The mechanism study on deep eutectic solvent for desilication of magnetite by reverse flotation

Zhan He [1,2], **Cai Liu** [1,2], **Guangjun Mei** [1,2,3], **Yuanyuan Zhao** [1,2], **Qian Cheng** [1,2,3], **Xianwei Song** [1,2]

[1] Hubei Key Laboratory of Mineral Resources Processing and Environment, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei 430070, China

[2] State Key Laboratory of Mineral Processing, Beijing 100080, China

[3] State Key Laboratory of Efficient Utilization for Low Grade Phosphate Rock and Its Associated Resources

Corresponding author: meiguangjun@aliyun.com (G. Mei)

Abstract: Magnetite reverse flotation using a new deep eutectic solvent synthesized by lactic acid and CTAC as the collector has been investigated in this work. The flotation test results were compared with dodecylamine. The CTAC/lactic acid DES increased the grade of total iron to 66.69%, and the reduce quartz content to 6.67%, which were preferable to dodecylamine (the grade of Fe in the concentrate is 63.47%, and the grade of quartz in the concentrate is 9.13%). The depression performance and adsorption mechanism of CTAC/lactic acid DES on surface of magnetite and quartz are investigated by FT-IR, zeta potential and XPS. The results show that the adsorption of CTAC/lactic acid DES on quartz surface is more effective than that of magnetite. Therefore, deep eutectic solvent is an effective reagent for reverse flotation of magnetite as collector.

Keywords: reverse flotation, deep eutectic solvents collector, desilication, magnetie, quartz

1. Introduction

Quartz is the most main impurity in iron ore. as early as the 1950s, iron ore was purified by flotation in industrial production (Mei et al., 2000). With the detailed research on various iron ores, the process with excellent separation performance was designed, and various high-efficiency flotation reagents are developed accordingly, which promotes the enormous development of iron ore flotation technology (Zhao et al.,2007). Nevertheless, how to achieve iron extraction and impurity removal greener, more effective, and lower investment is still a practical problem to be solved, and it is also one of the topics most concerned by researchers.

It was reported that the reverse flotation of iron ore is better than the direct flotation (Ren et al., 2004), and the reverse flotation includes anionic reverse flotation and cationic reverse flotation (Song et al., 2009), Anionic reverse flotation uses primary monoamines and their corresponding acetate or chloride derivatives as collectors (Sahoo et al., 2015), which can effectively avoid the influence of silicate minerals and impurity ions such as calcium and magnesium in the pulp. Compared with anionic reverse flotation, cationic reverse flotation is more effective for the separation of quartz and magnetite. Amine collectors are conventional agents in the process of cationic reverse flotation, especially dodecylamine. Li et al. (1997) further reverse flotation of iron concentrate with dodecylamine as collector, which has a significant effect on improving the quality of iron concentrate. The hydrocarbon chain length, structure, and group substitution position of the reagent are directly related to the reagent properties (Filippov et al., 2010). The research results of Liu et al. (2009) show that the substituents connecting nitrogen atoms in tertiary amine molecules are the main influencing factors, and then the flotation performance of tertiary amine collectors can be controlled by designing the electronic effect and steric hindrance of substituents. A new GE-601 (polyamine) collector was prepared by increasing the amount of amino. In

the process of reverse flotation, an iron concentrate with grade of 69.37% and recovery of 98.65% was obtained, and the grade of tailings was only 14.39% (Ge et al., 2004). In addition to aliphatic amines, ether amines are also the focus of beneficiation workers. Because the polar group –O– $(CH_2)_3$ is introduced, ether amine is more soluble in water than aliphatic amine, ether amine collector is easier to enter the solid-liquid and gas-liquid interface, and has good foam mobility (Araujo et al., 2005, Wei et al., 2005; Vieira et al., 2007). The research shows that under the condition that neither aliphatic amine nor condensed amine can make the SiO_2 content in iron concentrate reach the standard, and the optimal amount of ether amine can reduce the SiO_2 in concentrate below 4%, which has significant advantages in reverse flotation (Papiri et al., 2001).

In recent years, inspired by the combination of collectors, some new reverse flotation reagents have been developed (Nakhaei et al., 2018), especially in the application of ionic liquid collectors. Sahoo et al. (2014, 2015) have carried out the flotation test of quartz with methyl trioctylammonium chloride and TOMAS, and have proved the excellent collection performance.Li et al. (2019) synthesized an ionic liquid (composed of cetyltrimethylammonium bromide and sodium salicylate), compared with dodecylamine, reverse flotation is more effective in desilication. The preparation process of ionic liquid is complicated, usually needs to go through distillation, extraction, and other processes for about 2-3 days. Moreover, the viscosity of the preparation agent is large, which limits its popularization. Therefore, further improvement based on ionic liquid is the development direction of obtaining excellent cationic reverse flotation reagents.

The concept of deep eutectic solvent (DES) was first proposed by Professor Abbott and applied to metal surface treatment (Avalos et al., 2006). The essence of deep eutectic solvent is the combination of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) by a molecular hydrogen bond. Although it is close to the concept of ionic liquids, it is superior to ionic liquids in all aspects. Compared with ionic liquids, deep eutectic solvents are simpler in preparation, cheaper in price, higher in atom utilization, and extremely low in volatility. In terms of the basic concept of green chemistry and practical industrial applicability, deep eutectic solvents have more advantages (Li et al., 2016; Francisco et al., 2013; Wu et al., 2014).

Therefore, in this paper, the DES is used as the collector of magnetite by reverse flotation, and the feasibility of the application of the reagent in the flotation field is mainly investigated. The flotation performance of the DES collector under the influence of the dosage of reagent, pulp pH, and other factors is studied, and compared with the dodecylamine. The mechanism of reverse flotation was preliminarily revealed, and finally, the DES reverse flotation reagent with strong environmental protection and low toxicity was explored.

In this work, DES was synthesized using CTAC and lactic acid by stirring, whose molecular structure was characterized by FTIR and 1H-NMR. Then, the effects of DES dosage and pH value on the recovery of quartz and magnetite were explored, and the optimal process conditions were determined. On this basis, the experiment of artificial mixed minerals was carried out. Compared with dodecylamine, it can obtain the excellent effect of the increasing grade of iron and reducing the grade of silicon. In addition, the mechanism was analyzed by FTIR, zeta potential, contact angle measurement, and X-ray photoelectron spectroscopy (XPS), and a conceptual approach to the reaction of DES with minerals was proposed.

2.   Materials and methods

2.1.   Pure minerals and reagents

The quartz was obtained from Inner Mongolia, and the magnetite was purchased from NCS Testing Technology Co., Ltd, China. Quartz was crushed, ground, and wet-sieved to an appropriate size for the flotation tests.; magnetite was directly used for flotation without further processing. As shown in the cumulative distribution curve in Fig. 1 and Fig. 2, the median diameters d_{50} of quartz and magnetite were 54.5 μm and 35.4 μm, respectively, respectively. According to the chemical composition (Table 1), SiO_2 in quartz was 99.84%, while the TFe in magnetite was 70.69%, which indicated that these minerals are of high purity.

In this work, Cetyltrimethylammonium chloride (CTAC), lactic acid, starch, sodium hydroxide, and hydrochloric acid are all analytical grade originating from Sinopharm chemical reagent Co., Ltd, China. CTAC and lactic acid are used for the synthesis of DES. Starch is the inhibitor of mixed ore flotation test. Sodium hydroxide and hydrochloric acid adjust the pulp pH.
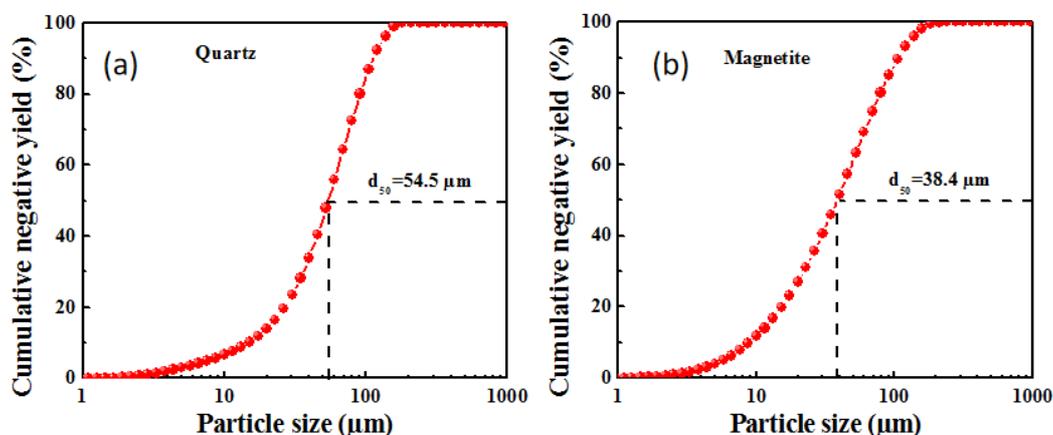

Fig. 1. Particle size distribution and cumulative distribution curve of quartz (a) and magnetite (b)

Table 1. Chemical compositions of minerals (wt%)

Minerals	TFe	SiO_2	Na_2O	Al_2O_3	CaO	K_2O	TiO_2
Quartz	0.05	99.84	0.009	0.05	0.0012	0.004	0.0013
Magnetite	70.69	0.293	0.010	0.32	0.066	0.012	0.535

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2.2. Synthesis deep-eutectic solvents

Cetyltrimethylammonium chloride was used as hydrogen bond acceptor, lactic acid was used as hydrogen bond donor and added into a 100ml beaker according to the molar ratio of 1:4. Then, stirring magnetically at 100℃ for 2 hours until clarification, the deep eutectic solvent was prepared (Zubeir et al., 2018). The obtained deep eutectic solvent was sealed and stored in a vacuum drying oven. The synthetic route of the designed DES is shown in Fig. 2.

Weigh a certain amount of synthetic deep eutectic solvent into a 50ml beaker, add a small amount of deionized water and stir it fully, and then configure it into a solution with a concentration of 1 mmol/L in a 1L volumetric flask as a deep eutectic solvent collector for flotation experiment.

2.3. Micro-flotation experiments

The flotation tests for each pure mineral and artificial mixed minerals were carried out in a XFG-type flotation machine with a 30 mL cell and the stirring speed of 1300rmp.In each test, 2 g of mineral sample was dispersed in the 30 mL cell with 20 mL deionized water. The pH of the pulp was adjusted to an appropriate value and stirring for 1min. Then, adding CTAC/lactic acid DES collector into pulp stirring
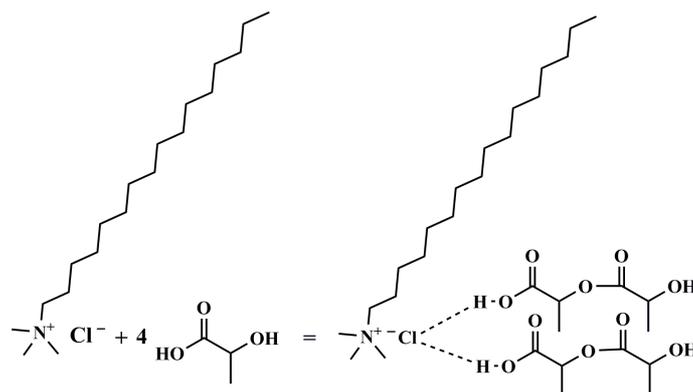
Fig. 2 The conceptual synthesis route of CTAC/lactic acid DES

for 2 min. The aeration flotation was conducted for 3-4 min. At last, the froth products and the tailings were collected and weighed after drying for calculating recovery and characterization. As for the flotation of mixed minerals, quartz and magnetite were mixed at the ratio of 1:3 as a feeding mineral sample. Flotation procedures were followed as above. The grade of Fe was analyzed by chemical titration and the recovery of magnetite was calculated. Finally, the beneficiation efficiency was calculated according to formula (1) through concentrate recovery, concentrate yield, raw ore grade, and pure mineral grade:

$$E = \frac{\varepsilon - \gamma}{1 - \alpha/\beta_{max}} \times 100\% \tag{1}$$

where, ε is the concentrate recovery rate; γ is concentrate yield; α and β_{max} are the grades of raw ore and pure mineral respectively.

2.4. FT-IR spectra analysis

Fourier transform infrared (FT-IR) spectra (Nicolet6700, Thermo Nicolet, America) were used to analyze the minerals samples (before and after adsorption with CTAC/lactic acid DES). 0.1g of mineral samples less than 5µm was added into 50 mL deionized water. The pure mineral was groud to less than 5µm, 0.1g of mineral sample was added into 50 ml aqueous solution with or without DES at 30℃, and then kept stirring for 30 min. After that, the mineral sample was vacuum filtered and dried in vacuum at low temperature.

2.5. Zeta potential measurements

Malvern Zetasizer Zeta-Nano (ZS90, Malvern, UK) was used to testing Zeta potentials of mineral samples before and after adsorption of CTAC/lactic acid DES. Firstly,0.1g of mineral samples less than 5µm was added into 100 mL deionized water. After the PH value was adjusted by 10% HCl and 10% NaOH solutions, ultrasonic dispersion was carried out. An appropriate amount of suspension was taken for testing the zeta potential of pure minerals. The average value of the three independent measurements was the result.

2.6. XPS measurements

X-ray photoelectron spectroscopy (Escalab 250XI, Thermo Fisher Scientific, USA) was used to analyze minerals after interaction with a DES. The results of XPS have been calibrated with C1s (284.80 eV).

2.7. Other characterizations

The particle size of quartz and magnetite was measured by Malvern Mastersizer (apa2000, Malvern, UK). Fourier transform infrared spectrometer (FTIR: Nicolet6700, Thermo Nicolet, America) and proton nuclear magnetic resonance (1H NMR: Bruker Avance III HD 500, Bruker, Germany) was used to analyze the the molecular structure of synthetic CTAC/lactic acid DES.

3.   Results and discussions

3.1. Characteristics of DES

The molecular structure of synthetic CTAC/lactic acid DES was analyzed by FTIR and 1H-NMR spectrum. The FTIR spectra of CTAC, lactic acid, and CTAC/lactic acid DES were recorded at room temperature and shown in Fig. 3(a). The characteristic peaks of cetyltrimethylammonium chloride (Wang et al., 2015; Huang et al., 2012) in the FTIR spectrum are observed obviously. Peak at 911.74 cm^{-1} and 965.29 cm^{-1} are assigned to the characteristic of C-N, while peak at 3015.21 cm^{-1}、2917.03 cm^{-1}, 2848.59 cm^{-1}, 1480.00 cm^{-1} and 727.27 cm^{-1} are for the symmetric, antisymmetric, and flexural vibrations of CH$_3$, CH$_2$, and CH. As for the single lactic acid, peak of 3355.54cm^{-1} and 1731.41cm^{-1} correspond to the vibration of C-OH and C=O respectively, while the remaining absorption peak is related to vibration of C-H (Wang, 2016; Zhang et al., 2016). Compared with a single agent, the absorption peaks in CTAC/lactic acid DES shifted to different degrees. Some deformation occurs in C-N vibrations, such as shifting from 911.74cm^{-1}and 965.29cm^{-1} to 911.13cm^{-1} and 967.20 cm^{-1}, respectively. The vibration peak at 2800-3000 cm^{-1} was weakened. In addition, an upward shift from 1731.41 cm^{-1} to 1741.21 cm^{-1} is observed at the vibration peak of C=O, and the vibration peak of C-OH at 3355.54 cm^{-1} was shifted to 3358.02cm^{-1}. This indicates that changes in conformation may be caused by the hydrogen bonding between the raw materials.

The 1H-NMR spectra of CTAC/lactic acid DES are presented in Fig. 3(b). The proton peak of cetyltrimethylammonium chloride are consistent with other information of standard peak. The methylene proton peak of carboxyl group in lactic acid and polylactic acid shifted, which hints that conformation of (poly)lactic acid changed obviously (Su et al., 2009; Liu, 2018; Xie et al., 2014). Hence, CTAC/lactic acid DES consists mostly of cetyltrimethylammonium chloride and lactic acid through hydrogen bonds.
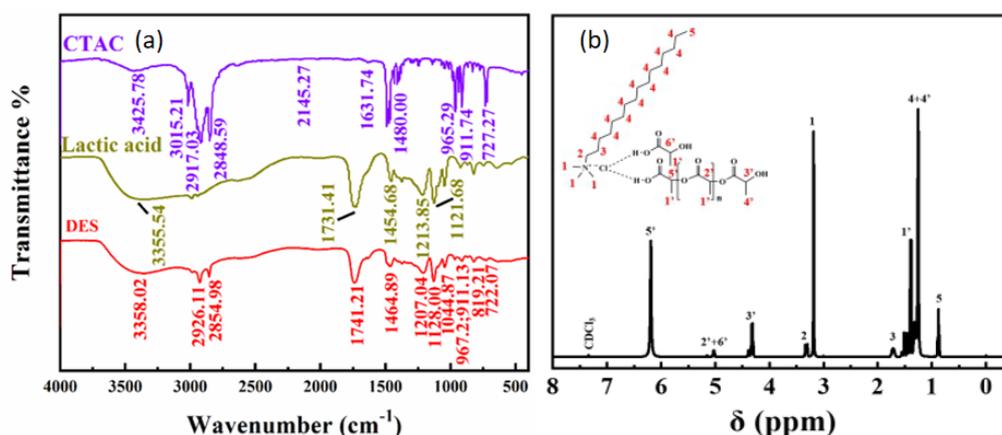

Fig. 3 FTIR of CTAC, lactic acid and CTAC/lactic acid DES

3.2. Micro-flotation results

The effects of DES collector concentration and pH of pulp on collecting efficiencies were investigated. In Fig. 4(a).With the increase of CTAC/lactic acid DES concentration, the recovery of quartz increased from 26.86% to 98.44%. When the CTAC/lactic acid DES concentration is 0.3mmol/L, the recovery of magnetite was 30.08%, which was far inferior to that of quartz under this condition. The flotation difference between quartz and magnetite by CTAC/lactic acid DES shows that the collector has the potential to separate quartz from magnetite. The results by calculating show that when the dosage of CTAC/lactic acid DES is 0.15 mmol/L, the difference value between the recovery of quartz and magnetite is the largest, reaching 85.95%. Therefore, the dosage of CTAC/lactic acid DES collector is set at 0.15mmol/L in the subsequent experiment.

Fig. 4(b) illustrates that the recovery of quartz is higher than that of magnetite in all pH of pulp conditions. In addition, the recovery of quartz reaches the peak in the near-neutral environment (93.77%), and then decreases, indicating that pH significantly affects the flotation of quartz. Because the

quaternary ammonium salt in CTAC/lactic acid DES contains amine cation (RNH_3^+), it plays an important role in reverse flotation. In alkaline condition, RNH_3^+ will be converted to RNH_2^+; while RNH_3^+ has a high concentration in acidic condition, so they can interact with each other through hydrogen bonds. Both of them weaken the adsorption capacity of RNH_3^+ on quartz. In conclusion, CTAC/lactic acid DES collector has good desilication performance in near neutral environment in the flotation.
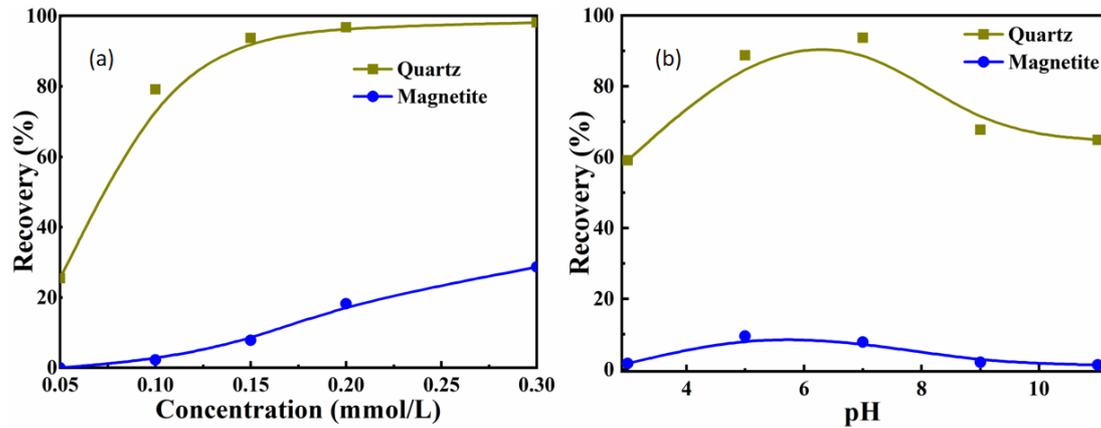

Fig. 4 The flotation recoveries of magenetite and quartz as a function of concentration of CTAC/lactic acid DES (a), and pH (b)
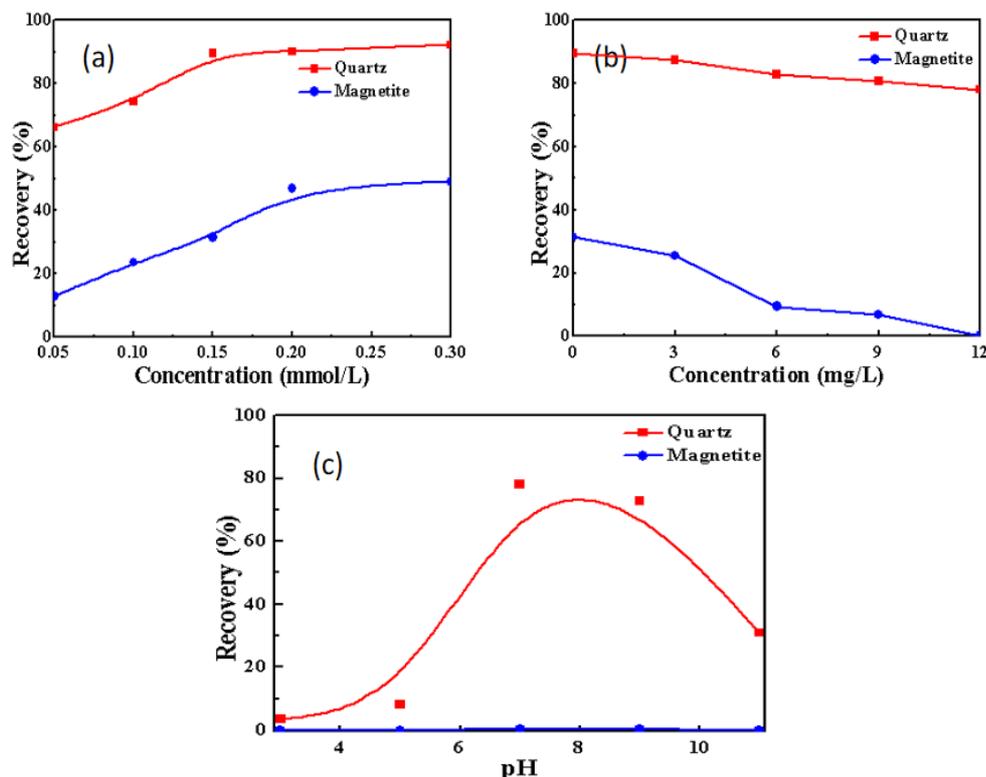

Fig. 5 The flotation recoveries of magenetite and quartz as a function of concentration of dodecylamine (a), concentration of starch (b) and pH (c).

The effect of dodecylamine concentration on the recovery of quartz and magnetite is shown in Fig. 5(a). When the dosage of the collector increases, the recovery of quartz and magnetite increases gradually. When the dosage of dodecylamine was 0.15 mmol/L, the recoveries of quartz and magnetite were 89.64% and 31.52%, respectively. When the concentration of dodecylamine is 0.3mmol/L, the

recovery of quartz is 92.30%, while the recovery of magnetite is 49.12%. The results show that sufficient dodecylamine can promote the recovery of minerals, but the appropriate concentration should be selected to avoid the waste of reagents in practical application. Based on the experiment results of floatability, the dosage of dodecylamine collector is set at 0.15mmol/L in the subsequent experiment. In Fig. 5(b), With the increase of starch concentration, the recoveries of quartz and magnetite gradually decrease, compared with quartz, the decline of recovery of magnetite more obvious, which indicates that starch is an effective and feasible depressant. The flotation depressant of starch is attributed to the competitive adsorption of starch and collectors on the mineral surface. When starch preferentially occupies the mineral surface, the interaction between collector and minerals will be significantly hindered, resulting in the decrease of recovery. To reduce magnetite being collected by dodecylamine as much as possible, the dosage of starch is set at 12mg/L in the subsequent experiment. In Fig. 5(c), The pulp pH has a significant effect on the flotation performance of dodecylamine collector. The recovery of quartz is 78.09% under the near-neutral condition (pH = 7). However, the recovery decreases obviously under the acidic or alkaline condition. For magnetite, the recovery of magnetite is close to 0% under all pulp pH conditions. As mentioned above, the effect pH of pulp on mineral recovery is also attributed to its effect on the morphology of amino groups in the collector. Hence, it is not necessary to adjust the pH when using dodecylamine.

Based on the results of the pure mineral flotation experiment, the best conditions for flotation were determined. The flotation of the artificially mixed minerals (quartz:magnetite=1:3) was carried out to further compare the flotation performance of CTAC/lactic acid DES and dodecylamine. Flotation results are shown in Table 2. According to the results in Table 2, when CTAC/lactic acid DES was used as collectors, the grade of TFe in the concentrate increases from 53.02% to 66.69%, and that of quartz decreased from 25.18% to 6.67%. which shows that the flotation performance is superior to that of dodecylamine(The grade of Fe in the concentrate is 63.47%, and the grade of quartz in the concentrate is 9.13%). The CTAC/lactic acid DES can effectively separate magnetite and quartz, at the same time, the concentrate yield is 79.86%, the recovery of TFe is about 94.67%, and the beneficiation efficiency is 72.07%. The results of the flotation test of the artificially mixed minerals show that the CTAC/lactic acid DES collectors have excellent flotation performance, and can effectively achieve desilication of magnetite.

Table 2. Comparison of results in the reverse flotation of artificial mixed minerals by using different collectors (quartz : magnetite = 1 : 3)

Collector	Product	Yield(wt.%)	Grade(%)		Recovery(%)		Efficiency(%)
			TFe	SiO$_2$	TFe	SiO$_2$	
CTAC/lactic acid DES	concentrate	75.00	66.69	6.67	94.16	19.83	72.07
	tailings	25.00	12.31	80.30	5.84	80.17	
	feeding	100.00	53.02	25.18	100.00	100.00	
Dodecyl-amine	concentrate	79.08	63.47	9.13	94.67	28.67	58.22
	tailings	20.92	13.53	85.85	5.33	71.33	
	feeding	100.00	53.02	25.18	100.00	100.00	

3.3. Mechanism of flotation

Fig. 6 shows the FT-IR spectra of quartz and magnetite before and after interaction with CTAC/lactic acid DES collector. In the infrared spectrum of quartz, peaks at 781.4 cm^{-1} and 463.06 cm^{-1} correspond to the flexural vibration of Si-O-Si, while the peak at 1169.64 cm^{-1} and 1082.78 cm^{-1} is assigned to its asymmetric stretching vibration, peak at 1880 cm^{-1} and 693.49 cm^{-1} is the stretching vibration absorption peaks of the silicon-oxygen tetrahedron and the vibration peaks of six-membered rin (Ming et al., 2004; Nayak et al., 2007), respectively. After interaction, The new peak of 2922.98 cm^{-1}、2854.55 cm^{-1} are related to the vibration of methyl and methylene of CTAC, while the peak of 1792.39 cm^{-1} is for the C=O of

lactic acid. In addition, the vibration absorption peaks of methyl and methylene shifted slightly, and the peaks at 2926.11 cm^{-1} and 2854.98 cm^{-1} shifted to 2922.98 cm^{-1} and 2854.55 cm^{-1}, respectively. However, compared with the spectrum of magnetite, CTAC was not adsorbed, and only lactic acid interacts with magnetite and adsorbs on the surface. Quaternary ammonium salt in CTAC plays an important role in changing the floatability of minerals because of the strong hydrophobicity of its tail. Therefore, CTAC/lactic acid DES exerts preferential adsorption for quartz than magnetite.
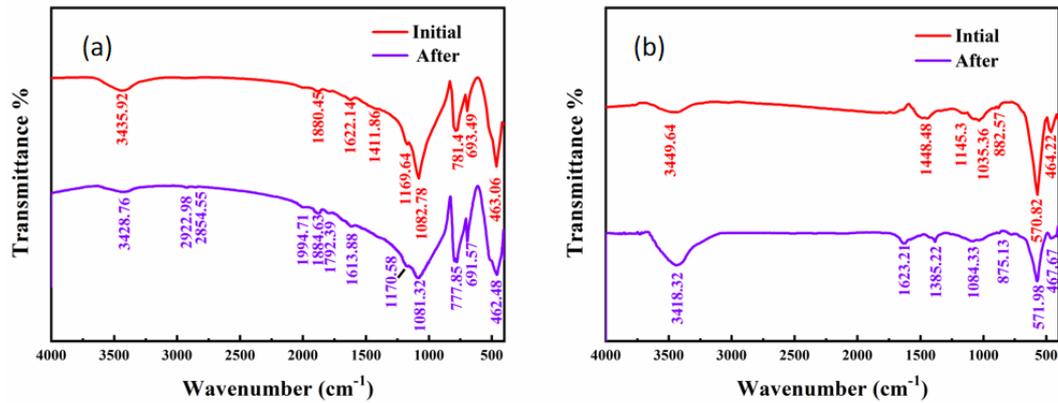

Fig. 6 FTIR of quartz (a) and magnetite(b) before and after adsorption with CTAC/lactic acid DES
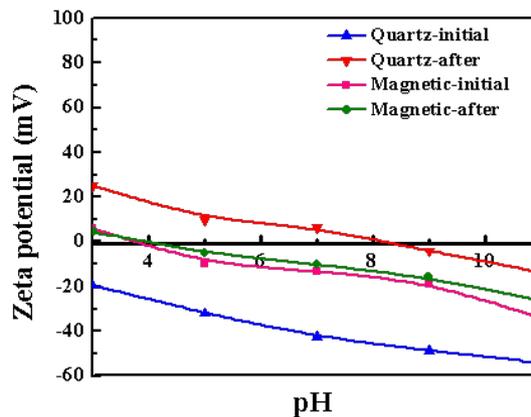

Fig. 7. zeta potential of quartz and magnetite before and after adsorption with CTAC/lactic acid DES
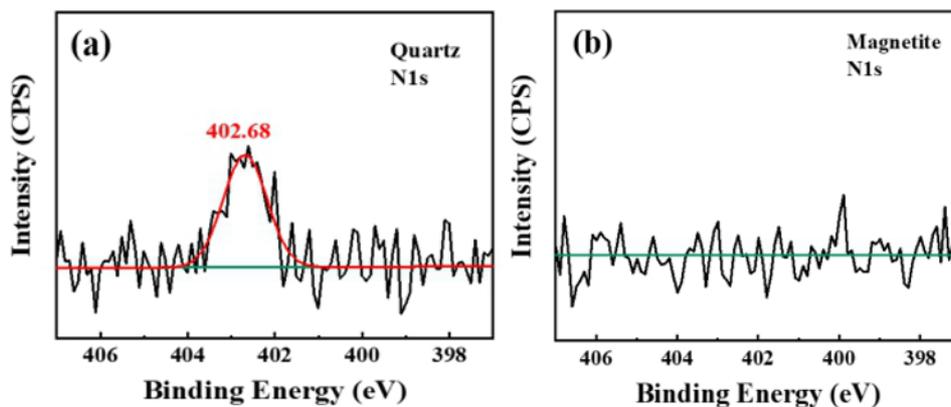

Fig. 8. XPS N1s of (a) quartz and (b) magnetite after adsorption by CTAC/lactic acid DES

To further understand the difference in flotation behavior of minerals, the changes of surface dynamic potential before and after the interaction between mineral and collector were analyzed. The

zeta potentials of quartz and magnetite before and after interacting with the CTAC/lactic acid DES are shown in Fig. 7. After quartz interacting with the CTAC/lactic acid DES, the zeta potentials of quartz increase from -48 mV to 13mV. As for magnetite after interaction, the zeta potential changes slightly, and the point of zero charge shifts slightly. The results show that DES collector has a more obvious effect on the surface properties and adsorption of quartz.

To further study the adsorption behavior of CTAC/lactic acid DES on the mineral surface, the quartz and magnetite after interaction with CTAC/lactic acid DES were analyzed by XPS. The N1s spectrum is mainly analyzed due to the N element in CTAC/lactic acid DES is the characteristic element, and the results are shown in Fig. 8. An obvious peak is observed in Fig. 8 (a), which indicates that there is an N element on the quartz surface, and CTAC/lactic acid DES is adsorbed on the surface of quartz. At the same time, it is found that the peak is located at 402.68 eV, which is consistent with the N1s characteristic peak of amino (Aydin, et al., 2013), and the amino is in the protonated state ($-NH_3^+$), which is easy to interact with negatively charged minerals through electrostatic interaction, which also explains the existence of CTAC/lactic acid DES component on the surface of quartz. However, in Fig. 8(b), the signal of N on the magnetite surface after interaction with DES is not detected, which indicates that the amino component of CTAC/lactic acid DES is not adsorbed on the magnetite surface. The infrared spectrum and change of zeta potential show that the surface of magnetite can only make lactic acid molecules stay through adsorption, which is similar to the function of traditional depressant, hindering the adsorption of CTAC components, resulting in the failure of N element detection. Therefore, the results indicate that the adsorption behavior and process of CTAC/lactic acid DES on quartz and magnetite are different.

Based on the flotation test and analysis, CTAC/lactic acid DES collector can realize desilication by reverse flotation, which is strongly related to the adsorption behavior of CTAC/lactic acid on the mineral surface. Firstly, CTAC/lactic acid is composed of CTAC and lactic acid by hydrogen bonding. Its quaternary ammonium salt has hydrophobicity and contains positively charged amino, which plays an important role in the collection. While the lactic acid has a hydrophilic and negatively charged carboxyl group, which cannot play a role in the collection. When the pulp pH is 7, both quartz and magnetite are negatively charged, which has the trend of adsorbing CTAC/lactic acid by static electricity. Therefore, they can be carried by bubbles to products in principle. However, the carboxyl group of lactic acid in CTAC/lactic acid DES will easily form stable complexes with Fe^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+}, Ca^{2+}, and other metal ions through chemisorption behavior, so it will preferentially occupy Fe sites when interacts with magnetite, and the electrostatic interaction between lactic acid and CTAC is limited, resulting in the lack of hydrophobic quaternary ammonium salts on the surface of magnetite, which is consistent with the analysis results of FTIR, zeta and XPS. In essence, lactic acid as an inhibitor preferentially occupies the surface of magnetite, making it difficult for CTAC as a collector to interact with magnetite, thereby achieve the purpose of selective collection. In the study of CTAB/NaOL separation of enstatite and magnetite, the corresponding phenomenon was also found (Yang et al., 2019). CTAB could not directly contact the surface of minerals owing to oleic acid selectively occupied the surface of magnetite, thus the purpose of mineral flotation separation was realized. To sum up, the adsorption behavior of lactic acid on quartz and magnetite is different, which leads to the change of surface properties of two minerals by DES collector showing specificity, and finally, accomplish the purpose of reverse flotation desilication.

4. Conclusions

In this paper, a new deep eutectic solvent collector CTAC/lactic acid DES was synthesized and successfully used in reverse flotation desilication. In the flotation experiment of the artificial mixed minerals, the most excellent flotation results were obtained at 0.15 mmol/L CTAC/lactic acid DES and neutral pH, the grade of TFe is increased from 53.02% to 66.69%, the quartz grade is reduced from 25.18% to 6.67%, and the beneficiation efficiency is 70.07%, all the indexes were preferable to dodecylamine.The adsorption mechanism of CTAC/lactic acid DES on quartz and magnetite surface was studied by FTIR, zeta potential and XPS. The results show that the adsorption of CTAC/lactic acid DES on quartz and magnetite is different. The hydrophilic carboxyl group in lactic acid preferentially occupies the Fe site through chemical adsorption, resulting in the lack of hydrophobic quaternary ammonium salt on the surface of magnetite, which inhibits the flotation of magnetite, while quartz does

not, so magnetite cannot be collected by CTAC. Thus, the reverse flotation of magnetite is realized.

Acknowledgement

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