998). Xanthate, due to its advantages including easy to be obtained and superior selectivity, remains the most promising collector for commercial applications of copper oxide minerals. In the past years, many studies have been devoted to improving the xanthate collection of chrysocolla after superficial sulfidization with diluted solutions of sodium hydrosulfide or sodium sulfide. However, this technique is often insufficient regarding the recovery of chrysocolla. One of the key factors is that chrysocolla is usually amorphous, and the adsorption layers of  $S^{2-}$  or  $HS^-$  are extremely limited and unstable on chrysocolla, which leads to weak interactions between Cu ions and xanthate (Aplan and Fuerstenau, 1984; Banza and Gock, 2003; Castro et al., 1974; Feng et al., 2017b; Raghavan et al., 1983). In addition, chrysocolla often appears a metal deficient surface in pulp due to its high solubility, which is detrimental for xanthate adsorption (Lee et al., 1998).

Surface modifications are widely conducted to improve the flotation. They can involve the use of additional active ions to increase the number of active sites on the mineral surface that is difficult to collect. This method significantly increases the reactivity of the original mineral surfaces, enhances the interaction between the collectors and mineral surfaces, and improves the mineral floatability (Feng et al., 2017a). Dithiocarbamates exhibit a strong complexation ability with metal ions and form highly stable metal-dithiocarbamate complexes (Gupta et al., 2015; Gupta et al., 2013; Ma et al., 2016). In the past few years, several investigations have been performed to use dithiocarbamates in ores flotation. Nagaraj et al. (NAGARAJ et al., 2001) reported that collector dimer as well as Fe-dithiocarbamate species were formed upon dibutyl dithiocarbamate adsorption on pyrite, but only the copper-dithiocarbamate complexes formed on chalcocite. In the study of (Moller et al., 2015), they measured the heat evolved during the reaction of sodium isobutyl dithiocarbamate and sodium ethyl xanthate and their mixtures with pyrite and chalcopyrite by using isothermal titration microcalorimetry. Chen et al. (Chen et al., 2013; Yekeler et al., 2004; Yekeler et al., 2006) investigated the adsorption of diethyl dithiocarbamate on galena and pyrite surface by using DFT, the results showed that interaction of diethyldithiocarbamate was via its sulfur atom bonding with metallic atoms on the mineral surfaces and the interaction with galena was stronger than that with pyrite. We hypothesize that the chelating ability of DDTC could be used for copper oxide minerals. For the chrysocolla that it is difficult to float, the DDTC may modify the surface structure and properties, and improve xanthate adsorption of chrysocolla. However, only few studies have been conducted on the effects of DDTC on xanthate flotation of chrysocolla.

The present study aims to evaluate the effect of DDTC on the chrysocolla flotation behavior in xanthate system. The effects and mechanism of DDTC on the flotation of chrysocolla were studied by Micro-flotation tests, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Zeta potential measurements and adsorption tests. The results showed that DDTC can effectively recover chrysocolla by improving the adsorption activity and stability of xanthate on the surface of chrysocolla. The study provides a new method and theoretical basis for the activation flotation of chrysocolla.

## 2. Materials and methods

### 2.1. Mineral samples and reagents

The chrysocolla samples were acquired from a mine in the Yunnan province, China. The ore was crushed into  $-1\text{mm}$  particles. Impurities in the chrysocolla were hand-removed under a microscope. The chrysocolla were ground through a three-head grinding machine (XPM- $\Phi 120 \times 3$ , China) and selected samples of  $38\text{-}74\mu\text{m}$  in size were sealed for preservation. The chemical analysis results of the sample are shown in Table 1. The sample contains 16.22%Si, 32.77%Cu, 1.68%Al, 0.47%Ca, 0.13%Mg, which is very close to the composition of pure chrysocolla and can be used for the experiments (RRUFF Database, 2011).

Table 1. Chemical multivariate analyses results of chrysocolla

Elements	Si	Cu	Al	Ca	Mg
Wt, %	16.22	32.77	1.68	0.47	0.13

All reagents used in the study were analytical grade, and deionized water with a resistivity of <math><18.0\text{ mS/m}</math> from Mill-Q50 (USA) was used throughout the tests. Sodium hydroxide and hydrochloric acid were used for pH controlling, both of which were purchased from Sinopharm Chemical Reagent Co., Ltd. DDTC and sodium sulfide were used as activator, and sodium isoamyl xanthate (IAX) was used as collector. They were purchased from Tianjin Kemi Chemical Reagent Development Center, China.

## 2.2. Micro-flotation tests

In each test, 2 g pure chrysocolla sample was combined with 40 mL deionized water and transferred into a 0.05 L XJC laboratory single-trough flotation machine (Jilin Prospecting Machinery Factory, China). Before aerating, an agitator was turned on to a revolving speed of 1200 r/min. The pH value of flotation pulp was adjusted with sodium hydroxide and hydrochloric acid solutions of various concentrations. After adding the required amount of DDTC or sodium sulfide, the suspension was agitated for 3 min. The IAX and pine oil were added and conditioned for 2 and 1 min, respectively. After aerating, the concentrate was collected for 5 min with a manual froth scraper and recovered on a filter. The flotation flow chart was shown in Fig. 1. Each test was repeated three times to average the results.

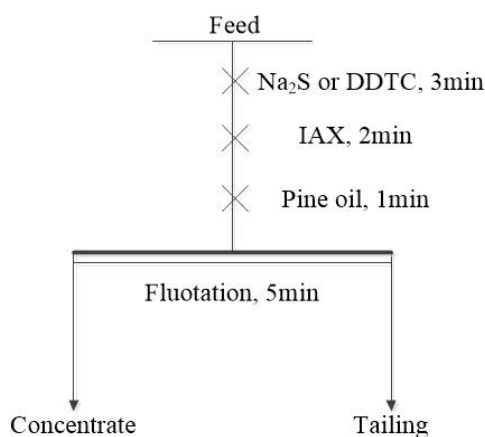


Fig 1. Flowsheet of single mineral flotation test

## 2.3. Vibrational spectrum

FT-IR spectra were collected on a Thermo Nicolet Nexus FT-IR spectrometer (TFS, USA) equipped with IR source optics, which provides a stable signal and  $0.5\text{ cm}^{-1}$  resolution. The spectrometer had a DTGS detector with KBr window and Ge-on-KBr beam splitter. Spectra were acquired in the range of  $500\text{--}4000\text{ cm}^{-1}$ .

## 2.4. XPS analysis

A PHI 5000 VersaProbe II system (PHI5000, ULVAC-PHI Inc., Japan) with a monochromatic Al-K X-ray source was employed for the XPS measurements. High-resolution C 1s, O 1s, Cu 2p, and S 2p XPS spectra were recorded to characterize the chemical nature of the modified chrysocolla samples. Before the XPS measurements, the samples were treated with the same flotation process that described in section 2.2 but without IAX addition. Then, the chrysocolla slurry was washed once with deionized water to remove any suspended colloidal particles. A centrifuge was used to separate solids and liquids. The solid part was air-dried in an oxygen-free glove box (i.e., Ar-saturated atmosphere) and then immediately introduced to the fore-vacuum of the XPS. To prevent the loss of volatile species

possibly formed on the sample surface, the samples were cooled with liquid N<sub>2</sub> before the pump-down and during analysis. The C 1s peak at 284.8 eV was used to correct the binding energies for electrostatic charging. The elemental atomic percentages were calculated from the peak area corrected via the MultiPak Spectrum software.

## 2.5. Zeta potential measurements

A Brookhaven ZetaPlus instrument was used to measure the zeta potential of the chrysocolla sample activated with DDTC in the absence and presence of IAX. The mineral suspension was prepared by adding 0.5 g of purified chrysocolla particles into a vessel with 100 mL deionized water containing  $5 \times 10^{-3}$  mol/L KCl background solution. The pH value of the mineral suspension was adjusted to a desired value using 0.10 mol/L H<sub>2</sub>SO<sub>4</sub> and 0.10 mol/L NaOH solutions. When needed, DDTC solution was added to the suspension at the beginning of conditioning period. The suspensions with and without IAX were allowed to settle for 10 min. The supernatant of the dilute fine-particle suspension was transferred to the measurement vessel for zeta potential measurements at room temperature. The zeta potential of each sample was measured three times, and the results were averaged.

## 2.6. Adsorption and desorption tests

A sample with 0.5 g chrysocolla and 40 mL water was poured into a 100 mL beaker, which was immersed into a thermostated water bath at 25 °C. After adjusting the pH values, the required amount of DDTC solution was added to activate the chrysocolla for 5 min. Subsequently, various IAX concentrations were added, and the suspension was agitated for 3 min. The residual concentrations of IAX were determined with an ultraviolet spectrophotometer (TOC-VCPH, Shimadzu, Japan). The adsorption amount of reagents on the surface of the chrysocolla sample was calculated from the difference between the original and residual concentrations:

$$Q = \frac{(C_0 - C)V}{m}, \quad (1)$$

where Q is the amount of absorbed reagents in the chrysocolla surface (mg/g), C<sub>0</sub> the initial concentration of reagents (mg/L), C the equilibrium concentration of reagents (mg/L), V the solution volume, and m the chrysocolla mass.

To survey the adsorption stability of IAX on chrysocolla surface, desorption tests was designed as follow. After adsorption test operations, the residual was rinsed with 40ml deionized water, the pulp was filtered; and the filtrate was stored. The rinsing operation was repeated twice to obtain other filtrates. The concentration of IAX in each filtrate was measured by using ultraviolet spectrophotometer. The desorption amount and desorption percentage in total adsorption were calculated via equation (2) and (3), respectively, which described the desorption of the IAX adsorbed on chrysocolla surface. Where Q<sub>d</sub> is the amount of desorbed reagents from the chrysocolla surface (mg/g), C<sub>n</sub> the reagents concentration of rinsing water (mg/L), n the numerical order of rinsing operation, V the volume of rinsing water.

$$Q_d = \frac{C_n V}{m}, \quad (2)$$

$$D = \frac{Q_d}{Q} \times 100\%. \quad (3)$$

## 3. Results and discussion

### 3.1. Micro-flotation tests of chrysocolla

Fig. 2 shows the effect of pH values on the flotation recovery of chrysocolla. For comparison with the traditional flotation of copper oxide mineral, the sulfidization and xanthate flotation was also evaluated. From Fig. 2, when the DDTC concentration is 800mg/L, the flotation recovery of chrysocolla increases gradually with increasing pH but begins to decrease at pH > 9. The suitable pH range for the chrysocolla flotation was 8-9 for DDTC and 10.5-11.5 for Na<sub>2</sub>S.

The flotation performance of chrysocolla as a function of flotation reagents is presented in Fig. 3 and 4. From Fig. 3, regardless of the modification type, the chrysocolla recovery presents a positive

correlation with the collector concentration until a maximum is reached. Xanthate is a common collector for the enrichment of copper minerals because it prefers to interact with copper ions to form hydrophobic Cu-xanthate precipitate. However, only approximately 5% chrysocolla is floated in the IAX solution, indicating that IAX collector exhibits a weak collection capability for chrysocolla without any modifier. In general,  $\text{Na}_2\text{S}$  is used to sulfurate copper oxide surfaces to enhance xanthate adsorption because of the formation of sulfide film on the surface of copper oxide and the decrease of its solubility (Bessi re and Housni, 1991; Zhang, 1994). It can be seen in Fig. 3 that increasing  $\text{Na}_2\text{S}$  concentration improves the chrysocolla floatability. The chrysocolla recovery reaches approximately 23% at a  $\text{Na}_2\text{S}$  concentration of 800 mg/L. Further increasing  $\text{Na}_2\text{S}$  concentration, the chrysocolla is depressed owing to the excess  $\text{Na}_2\text{S}$  in pulp (Lee et al., 1998; Lee et al., 2009). The flotation data show that although  $\text{Na}_2\text{S}$  can improve the floatability of chrysocolla when xanthate is used as a collector, the flotation of chrysocolla is difficult with a maximal recovery of only 23%.

Please note that the chrysocolla recovery is approximately 0% in the DDTC solution that without IAX. However, approximately 5% chrysocolla is floated recovery when IAX alone. This may be attributed to that the hydrophobic group (alkyl chain) in IAX is longer than that in DDTC. The recovery is enhanced by the modification of the mineral surface with DDTC for high IAX concentrations (Fig. 4). These observations suggest that DDTC has no collection power but exhibits excellent activation for chrysocolla. The superior flotation results of chrysocolla modified with DDTC can be attributed to the increasing of surface activity and the facilitation of xanthate adsorption on the mineral surface.

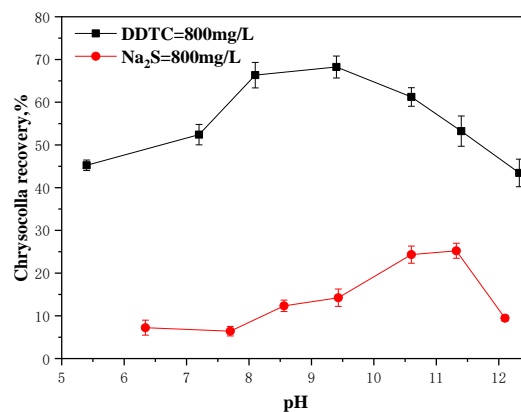


Fig 2. Chrysocolla recovery as function of pH; IAX concentration of 500 mg/L

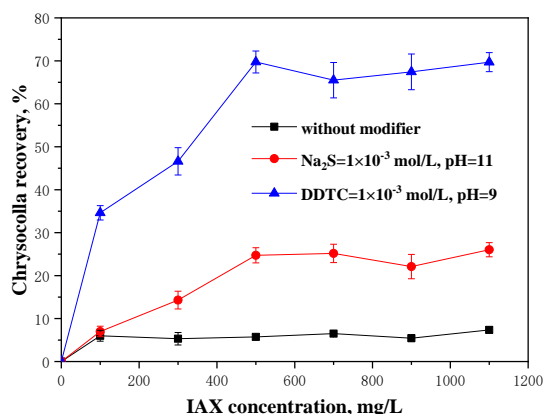


Fig 3. Chrysocolla recovery as function of collector concentration

### 3.2. FT-IR analysis

To determine the chemical composition and structure on the chrysocolla surfaces with and without DDTC, FT-IR was employed in this study. The FT-IR spectra of DDTC and the chrysocolla sample before and after DDTC treatment are presented in Fig. 5. According to Fig. 5(a), the O-H stretching

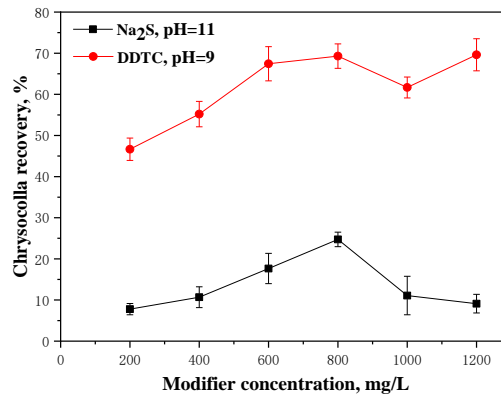


Fig 4. Chrysocolla recovery as function of modifier concentration; IAX concentration of 500 mg/L

vibration is a broad composite peak characteristic of water-like O–H ( $3400\text{ cm}^{-1}$ ) due to the bonding of the copper in chrysocolla to hydroxide units within the amorphous matrix of partially hydrated silicate rather than discrete copper hydroxide units (Hope et al., 2012a), while the O–H bending vibration at  $1639\text{ cm}^{-1}$ . The Si–O stretching vibration and bending vibration absorption regions are observed at  $1031.14\text{ cm}^{-1}$  and  $795.62\text{ cm}^{-1}$ , respectively, which are the typical characteristic peak of silicate minerals. Therefore, this sample presents in a  $\text{SiO}_4$  structure. Further, C–H stretching vibrations in (b) and (c) appear at approximately  $2950\text{ cm}^{-1}$ ;  $\text{CH}_2$  wagging and twisting vibrations at approximately  $1200\text{ cm}^{-1}$  and C–H symmetrical deformation at approximately  $1180\text{ cm}^{-1}$  can be observed in the FT-IR spectra. Regarding the chrysocolla sample with DDTC treatment, a new band at approximately  $1508\text{ cm}^{-1}$  appears. It could be attributed to the enhanced C–N stretching vibrations of the DDTC group. In addition, the complex vibrations of the  $-\text{N}-\text{C}(=\text{S})\text{S}-$  functional group inside DDTC at approximately  $1433\text{ cm}^{-1}$  shifted to  $1424\text{ cm}^{-1}$ . Such a shift can be explained by a Cu–DDTC precipitate cover on the chrysocolla surface in the form of  $-\text{N}-\text{C}(=\text{S})\text{S}-\text{Cu}$  (Ma et al., 2016).

DDTC is normally hydrophobic and has a strong chelating performance with many metals such as Cu, Pb, Ni, Au, Ag, Zn, Hg, Fe, Sn, Pt, Pd, and In (Ganguli et al., 2002; Gupta et al., 2015; Gupta et al., 2013; Leipoldt and Coppens, 2002; Luca et al., 2006). The FT-IR results indicate that DDTC can interact with Cu atoms of chrysocolla surface. However, it exhibits an insignificant collection capability for chrysocolla, as show in Fig. 3. This can be attributed to the abundant amorphous silicon in the chrysocolla, which shields the weak hydrophobicity of DDTC adsorbed on chrysocolla surface, i.e. lead to dominant hydrophilicity of the whole chrysocolla surface. The flotation and FT-IR results imply that the DDTC plays a modification and activation role for chrysocolla flotation.

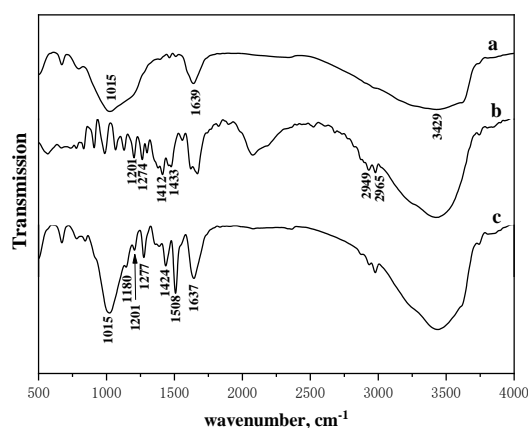


Fig 5. FT-IR spectra of (a) pure chrysocolla, (b) DDTC and (c) chrysocolla after DDTC treatment of 1 h

### 3.3. XPS analysis

The XPS technique can determine the chemical states of elements, which is valuable to further analyse the adsorption structure on a mineral surface during flotation. Fig. 6 presents the survey spectra of the

chrysocolla sample without or with DDTC adsorption over a binding energy range of 0–1400 eV. Regarding (a), the expected elements of pure chrysocolla (C, O, Cu, Si and Al) was detected, and no evidence of impurities from other elements can be found. The spectra (b) and (c) present the expected elements for DDTC: C, O, N, and S. The atomic concentrations for S 2p, O 1s, N 1s, Al 2p and Cu 2p determined via XPS are summarized in Table 2. The results show that the atomic Cu concentration on surface is much lower than that in the bulk, suggesting that the Cu amount on the surface of the untreated chrysocolla was prominently scarce. This might be one of key cause for the low surface activity of chrysocolla, which leads to a weak collector adsorption and floatability of the chrysocolla with xanthate only.

It is noteworthy that the atomic Cu concentration is somewhat decreased after the DDTC treatment and further decreases with increasing DDTC concentration. This seems to be a disadvantage for the adsorption of xanthate on the chrysocolla surface. However, the flotation tests do not support this conclusion. After the DDTC adsorption, the atomic concentration ratio of S and N increased and that of Si and O decreased, confirming the coverage of chrysocolla by DDTC, which can lead to the weaker Cu 2p XPS spectrum intensity. Similar result were obtained in Liu et al. study (Liu et al., 2017). The activation mechanism of DDTC needs to further investigate the surface structures.

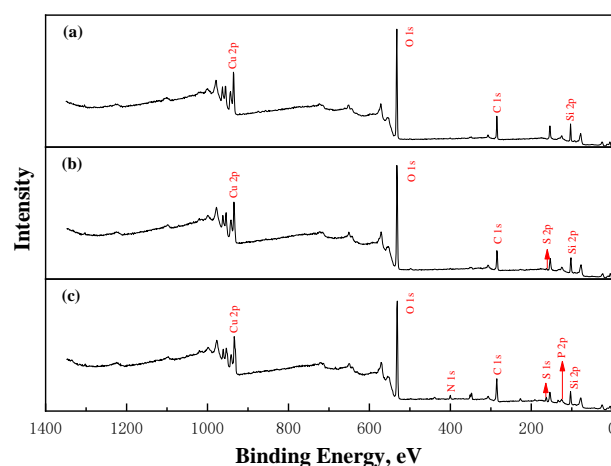


Fig 6. XPS scans of (a) pure chrysocolla, (b) chrysocolla treated with 800 mg/L DDTC and (c) chrysocolla treated with 1200 mg/L DDTC; pH=9

Table 2. Relative contents of representative elemental constituents on chrysocolla surfaces

Chrysocolla	Atomic concentration, %						
	N 1s	O 1s	Cu 2p	Si 2p	S 2p	Al 2p	C 1s
Before adsorption	/	47.02	9.21	15.23	/	2.75	25.79
After DDTC adsorption (800 mg/L)	0.76	45.58	8.56	16.17	1.33	2.69	24.91
After DDTC adsorption (1200 mg/L)	1.28	40.32	6.89	11.85	2.65	2.43	34.58

The high-resolution XPS spectra of Cu2p are presented in Fig. 7. Regarding the pure chrysocolla surface of Fig. 7a, the Cu 2p spectrum contain a component at 933.41 eV and the principal component at 935.65 eV. In addition, a satellite peaks appears in the Cu2p spectrum, indicating the existence of Cu oxide on the chrysocolla surface. Combined the result of IR, the higher band energy can be described as consisting of Cu(II)( cupric) bound to hydroxide units within the amorphous matrix of partially hydrated silica. The low band energy attributes to Cu(I) (cuprous) species, and it is formed via the loss of surface hydroxy water; i.e., that reduction of Cu(II) to Cu(I) by secondary electrons occurred on surface layers of the mineral (Grift et al., 1989; Hope et al., 2012a), as shown in Eq (4). After DDTC

treatment, the state satellite intensity is much lower (Fig. 7b), and the binding energies of the Cu(II) and Cu(I) species shift to lower values of 934.87 eV and 932.26 eV, respectively. This indicates different electronic environments in the pure and DDTC modified chrysocolla surfaces, suggesting that the Cu(II) bond to DDTC rather than O atom (Liu et al., 2016; Liu et al., 2017). In addition, the increasing of the relative Cu(I) to the total Cu amount suggests that some electron reduction of Cu(II) to Cu(I) is possibly facilitated by DDTC, as shown in Table 3. These results indicate that the surface modification with DDTC increases the relative ratio of Cu(I) species in total Cu, and transforms the original Cu oxide species to Cu-DDTC. From the Fig. 7(c), when the DDTC concentration is increased 1200 mg/L, the binding energy of Cu peaks further shifted to lower band energies of 931.91 eV and 934.23 eV, respectively, and the intensity of the Cu(I) peak was significantly increased. These results indicate the interaction between DDTC and Cu atoms was enhanced with the increasing of DDTC concentration.

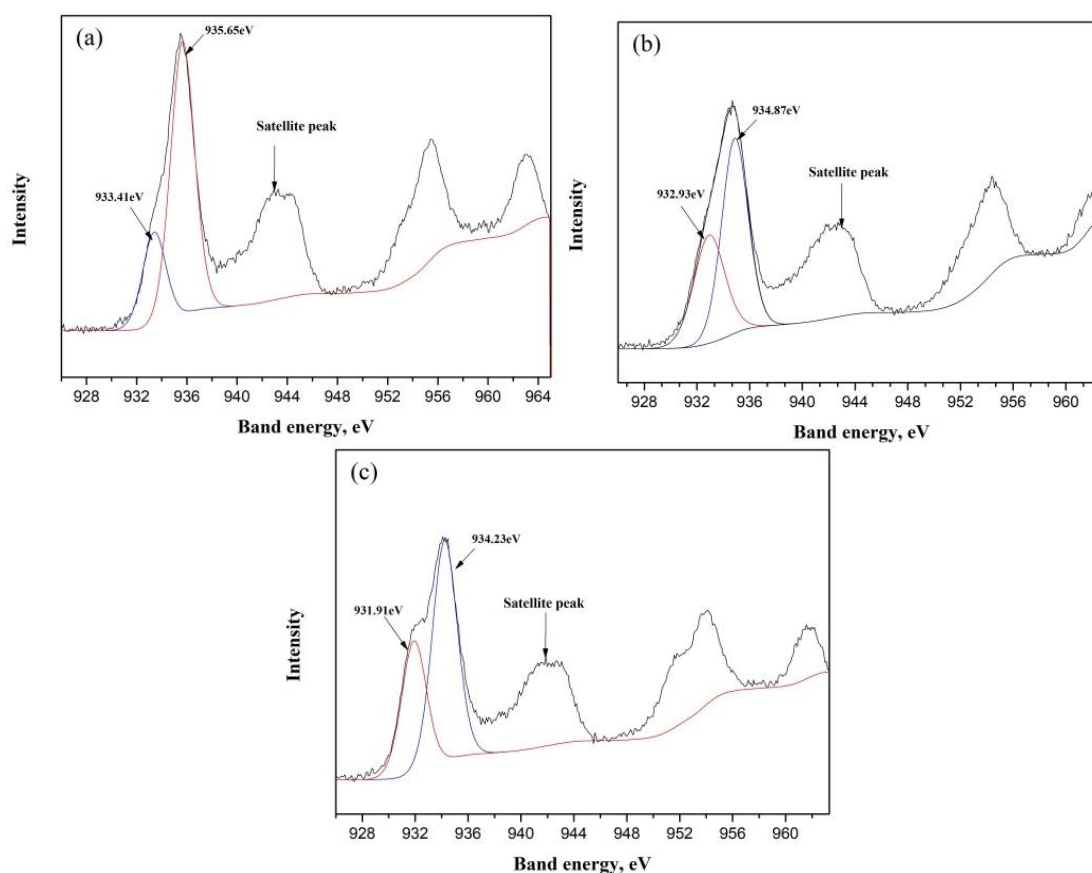
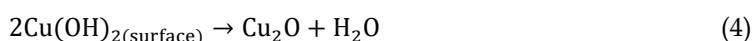


Fig 7. Cu 2p XPS spectra of (a) pure chrysocolla, (b) chrysocolla treated with 800 mg/L DDTC, (c) chrysocolla treated with 1200 mg/L DDTC; pH=9

Table 3. Binding energy, relative content, FWHM, and percentage in total Cu of different Cu species on (a) pure chrysocolla, (b) chrysocolla treated with 800 mg/L DDTC and (c) chrysocolla treated with 1200 mg/L DDTC; pH=9

Samples	Species	Cu 2p <sub>3/2</sub> band energy, eV	FWHM, eV	Relative content of Cu species, %	Percentage in total Cu, %
a	Cu(II)	935.58	2.29	8.37	76.34
	Cu(I)	933.41	2.29	0.84	23.66
b	Cu(II)	934.87	2.48	5.91	69.10
	Cu(I)	932.26	2.88	2.65	30.90
c	Cu(II)	934.23	2.34	4.31	62.52
	Cu(I)	931.73	2.77	2.58	37.48



The S 2p spectra are further analyzed to thoroughly understand the effect of DDTC on the modification of chrysocolla. The results are presented in Fig. 8. Regarding the chrysocolla sample treated with a 800 mg/L DDTC solution in Fig. 8a, the S 2p<sub>3/2</sub> XPS bands at around 160.88 eV and 161.98 eV can be related to the S atoms in the (-S-) and C=S groups, respectively (Acres et al., 2010; Han et al., 2009; Ma et al., 2016; Szargan et al., 1999). The high band energy located at 162.98 eV is indicative of S<sub>n</sub><sup>2-</sup>, suggesting that the S was undergone oxidation during DDTC modification, and it is advantageous to the activation of mineral (Chen et al., 2014; Smart et al., 2015). The percentages of each S species are shown in Table 5. From Table 5, it can be seen that Cu-S and C=S bonds relative to the total S amount are 19.93% and 23.71%, respectively. After the chrysocolla was modified in the 1200 mg/L DDTC solution, as shown in Fig. 8b, the binding energy of S shifted approximately 0.2 eV to high value and the percentages of Cu-S and C-S relative to the total S amount are 33.77% and 42.57%, respectively. Combined with the Cu2p spectra, it is believed that a strong redox reaction occurred between the Cu(II) and S atom of DDTC in the solution, as written in Eq (5) and (6).

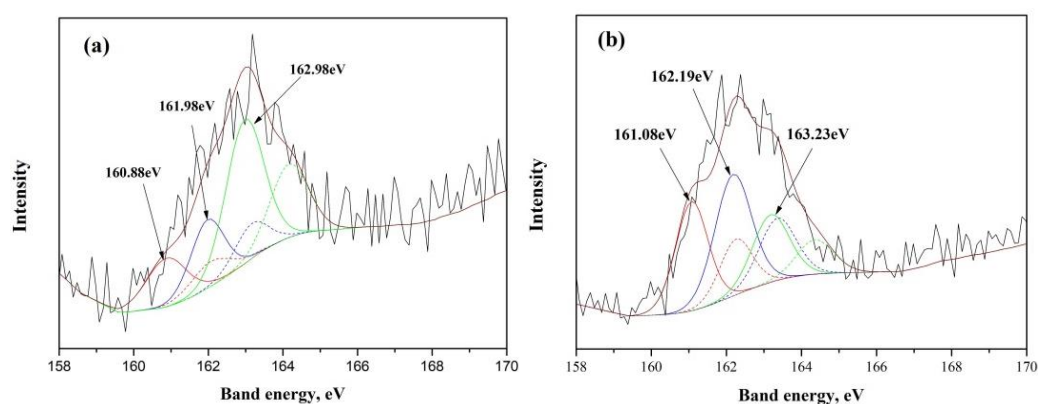
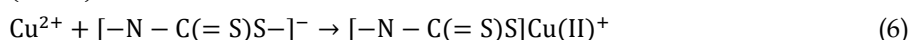
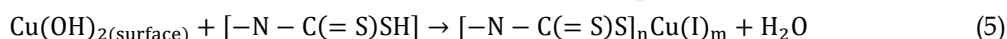


Fig 8. S 2p XPS spectra of (a) chrysocolla treated with 800 mg/L DDTC, (b) chrysocolla treated with 1200 mg/L DDTC; pH=9

Table 4. Binding energy, relative content, FWHM, and percentage in total S of different S species on (a) chrysocolla treated with 800 mg/L DDTC and (b) chrysocolla treated with 1200 mg/L DDTC; pH=9

Samples	Species	S 2p <sub>3/2</sub> band energy, eV	FWHM, eV	Relative content of Cu species, %	Percentage in total Cu, %
a	S <sup>2-</sup>	160.88	1.27	0.26	19.93
	S <sub>2</sub> <sup>2-</sup>	161.98	1.07	0.32	23.71
	S <sub>n</sub> <sup>2-</sup>	162.98	1.48	0.75	56.36
b	S <sup>2-</sup>	161.08	1.02	0.89	33.77
	S <sub>2</sub> <sup>2-</sup>	162.19	1.15	1.13	42.57
	S <sub>n</sub> <sup>2-</sup>	163.23	1.15	0.63	23.66

From Table 2 and Cu2p spectra, although the atomic Cu concentration is somewhat decreased after the DDTC treatment and further decreases with increasing DDTC concentration. However, the result of high-resolution Cu2p and S2p spectra reveal that the inert Cu oxide species covered on pure chrysocolla surface are modified to active surface with high number Cu-S sites, i.e. the ratio of active Cu sites is increased. Such sites prefer to interact with xanthate than that Cu oxide species (Liu et al., 2017).

### 3.4. Adsorption of xanthate on chrysocolla surface

The adsorption amount of IAX for different pH values with or without DDTC is presented in Fig. 9. According to Fig. 9, the adsorption quantity of IAX gradually increases with increasing pH value but decreases for pH>9. The preferable pH value for IAX adsorption is therefore approximately 9.

Fig. 10 presents the IAX adsorption amount with respect to the initial IAX concentration. The adsorption amount on the chrysocolla surface in the presence of DDTC is approximately doubled with respect to that without DDTC. Hence, the floatability of chrysocolla can be improved via an increase in the collector adsorption amount on the chrysocolla surface in the presence of DDTC.

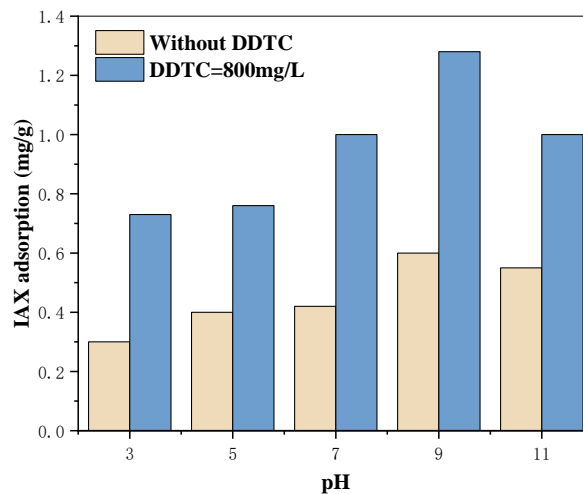


Fig 9. Adsorption amounts of IAX on chrysocolla surface with respect to pH; IAX=500mg/L

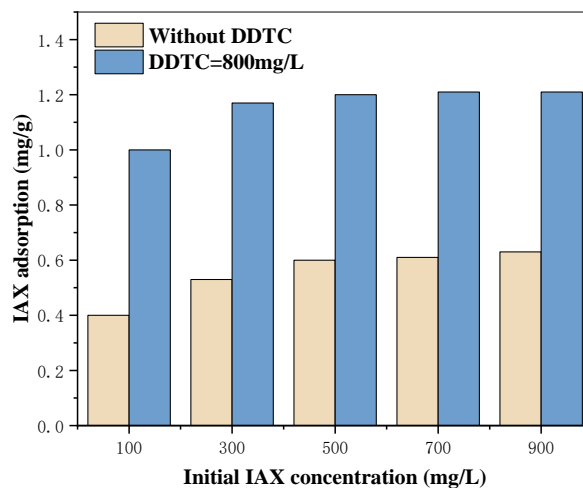


Fig 10. Adsorption amounts of IAX on chrysocolla surface respect to initial IAX concentration; pH=9

### 3.5. Zeta potential

Zeta potentials of the chrysocolla sample with and without DDTC were investigated to determine the adsorption states of xanthate on the chrysocolla surface (Fig. 11). In the absence of DDTC, the zeta potential decreases considerably less. Hence, only low adsorption of IAX anions occurs on the chrysocolla surface in the absence of DDTC. The zeta potential of chrysocolla in the presence of DDTC is more negative than that without DDTC. Hence, the surface modification of the chrysocolla sample with DDTC increases the number of active xanthate sites on the activated mineral surface.

As shown in Fig. 2, the chrysocolla flotation recovery is approximately 5% in the IAX solution without DDTC. This is consistent with the zeta potential measurement. The adsorption of the collector on the chrysocolla surface is negligible in this case. However, according to Fig. 9 and 10, the IAX collector was obviously absorbed by the mineral surface without DDTC modification. A possible explanation exists for this phenomenon. The hydrophobicity of minerals depends on the attachment of collectors to the mineral surface. The adsorption IAX on the chrysocolla surface without DDTC is achieved via the attachment of electrically neutral IAX molecules. Namely, IAX molecules most likely react with their conjugate-base anions adsorbed by hydrogen bonding due to the abundant hydroxyl

on the pure chrysocolla surface, and a predominant physical multilayer adsorption model is proposed to illustrate the adsorption on the chrysocolla surface. Such IAX molecules adsorbed on the chrysocolla surface obviously change in the residual IAX solution rather than the zeta potential. In addition, the hydrogen-bonding interaction between IAX molecules and anions is unstable, and it is easily desorbed by the chrysocolla surface in the flotation process. As a result, the flotation recovery is only approximately 5% for the IAX solution without DDTC. In the presence of DDTC, the IAX adsorption on chrysocolla surface most likely occurs as physical and chemical adsorption. This not only increased the contents of xanthate adsorption on the mineral surface but also observably decreased the zeta potential of chrysocolla. The chemical adsorption of collector can enhance the stability of the hydrophobicity species.

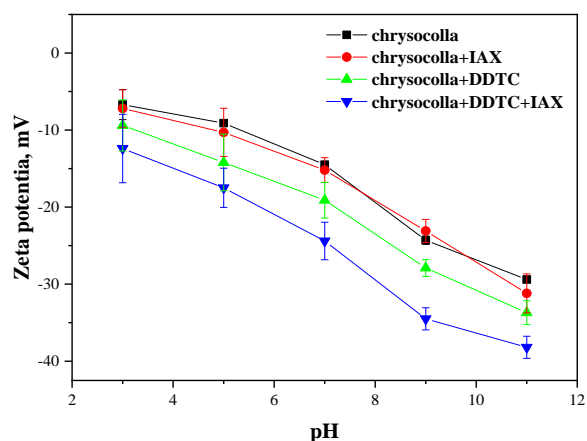


Fig 11. Zeta potential of chrysocolla as function of pH

### 3.6. Desorption of xanthate on the chrysocolla surface

The stability of xanthate adsorption can be evaluated via determination of xanthate desorption. Table 5 shows the desorption of adsorbed xanthate from chrysocolla surface with the deionized water rinsing. It can be seen that the desorption percentage of IAX without DDTC modification is much higher than that with DDTC modification. This indicates that the IAX product on chrysocolla surface is relatively more stable after DDTC modification.

Table 5. Desorption of IAX from the chrysocolla surface via deionized water rinsing; initial IAX concentration of 500 mg/L

Rinsing time	Desorption amounts, $\times 10^{-2}$ mg/g		Desorption percentage in total adsorption, %	
	Without modification	Modification	Without modification	Modification
1	40.41	32.41	60.31	25.52
2	5.07	4.66	7.56	3.67
3	1.41	1.31	2.11	1.03
<b>Total</b>	<b>46.89</b>	<b>38.38</b>	<b>69.98</b>	<b>30.22</b>

Based on the results and analyses above, the adsorption model for DDTC and xanthate on chrysocolla surfaces is presented in Fig. 12. The Cu-DDTC precipitate on the chrysocolla surface does not exhibit its hydrophobicity in chrysocolla flotation due to the large amount of amorphous and hydrophilic silicon in chrysocolla; it most likely causes the modification and activation for xanthate adsorption. The DDTC used its functional groups ( $-N-C(=S)S-$ ) to bond copper atoms via the formation of  $-N-C(=S)S-Cu(II)-$  bonds, which can increase the reactivity of chrysocolla surfaces for xanthate adsorption. In addition, the much more Cu(II) species can be reduced to Cu(I) species on chrysocolla surfaces with DDTC modification, which is preferred to bond to xanthate ions. The hydrophobic product of DDTC-Cu(II)-IAX and  $-Cu(I)-IAX$  formed via interaction between IAX and

chrysocolla surfaces after DDTC modification has higher strength and stability than that without DDTC modification. As a result, DDTC improved the flotation recovery of chrysocolla.

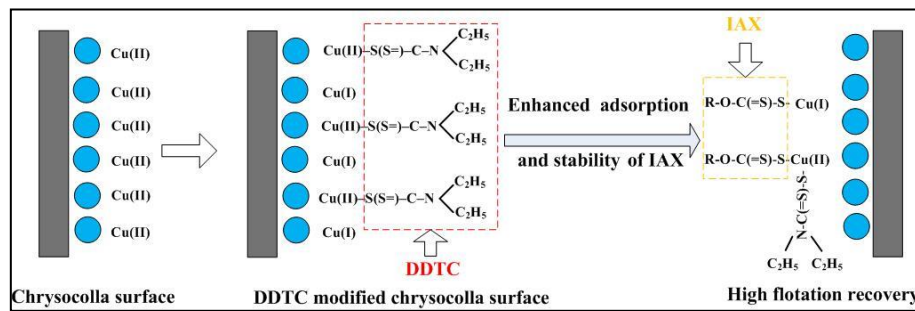


Fig 12. Potential structure configuration of DDTC activation; R is alkyl group

#### 4. Conclusions

The present study investigated the modification of DDTC on chrysocolla flotation. The following conclusions can be drawn:

(1) Chrysocolla cannot be collected well via DDTC or xanthate, while excellent flotation recovery was achieved when chrysocolla was modified with DDTC prior to IAX collection. It is believed that DDTC exhibits activation rather than collection in chrysocolla flotation.

(2) FT-IR and XPS results revealed that DDTC bonded to the surface copper atoms of chrysocolla, and more Cu(II) species on the mineral surface were reduced to Cu(I) species after the chrysocolla was modified with DDTC, and thus leading to the formation of larger amounts of  $-N-C(=S)S-Cu(II)-$  bonds and Cu(I) species. The number of  $-N-C(=S)S-Cu(II)-$  bonds and Cu(I) species on the modified mineral surface increased with increasing DDTC amount. This increase was beneficial for the adsorption of xanthate ions.

(3) The adsorption experiments and zeta potential measurements indicate that surface modification with DDTC not only increased the contents of xanthate products on chrysocolla surface but also enhanced the stability of the hydrophobicity products, thereby improving the sample floatability.

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