

Received September 20, 2017; reviewed; accepted October 25, 2017

Structural modification of cellulose to enhance the flotation efficiency of fine copper oxide ore

, Guohua Gu¹, Renfeng Zhu^{1,2}, Zhixiang Chen¹

¹ School of Minerals Processing and Bio-engineering, Central South University, Changsha 410083, Hunan, China

² Institute of Multipurpose Utilization of Mineral Resources, Chinese Academy of Geological Sciences, Chengdu 610041, Sichuan, China

Corresponding author: 165612115@csu.edu.cn (Zhixiang Chen)

Abstract: Using more efficient collector to improve the recovery efficiency of fine copper oxide has become imperative as the shortage of copper mineral resources. In this study, the new collector 3-hydroxy butyrate-carboxy methyl cellulose xanthate (HCMCX) was synthesized by carboxy methyl cellulose, 3-hydroxy butyrate and carbon disulfide, all of which as raw materials. The structural characteristics of HCMCX was detected by both infrared spectrum and ultraviolet spectrum. Besides, the interacting behavior between HCMCX and fine malachite was investigated through particle size analysis, contact angle measurements, and flotation tests. Particle size analysis indicated that the mean size of malachite was increased by 8 μm while the HCMCX concentration at 200 mg/dm^3 . The contact angle measurements demonstrated that, comparing with the collector AX at a same dosage, the mineral surface of malachite showed a stronger hydrophobicity after interacting with HCMCX. Microflotation tests results exhibited that the recovery of malachite was about 94% when the pulp pH 8 and collector concentration at 200 mg/dm^3 . The results of practical ore flotation tests showed that HCMCX could as an excellent collector for flotation of fine malachite, finally to achieve the concentrates containing 20% Cu and 88% Cu recovery.

Keywords: fine malachite, collector, sulfuration flotation, contact angle, mean size, flocculation

1. Introduction

Recovering of copper oxide minerals still is a technical challenge around the world, since most of oxide minerals are existed in a states of "micro-disposal" or "ultramicro-dispersal" dotted in the gangue minerals (Fang et al., 2002). Malachite, for example, is one of them. Therefore, fine particles are inevitable produced during the grinding process for achieving complete liberation of valuable minerals (Shibata et al., 2003). While the malachite are vulnerable to be over crushed after a long time process of grinding, especially when the ore existed argillaceous gangues. (Chen et al., 2010). Liu et al indicated that there about one-sixth copper mineral are losing in the form of fine granularity in tailings per year in the globe (Liu et al., 2010). Therefore, the problem to recover the fine (6–50 μm) and ultra-fine (<6 μm) valuable minerals is still as a mainly challenge for researchers up to now (Sun et al., 2009).

The different fine minerals showed their specific surface characteristics. Low recovery of fine particles are often attributed to their less quality and inertia, leading to small probabilities of particles colliding with bubbles since the particles follows bubble fluid streamlines (Schulze et al., 1989). The other reason for the low floatability of fine particles is insufficient kinetic energy (due to low mass) to displace the thin water film between the colliding particle surface and bubbles and formed the three-phase contact line.

On the other hand, the mechanical entrainment of hydrophilic minerals also is a severe problem in the froth flotation progress of fine particles. Generally speaking, mechanical entrainment of gangue becomes more obvious when the particle size smaller than 30 μm , and the entrainment ratio is proportional to the recovery of water (Warren et al., 1984). Many studies have been and are being

conducted to investigate froth draining behavior with the objective of lowering water recovery into the froth thus alleviate mechanical entrainment into the froth products (Liu et al., 2006).

Besides, researchers are dedicated to develop new collectors what can improve the flotation recovery efficiency of fine malachite from complex gangue minerals during the latest ten years. Meanwhile, a large kinds of collector, including the naturally abundant cellulose, have been investigated in order to achieve this target. (Shen et al., 2017). Cellulose, the most abundant natural organic renewable resource on the earth, was extracted from the cotton, wood, hemp and various straw as well as other plant fibers. It is a long linear chain macromolecule, with β -D-glucose as the unit and polymerized by 1,4-glycosidic bonds. Each of the glucose residues in the cellulose macromolecules contains three alcoholic hydroxyl groups, namely the secondary alcohol hydroxyl groups of the C(2), C(3) positions and the primary alcohol hydroxyl groups at the C(6) position, which play a decisive role in the properties of cellulose. It could take place oxidation, esterification, and etherification reactions, as well-formed hydrogen bonds between molecules (D.K et al., 2005).

Cellulose, after chemical modification, could be introduced some high-affinity functional groups like sulfur-bearing group what always has a higher affinities with heavy metals but adverse results for light metals (Li et al., 2015; Ge et al., 2015). The common sulfur-bearing collectors include thiols, dithiocarbamates, dithiophosphates and xanthates. Among of them, the xanthates was widely used as a collector of sulfide ore since it was easy to synthesize by using some inexpensive raw materials, as well as the ability to form stable xanthate-metal complexes with heavy metal ions (Pillai et al., 2013; Bediako et al., 2015).

The previous test results indicated that the recovery efficiency of fine malachite was dissatisfactory when the modified collector (CMCX) was used (CMCX, obtaining through alkalization of CMC and then xanthate by carbon disulfide). The contact angle and adsorption experiment results demonstrated that the hydrophobicity of malachite surface was insufficient although the adsorption capacity of CMCX on the surface of fine malachite was powerful. Therefore, adding some non-polar groups in this synthetic material is considered in this research, further to strengthen the surface hydrophobicity of malachite. After the structure modification, CMCX could be developed into an ideal collector for recovering of the copper oxide ore.

The objective of the study is to investigate the influence of the new synthetic collector 3-hydroxy butyrate-carboxy methyl cellulose xanthate (HCMCX) for fine malachite mineral, comparing the recovery efficiency with traditional collector amyl xanthate (AX) as well. The collector performance in different conditions like pulp pH and reagent concentration is studied by single and practical malachite mineral flotation, and the optimum value of these parameters were discussed in this research.

2. Experimental

2.1 Materials

The sample of single malachite was purchased as a hand-picked lump from Dongchuan dressing plant, where is located in Yunnan province, China. It was prepared by means of a hammer and dry ground (these minerals were ground in a porcelain ball mill with Zirconia balls) up to the mean size was about 25 μ m. XRD spectrums (showed in Fig. 1) and chemistry analysis results confirmed that the malachite sample was over 98% pure. The complex copper oxide ore using in this study was conducted for different deposits of Dongchuan Copper Mine (Yunnan, China), and the final particle size -18mm accounted for 100% after crushing, what as the feed of grinding.

Carbon disulfide (CS₂), 3-hydroxy butyrate and carboxy methyl cellulose were purchased from IMUMR Flotation Reagents Co., Ltd, China. Sodium hydroxide (NaOH) powders and hydrochloric (HCl) were obtained from Guoyao Chemical Reagents Co., Ltd. All the above chemicals used in the tests were of analytical grade. Amyl xanthate (AX), terpenic oil (TO), sodium sulfide (Na₂S) and sodium silicate were supplied from Dongchuan Copper ore dressing plant. Distilled water was used throughout the experiments, and all samples were weighed on an electronic balance (Precisa EP 220A, Switzerland). All pH measurements were done using a pH meter (TOADKK HM-30R, Japan) and the readings were taken in the range of ± 0.1 .

2.2. Methods

2.2.1 Synthesis of cellulose xanthate

The collector, 3-hydroxy butyrate-carboxy methyl cellulose xanthate (HCMCX), was synthesized by two steps (Fig. 2):

- Step I: 3g carboxy methyl cellulose and 100cm³ NaOH solution(mass concentration, 20%) were mixed in a 500cm³ three-neck round bottom flask for alkaline reaction, in order to make the cellulose fully expanding and dissolving. Simultaneously, 50 cm³ of the 3-hydroxy butyrate was added to react with the cellulose. In this step, the complex solution was constantly stirred (300rpm) for 1 hour in the desired temperature (296K), after that the non-polar hydrophobic group was formed by esterification.

- Step II: carbon disulfide (5.04g) was dropwise added to the round bottom flask with constantly stirring at 300rpm. After the addition process finished, the mixture was continued stirred (300rpm) for 4 hours at a constant temperature 303K, making the products receive selective collector groups (Kim et al., 1999; Dos Santos et al., 2011; Li et al., 2015; Ma et al., 2017).

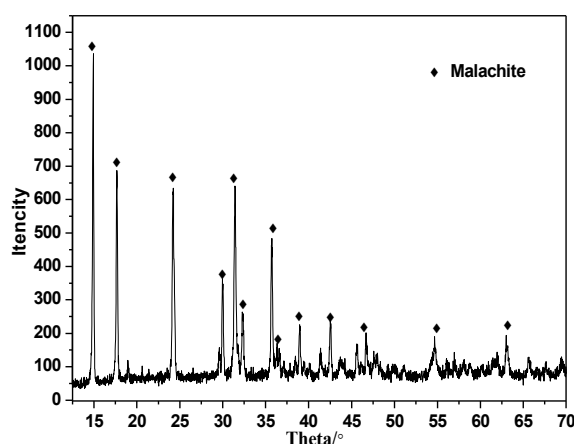


Fig. 1. The XRD spectrum of the malachite sample used for flotation tests

2.2.2 Flotation tests of pure malachite mineral

The flotation tests were carried out in the XFG-1600 type flotation machine, using the agitation speed at 1500r/min. The pulp pH was adjusted to a desired value by the addition of HCl and NaOH. Froth products and tails were weighed respectively after filtration and drying, and the recovery was calculated based on the mass of the products.

Some of the tests were repeated to evaluate the reproducibility of the experimental data. For these tests, the values presented have been averaged across all experimental runs under the same conditions. The error bars provided represent 95% confidence intervals calculated based on the standard deviation of the values.

2.2.3 Flotation tests of Dongchuan copper ores

Laboratory experiments were conducted using different deposits of Dongchuan Copper Mine (Yunnan, China). Results of chemical analysis and X-ray diffraction were shown in Tables 1 and 2, respectively. In each test, 1000g test sample was ground in a conical ball mill, and the concentration of pulp was 62%. The flotation tests were conducted as in the flow sheet shown in Fig. 2.

2.2.4 Particle size analysis

For the particle size analysis, 2.0 g of single mineral was taken and made up to 40 cm³ after the addition of distilled water in 1000-cm³ beaker. The corresponding flotation agents, which were the same types as those used in the flotation test, were added into the pulp and stirred for 5 min. The mean size of the pulp was then measured with a laser particle size analyzer at a spindle speed of 1900 rpm (MasterSizer 2000, Malvern, UK).

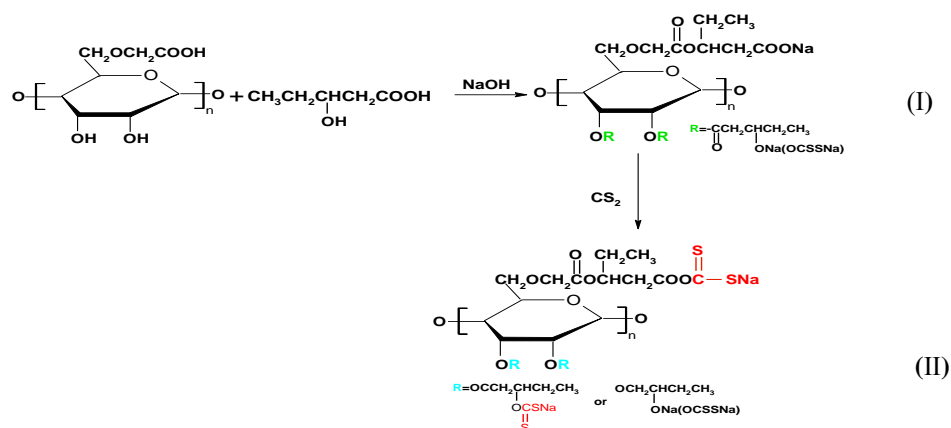


Fig. 2. Scheme synthesis of the HCMCX

2.2.5 Contact angle measurements

Static contact angles of the probe liquids on the sample surfaces were measured using GBX contact angle meter (France) equipped with a digital camera and computer software for the contact angle calculation from the shape of the settled droplet. The surface of the bulk mineral was cut and polished before the treatment of the reagents, in order to minimize the effect of surface defects on the experiments (Gao et al. 2013; Gao et al. 2014). A liquid drop of about $3.5 \times 10^{-3} \text{ cm}^3$ was placed on the sample surface, and the reading of contact angles was taken automatically on the left and right sides of the water droplet profile by computer software. Measurements of the contact angles were conducted at room temperature of 25 °C. At least 3 contact angle measurements were taken for each probe liquid on each sample surface.

2.2.6 UV Spectra

Various levels of the collector solution were mixed with the malachite, and the concentrations of two solutions were both $1 \times 10^{-4} \text{ mol/dm}^3$. Then, the mixture was sufficiently oscillated. Absorption spectra between 200 and 450nm were recorded for the supernatant using an Ultraviolet Spectrometer (UV-1750, Shimadzu, Kyoto, Japan).

Table 1. Chemical analysis of the ore. All percentages are given as weight percentage of the total

Elements	Cu	As	S	Fe	Au (g/Mg)	Ag (g/Mg)
Composition (%)	1.26	0.05	0.13	2.15	0.02	< 2

Table 2. Ore type for copper minerals

Species	Sulfides	Oxides	Total Cu
Mass Fraction (%)	0.01	1.25	1.26
Distribution Ratio (%)	0.08	99.2	100

2.2.6 Infrared spectrum studies

The following procedure was used for FT-IR spectroscopy experiments by a AVATAR360 FT-IR instrument (Nicolet Co., Madison, WI, USA). The untreated pure mineral particles were used as a reference spectrum. One gram of pure mineral particles was added into 30 mL aqueous solution with or without 200 mg/L collector HCMCX at pH 8, and then ultrasonicated for 5 min. Next, the solutions were magnetically stirred for 40 min and settled for another 40 min. After filtering, the precipitate was washed three times with distilled water and then vacuum dried at 40 °C. Fourier transform infrared (FT-IR) spectra of solids were recorded using a FT-IR spectrometer at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$). The spectra were recorded with 30 scans at a resolution of 2 cm^{-1} .

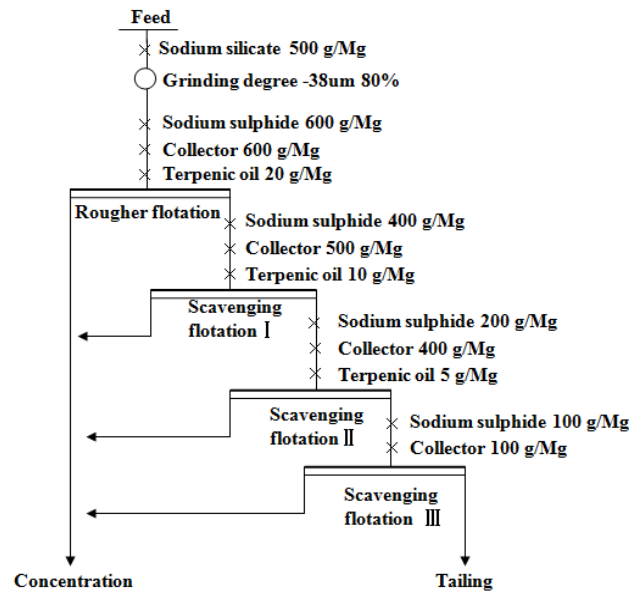


Fig. 3. Flow sheet flotation tests

3. Results and discussions

3.1 Characterization of the products

Fig. 4 presents the FTIR spectrum of CMC and HCMCX. In the IR spectrum of CMC, the peaks at 3413 and 2920 cm^{-1} are the stretching vibration of $-\text{OH}$ and $-\text{CH}_2$, respectively. The peak at 1021 cm^{-1} is attributed to the stretching vibration of C-O. The peak at 1256 cm^{-1} is attributed to the stretching vibration of aliphatic acid groups. Besides, the peak at 1646 cm^{-1} is produced by the asymmetric stretching vibrations of C=O (Derrick et al., 1999; Yang et al., 2011; Li et al., 2014).

In the IR spectrum of HCMCX, the peaks at 3387 and 2930 cm^{-1} are the stretching vibration of $-\text{OH}$ and $-\text{CH}_2$, respectively. The peak at 1658 cm^{-1} is produced by the asymmetric stretching vibrations of C=O. Besides, the new peak at 1132 cm^{-1} is produced by the stretching vibrations of S-C-S, while the peaks at 1066 and 530 cm^{-1} belong to the stretching vibration of C=S and C-S, respectively (Kong et al., 2015; Pillai et al., 2013).

In addition, the new peak of $-\text{CH}_3$ at 1,375 cm^{-1} was responsible for methyl bending vibration. A beta glycosidic linkage of the glucose ring is shifted from 915 to 879 cm^{-1} (Zawawy et al., 2014). The UV spectra results of the raw cellulose CMC and the synthetic product HCMCX in the wavelength range of 200-450 nm is shown in Fig. 5. It was indicated that the HCMCX has a maximum absorption peak at 303 nm arose from the cellulose xanthate group (Dux et al., 1965). Therefore, according to the analysis above could be confirmed that the synthesis product was the target collector.

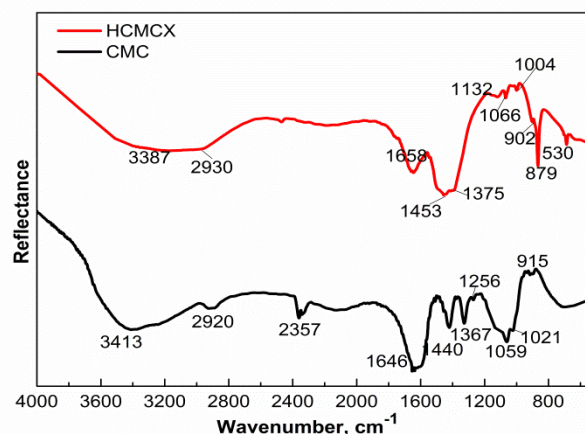


Fig. 4. Infrared spectra of CMC and HCMC

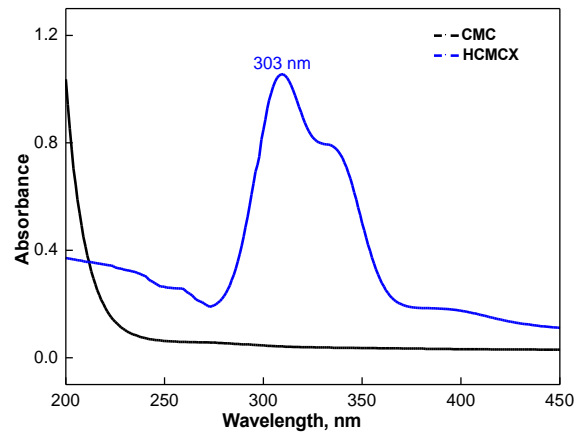


Fig. 5. Ultraviolet absorption spectra of CMC and HCMCX

3.2. Micro flotation

The effects of fine malachite in different collectors concentration were presented in Fig. 6 (a). It was indicated that a good flotation performance of fine malachite could be achieved, the recovery was about 94%, as the HCMCX concentration at 200 mg/dm³. Besides, the flotation recovery of malachite were obviously higher than AX throughout the dosage. As the concentration of AX over 300mg/dm³, the recovery of malachite hold steady at about 75%. All of the results proved that the HCMCX showed a stronger collecting ability than AX.

The effects of pH on fine malachite in the presence of either AX or HCMCX were showed in Fig. 6 (b). The results indicated that the flotation recovery in the presence of HCMCX was increased with the pulp pH rising gradually, especially, the optimum recovery of malachite was about 94% as pH = 8. Furthermore, the HCMCX exhibited a stronger collecting ability than AX throughout pH values. Liu et. (2012) proved that HS⁻ ions, major ionized component of sodium sulfide at pH 7~12, play a major role in the vulcanization process of malachite, as showed in Fig. 7. The HS⁻ was conducive to the formation of hydrophobic film on the surface of copper oxide. However, excessive HS⁻ concentration was detrimental to the recovery of malachite of vulcanization due to the strong inhibitory impact on the sulfide ore. Besides, the HCMCX probably possess strong flocculation capacity for fine particles. It was the reason why HCMCX always shows higher collector ability than AX in different conditions.

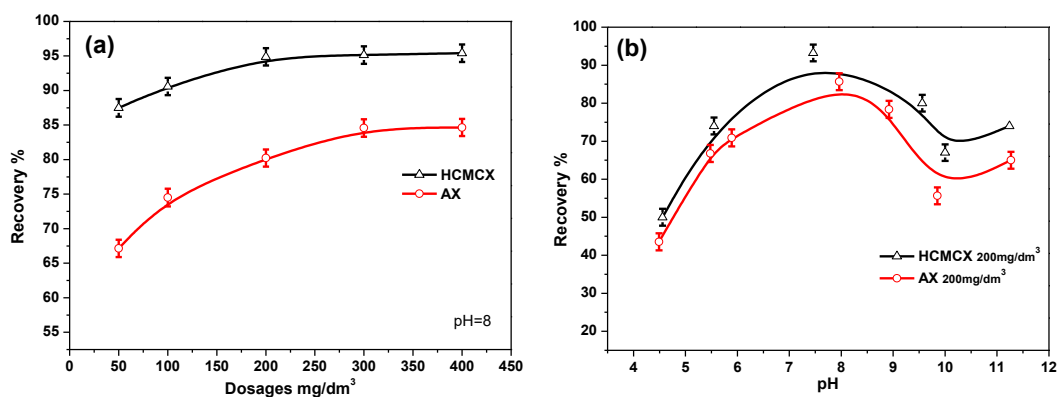


Fig. 6. Effects of (a) concentration of AX and HCMCX and (b) pH values on the flotation recovery of fine malachite (Na₂S 200mg/dm³, TO 20mg/dm³)

Three-dimensional contour plots were applied to demonstrate the interactive effects of operational parameters on the recovery of fine malachite. Fig. 8 shows the corresponding contour of the combined effect of pH and dosage of HCMCX or AX, while Na₂S 200mg/dm³, TO 20mg/dm³. From the contours, it was clear to understand the interactive effects between the two independent variables and further to decide the optimum levels. In Fig. 8, the red region represents the higher copper recovery and the deep

blue region represents the lower one. The results indicated that the slurry pH has a huge influence on the recovery of malachite, and the copper recovery was better at pH = 7~9 with both collector either AX or HCMCX; meanwhile, the effect of the collector dosage was also play a significant role until it exceeds 200mg/dm³ and 300 mg/dm³ for HCMCX and AX, respectively.

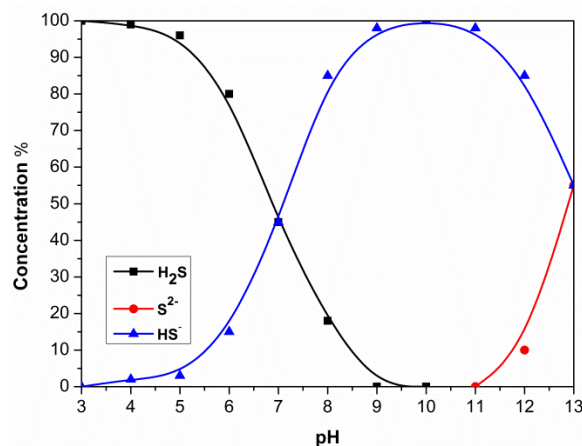


Fig. 7. Distribution of concentration of HS⁻, HS²⁻, S²⁻ as a function of pH

In order to assess the proportion of the hydraulic entrainment in the overall recovery of fine malachite, The portion of recovery associated with the hydraulic entrainment was studied in this part. In the experiment, no frother was added during the flotation process, measuring the fine malachite recovery and the weight of the water in the froth products as a function of different collector concentrations (Shen et al, 2017), as showed in Fig. 9. It can be seen that the water recovery in the presence of the HCMCX basically unchanged to compare with the AX. Therefore, it can be ensured that the improvement of recovery efficiency was mainly attributed to the stronger collecting ability of HCMCX.

3.3. Batch flotation tests

Batch flotation tests were designed to investigate the flotation effects by the synthesized collector HCMCX in the Dongchuan copper oxide ore. The yields of concentrate, copper grade and recovery are listed in Table 3, respectively. It was noted that the copper recovery efficiency was improved by the HCMCX. Meanwhile, the terpenic oil and sodium silicate were used as frother and depressant, respectively. The results showed that HCMCX achieved an better concentration products, containing the Cu grade 20.19% and the recovery 88.39% . Especially, the recovery of copper was increased by 5.69% comparing with AX.

3.4. Mean size of particles

Fig. 10 shows the effects of HCMCX and AX concentration as well as pulp pH values on the mean size of fine malachite. Fig. 10(a) can be seen that the mean size of malachite basically unchanged throughout the concentration of AX, while increasing from 25μm to 33μm as the concentration of HCMCX increased from 0 to 200 mg/dm³. However, the particle mean size was decreased slightly as the concentration of HCMCX over 200 mg/dm³. It was probably attributed to form covalent bonds or coordination bonds between the xanthate group of the HCMCX and the mineral surface, causing the collector adsorption on the surface of malachite, and finally flocculating into the clusters. Some of the previous researches denoted that, as the amount of the polymer to adsorb on the surface of malachite equal to half of the saturated adsorption capacity, the highest flocculated efficiency and the most stable flocs was achieved. If the absorbed concentration of the polymer continually to increase, the fragmentation rate of flocs will greater than the flocculation rate and leads to a decrease trend of mean particle size (Chen et al, 1985). It was the main reason why the flocculation efficiency of fine malachite was weakened when the dosage of the HCMCX exceeds a certain concentration.

The effects of pH on the mean size of malachite using different collectors were shown in Fig. 10 (b). It was indicated that the mean size, using HCMCX as the collector, was higher than AX in the entire range of pH values. Besides, the mean size was increased as pH climbed from 4 to 8 in the presence of HCMCX. And the most efficient flocculation of mineral particles was at about pH 7~9.

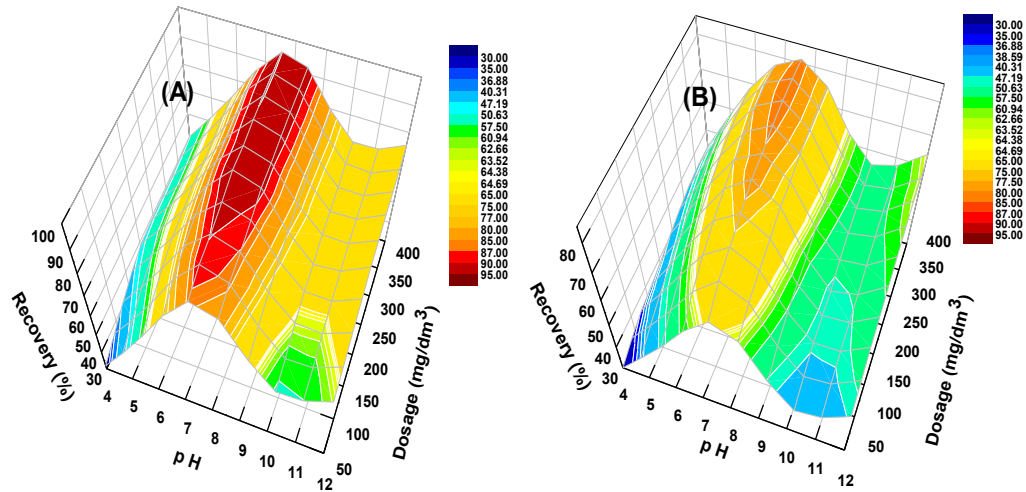


Fig. 8. Recovery response surface plots with both the slurry pH and collector dosage: (A) HCMCX and (B) AX

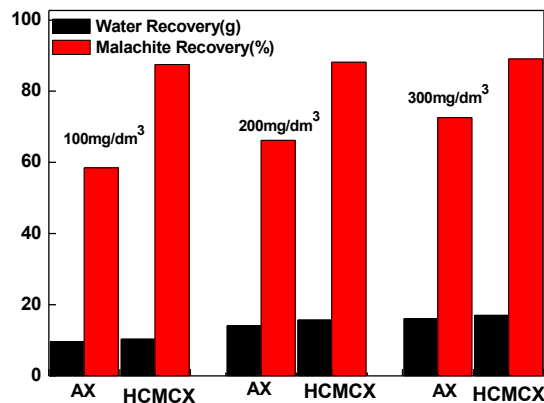


Fig. 9. Fine malachite recovery and water recovered for batch flotation as a function of collector concentration in the presence of AX and HCMCX. (Na_2S 200 mg/dm³, pH =8)

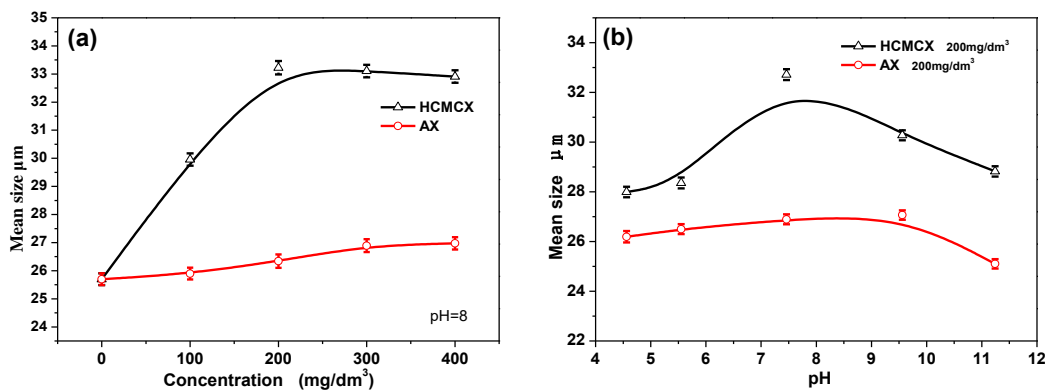


Fig. 10. Effects of (a) HCMC and AX concentration and (b) pulp pH on the particle size of fines malachite (Na_2S 200 mg/dm³)

The summation of adsorption and cohesion of the polymer on the mineral surface were higher than the electrostatic repulsion between the particles. Therefore, the polymer could adsorbed on the mineral

surface, as a bridge to flocculate fine particles, causing the mean size of the particles to increase significantly. On the other hand, the average particle size was changed with the alteration of pulp pH, which may be related to the amount of adsorption sites of HCMCX on the particle surface. The highest vulcanization efficiency of malachite was achieved at pH 7~9. After that, the mineral surface could provide more adsorption sites for HCMCX, which caused the flocculation capacity of fine particles to enhance significantly. Furthermore, the zeta potential of malachite was changed with a variety of pH values. Chen et al (1985) pointed that the dispersion-flocculation efficiency of fine particles was closely related to the zeta potential of mineral, the results was showed in Fig. 11. The mineral particles were dispersed as pH at 5~7 while flocculated at pH 7~9.

Table 3. Comparative Cu recoveries by AX and the synthesized products

Collector dosage (g/Mg)	Entry	Product	Yield (%)	Grade of Cu (%)	Recovery of Cu (%)	
HCMCX (600+500+300+100)	1	Concentrate	5.45	20.21	88.4	
		Tailing	94.55	0.152	11.6	
		Feed	100	1.248	100	
	2	Concentrate	5.46	20.11	88.28	
		Tailing	94.46	0.154	11.72	
		Feed	100	1.245	100	
	3	Concentrate	5.46	20.24	88.5	
		Tailing	94.55	0.151	11.5	
		Feed	100	1.249	100	
	Average				20.19	88.39
	AX (600+500+300+100)	4	Concentrate	5.3	19.77	84
			Tailing	94.7	0.21	15.6
Feed			100	1.248	100	
5		Concentrate	5.1	19.64	80.92	
		Tailing	94.9	0.25	15.6	
		Feed	100	1.24	100	
6		Concentrate	5.2	19.75	83.2	
		Tailing	94.8	0.22	16.8	
		Feed	100	1.248	100	
Average				19.72	82.7	

3.5. Wettability of fine malachite

In order to investigate the wettability of the surface of malachite in the presence of AX or HCMCX, the contact angle tests were carried out in the study and the results were presented in Fig. 12. It is indicated that the contact angle of both collectors were increased as the collector concentration was increased. The surface of malachite shows a strong hydrophilic before the vulcanization treatment, and the contact angle was about 15 degrees (the error is 2 degrees) (Liu et al, 2012). After vulcanization, increasing the dosage of collector HCMCX or AX, the contact angle was increased gradually. At a same collector dosage, comparing with AX, the mineral surface of malachite exhibited a stronger hydrophobicity after interacting with HCMCX. Bediako et al (2015) exposed that the surface of the modified cellulose showed a loose, porous, rough and wrinkled structure with expanding specific surface area, as showed in Fig. 13 (Zhang et al, 2016). Adsorbent morphology under that structure condition is favorable for the adsorption performance on the mineral surface.

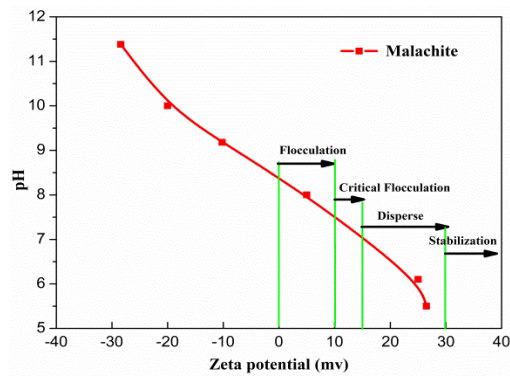


Fig. 11. The relationship between dispersion-flocculation of particles and zeta potential at different pH values

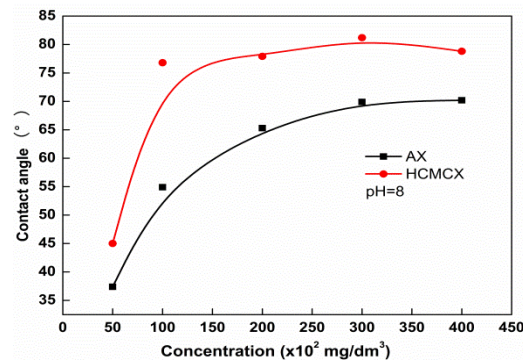


Fig. 12. Effects of HCMCX and AX concentration on the contact angle of fine malachite (Na_2S 200mg/dm³)

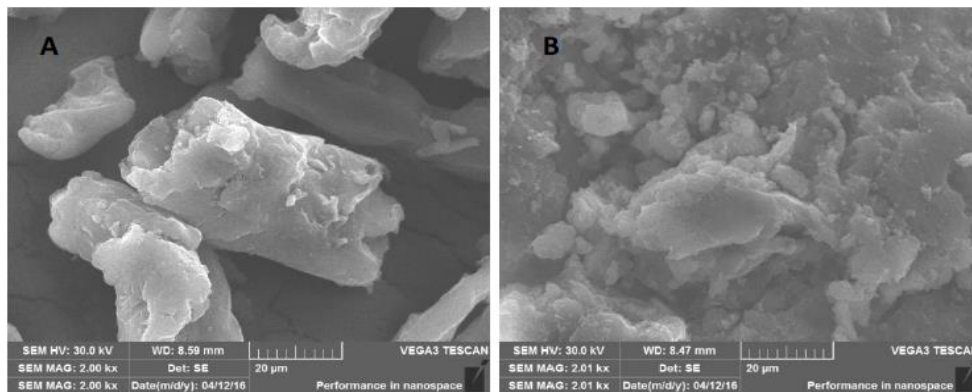


Fig. 13. SEM of CMC (A) and HCMCX (B) (Zhang et al, 2016)

3.6. FTIR analysis

The FTIR spectra of fine malachite before and after conditioning with HCMCX are plotted in Fig. 14. After vulcanization, the spectrum of malachite indicated that peaks appeared at 3410 cm^{-1} , 3314 cm^{-1} which were stretching vibration of hydroxyl group (-OH). Asymmetry bending vibration absorption peaks of -OH occur at 1505 cm^{-1} and 1387 cm^{-1} . Besides, the peak at 883 cm^{-1} , 753 cm^{-1} were assigned to the characteristic absorption peaks of CO_3^{2-} (Liu et al., 2009; Biedako et al., 2015). The band was observed at 2363 cm^{-1} , as a result of the chemical adsorption of Na_2S on the malachite surface. After the reacting of HCMCX with malachite, the C=S peaks at 1066 cm^{-1} (in Fig. 4) shifted to 1024 cm^{-1} (Socrates, 2004). The shift may attributed to the group of C=S bonded with the active atoms on the malachite surface through chemical adsorption (Socrates, 2004; Ma et al., 2017). Besides, the new peaks appear at 1651 cm^{-1} after reacting with HCMCX, due to the metal coordination complex was occurred during the

reacting process (Socrates, 2004). These results suggest that the HCMCX indeed was adsorbed on the malachite surface by chemical adsorption.

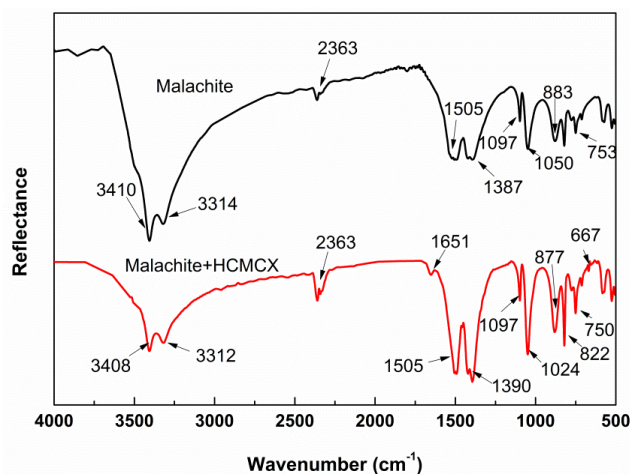


Fig. 14. FTIR spectra of fine malachite before and after conditioning with HCMCX

4. Conclusions

In this study, chemical modification of carboxy methyl cellulose was carried out aiming to introduce high-affinity functional groups, including sulfur-bearing groups and hydrophobic groups, to improve the flotation performance of fine malachite. The modification product were confirmed by FTIR analysis. Once the new peaks close to $1,375\text{ cm}^{-1}$ and $1,004\text{ cm}^{-1}$, it could be proved that the group $-\text{CH}_3$ and $\text{C}=\text{S}$ were included in the product. UV Spectra has a maximum absorption peak at 303 nm arose from the cellulose xanthate group, which confirmed that the target group 'thiocarbonyl group' was included in this product.

The mean size of malachite essentially unchanged throughout the different concentration of collector AX, while increasing from $25\mu\text{m}$ to $33\mu\text{m}$ as the concentration of HCMCX increased from 0 mg/dm^3 to 200 mg/dm^3 . In addition, comparing with AX, the surface of malachite showed a stronger hydrophobicity in the presence of HCMCX at the same dosage.

The micro flotation tests of pure malachite mineral with the collector HCMCX indicated that: under the flotation condition of $\text{pH}=8$ and collector concentration at 200 mg/dm^3 , the recovery of malachite reached 94%. The results of flotation tests of Dongchuan copper ore showed that the HCMCX could as an excellent collector for flotation of fine malachite, finally to achieve the concentrates containing 20.19% Cu with 88.39% Cu recovery.

Acknowledgements: The authors acknowledge the support of the National Natural Science Foundation of China (No. 51404218), the National Key Technology R&D Program (No.2015BAB12B02) and the Science and Technology Planning Project Guangdong Province, China (No.2013B090800016),the Fundamental Research Funds for the Central Universities of Central South University (No. 2018zzts078).

References

- ATTIA, Y.A., KITCHENER, J.A., 1975. *Development of complexing polymers for the selective flocculation of copper minerals*, 11th International Mineral Processing Congress, Cagliari, Italy,197.
- BEDIKO, J. K., WEI, W., KIM, S., YUN, Y.S., 2015. *Removal of heavy metals from aqueous phases using chemically modified waste lyocell fiber*. J. Hazard. Mater., 299, 550-561.
- CHEN, X.L., LIU, X.S., QIN, G., 2010. *Experimental study on Beneficiation of a new type of oxidized copper ore collector OK2033*. Nonferrous Min. Metall., 26(5), 17-19.
- CHEN, J., XU, Z. H., 1985. *Advances in selective flocculation theory*. Nonferrous Met. (English Edition) (01), 16-24.
- DERRICK, M.R., STULIK, D., LANDRY, J.M., 1999. *Infrared Spectroscopy in Conservation Science*, 1st ed., The Getty Conservation Institute, L/A, USA.
- DUX, J.P., PHIFER, L.H., 1957. *Determination of Xanthate Sulfur in Viscose*. Anal. Chem., 29(12), 1842-1845.

- FANG, J., 2002. *Study on the material composition and flotation process of refractory oxidized copper ore in Dongchuan*. Doctoral dissertation, Kunming university of science and technology.
- GAO, Z., SUN, W., HU, Y., LIU, X., 2013. *Surface energies and appearances of commonly exposed surfaces of Scheelite crystal*. *Trans. Nonferrous Met. Soc. China*, 23(7), 2147-2152.
- GAO, Z., SUN, W., HU, Y., 2014. *Mineral cleavage nature and surface energy: anisotropic surface broken bonds consideration*. *Trans. Nonferrous Met. Soc. China* 24(9), 2930-2937.
- GE, Y., XIAO, D., LI, Z., CUI, X., 2015. *Dithiocarbamate functionalized lignin for efficient removal of metallic ions and the usage of the metal-loaded bio-sorbents as potential free radical scavengers*. *J. Mater. Chem. A*, 3(14), 7666-7666.
- HU, Y.H., LIU, G.X., WANG, D.Z., 1986. *Sulfur non-ionic flotation of copper oxide polar catch*. *Nonferrous Met. Eng.* (02), 30-35.
- KIM, H. T., LEE, K., 1999. *Application of insoluble cellulose xanthate for the removal of heavy metals from aqueous solution*. *Korean Journal of Chemical Engineering*, 16(3), 298-302.
- KLEMM, D., HEUBLEIN, B., FINK, H.-P., BOHN, A., 2005. *Cellulose: fascinating biopolymer and sustainable raw material*. *Cheminform*, 44(22), 3358-3393
- KONG, Y., GE, Y., 2015. *Synthesis of porous lignin xanthate resin for Pb²⁺ removal from aqueous solution*, *Chem. Eng. J.* 270, 229-234.
- LI, X., HU, Y., ZHANG, B., 2014. *Kinetics and equilibrium adsorption of copper(II) and nickel(II) ions from aqueous solution using sawdust xanthate modified with ethanediamine*, *Trans. Nonferrous Met. Soc.* 24, 868-875.
- LI, Z., KONG, Y., GE, Y., 2015. *Synthesis of porous lignin xanthate resin for Pb²⁺, removal from aqueous solution*. *Chem. Eng. J.*, 270, 229-234.
- LIU, CH., 2012. *Study and application of sulfide flotation of typical oxidized copper ores*. Doctoral dissertation, Jiangxi University of Science and Technology.
- LIU, D.W., SHANG, X., FANG, J., 2010. *Study on mineral flotation of fine particles of copper oxide*. *China Min.*, 19(1), 79-81.
- LIU W., WEI D. Z., WANG B. Y., 2009. *A new collector used for flotation of oxide minerals*. *Transactions of Nonferrous Metals Society of China*, 19(5):1326-1330.
- LIU, Q., WANNAS, D., PENG, Y., 2006. *Exploiting the dual functions of polymer depressants in fine particle flotation*. *Int. J. Miner. Process.*, 79(2), 244-254.
- MA, X., XIA, L., WANG, S., ZHONG, H., JIA, H., 2017. *The structural modification of xanthate collectors to enhance the flotation selectivity of chalcopyrite*. *Industrial & Engineering Chemistry Research*, 56(21), 6307-6316.
- PILLAI, S.S., DEEPA, B., ABRAHAM, E., GIRIJA, N., GEETHA, P., JACOB, L., KOSHY, M., 2013. *Biosorption of Cd(II) from aqueous solution using xanthated nano banana cellulose: equilibrium and kinetic studies*, *Ecotoxicol. Environ. Saf.*, 98, 352-360.
- SCHULZE, H.J., RADOEV, B., GEIDEL, T., STECHEMESSER, H., TOPFER, E., 1989. *Investigations of the collision process between particles and gas bubbles in flotation - a theoretical analysis*. *Int. J. Miner. Process.*, 27, 263-278.
- SHEN L., ZHU, J., LIU, L., 2017. *Flotation of fine kaolinite using dodecylamine chloride/fatty acids mixture as collector*. *Powder Technol.*, 312, 159-165.
- SHIBATA, J., FUERSTENAU, D.W., 2003. *Flocculation and flotation characteristics of fine hematite with sodium oleate*. *Int. J. Miner. Process.*, 72(1-4), 25-32.
- SUN, W., DENG, M.J., HU, Y.H., 2009. *Fine particle aggregating and flotation behavior induced by high intensity conditioning of a CO₂ saturation slurry*. *Int. J. Min. Sci. Technol.*, 19(4), 483-488
- SANTOS, V. C. G. D., SOUZA, J. V. T. M. D., TARLEY, C. R. T., CAETANO, J., DRAGUNSKI, D. C., 2011. *Copper ions adsorption from aqueous medium using the biosorbent sugarcane bagasse in natura and chemically modified*. *Water Air Soil Pollut.*, 216(1-4), 351-359.
- SOCRATES, G., 2004. *Infrared and Raman Characteristic Group Frequencies*. John Wiley & Sons: Chichester, U.K.
- WARREN, L.J. 1984. *Ultrafine particles in flotation*. In: Jones, M.H., Woodcock, J.T. (Eds.), *Principles of Mineral Flotation*. Australian IMM, Melbourne, pp. 185-214.
- YANG, S.P., FU, S.Y., LIU, H., ZHOU, Y.M., LI, X.Y., 2011. *Hydrogel beads based on carboxymethyl cellulose for removal heavy metal ions*. *J. Appl. Polym. Sci.* 119, 1204-1210.
- ZAWAWY, W.K., 2006. *Blended graft copolymer of carboxymethyl cellulose and poly(vinyl alcohol) with banana fiber*, *J. Appl. Polym. Sci.* 100, 1842-1848.
- ZHANG, Y., LUO, C., WANG, H., HAN, L., WANG, C., JIE, X., et al. 2016. *Modified adsorbent hydroxypropyl cellulose xanthate for removal of Cu²⁺ and Ni²⁺ from aqueous solution*. *Desalin. Water Treat*, 1-13.