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Study of N, N-bis (2-hydroxyethyl) -N-methyl dodecyl ammonium chloride as the novel collector in selective flotation separation of quartz and hematite

Wenbao Liu, Wengang Liu, Qiang Zhao, Xinyang Wang, Hao Duan, Xiangyu Peng, Benying Wang

School of Resources and Civil Engineering, Northeastern University, Shenyang, China 110819

Corresponding authors: liuwengang@mail.neu.edu.cn (W.G Liu), m15829479570@163.com (X.Y. Peng)

Abstract: A quaternary ammonium salt, N, N-bis (2-hydroxyethyl)-N-methyl dodecyl ammonium chloride (BHMDC), with high surface activity, was screened and firstly introduced in the reverse flotation of hematite ores based on Density Functional Theory (DFT) calculation and surface tension measurement. The interaction mechanism of BHMDC on the surfaces of quartz and hematite was studied by zeta potential measurement, X-ray photoelectron spectroscopy (XPS) and Fourier transforms infrared spectroscopy (FTIR), respectively. The results of DFT calculation and surface tension measurement indicated that BHMDC had higher selectivity and hydrophobicity than dodecylamine (DDA). The analyses of zeta potential measurement, FTIR, and XPS demonstrated that the adsorption of BHMDC on hematite and quartz surfaces were mainly dependent on hydrogen bonding and electrostatic interaction. Due to the more active sites (O atoms), the weaker charge and larger size of polar groups, BHMDC had better simulation results in performance than DDA, especially in selectivity. The flotation tests showed that BHMDC exhibited better flotation performance, which was consistent with the results of DFT calculation. And the efficient separation of hematite and quartz within the wide pH value range (4.0-10.0) was determined, which was also confirmed by zeta potential measurement. It also indicated that BHMDC was an excellent collector in the reverse flotation of hematite ores with great industrial potential, which could obtain the concentrate with the Fe grade of 65.37% and recovery of 88.92%.

***Keywords*:** quaternary ammonium salts, high surface activity, quartz, hematite, interaction mechanism, flotation separation

1. Introduction

Iron and steel industry is a pillar industry in national economy. The sustainable development of iron and steel industry cannot be separated from the exploitation and utilization of iron ore resources (Pattanaik and Rayasam, 2018; Rodrigues et al., 2013). With the over-exploitation and over-depletion of high-grade iron ore (iron grade>55.0%) deposits, the low-grade ores (iron grade<30.0%) keep increasing for years, especially in China, whose iron ores are characterized by poverty, fineness and miscellaneous (Filippov et al., 2014; Zhang et al.; 2017b, Tang et al., 2019). Beneficiation of iron ore by traditional physical processes (gravity and magnetic separation, etc.) cannot meet the increasing demand of iron and steel enterprises, and flotation has been an effective method of iron ore beneficiation with high grade (Filippov et al., 2014; Mowla et al., 2008). In particular, the cationic reverse flotation process of hematite has attracted increasing attention because of its simple reagent system, low-temperature resistance, and high-grade iron concentrate (Zhang et al., 2019a; Liu et al., 2016; Luo et al., 2017).

The development of cationic collector research is the key to the cationic reverse flotation of hematite (Liu et al., 2018). The common cationic collector is amine surfactants which often contains at least one polar group and one hydrophobic long alkyl chain. In recent years, with the deepening concept of

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energy-saving and environmental protection, a large number of new and efficient cationic surfactants have been investigated and used in the separation of the ore (Liu et al., 2017; Pattanaik and Venugopal, 2018). Amine collectors have also been developed from single aliphatic amines to ether amines, amides, polyamines, condensation amines, aromatic amines, morpholine, and quaternary ammonium salts (Araujo et al., 2005; Filippov et al., 2014; Liu et al., 2017; Liu et al., 2016; Medeiros and Baltar, 2018; Papini et al., 2001; Pattanaik and Venugopal, 2018). Quaternary ammonium salt with four alkyl groups on the central cationic N atom (R_4N^+) is not only widely used as the surfactant, but also a common cationic collector in mineral flotation, because of its strong surface activity (Yang et al., 2015). Due to their excellent antimicrobial properties, they are widely applied for food, medicine, cosmetics, and other industries (Yang et al., 2015). Although more and more kinds of new quaternary ammonium cationic surfactants have been developed, novel quaternary ammonium salts used as the collector for flotation are investigated rarely (Hu et al., 2011; Weng et al., 2013). As we all know, compared with other kinds of amine collectors, quaternary ammonium salts have better water solubility and less influence by acid-based solution (Weng et al., 2013). Recent studies have shown that quaternary ammonium salts exhibited better selectivity than the mono-amines (Araujo et al., 2005; Sahoo et al., 2015; Wang and Ren, 2005; Weng et al., 2013; Xia et al., 2009). Hence, the application of new high-efficiency quaternary ammonium salt collectors is conducive to the development and utilization of low-grade refractory mineral resources. In recent years, many studies have been focused on the introduction of the hydroxyl group into cationic surfactants, which showed that some changes could be made in its properties when the methyl group in dodecyl trimethyl ammonium chloride (DTAC) was replaced by a hydroxyl group. For example, the surface activity, hydrophobicity, compatibility with anionic surfactants, foam synergy, and thickening are improved, while the toxicity weakens or even disappears (Dai et al., 2016; Jordan et al., 2012; Li et al., 2011; Wei et al., 2013). However, up to now, there is still no report on the use of the quaternary ammonium salts containing a hydroxyethyl group with a high surface activity in the flotation separation of mineral ores.

In this paper, a quaternary ammonium salt containing two hydroxyethyl groups as the novel collector was designed, screened, and firstly introduced into the reverse flotation of hematite ore. The performance of N, N-bis (2-hydroxyethyl)-N-methyl dodecyl ammonium chloride (BHMDC) was pre-evaluated by Density Functional Theory (DFT) calculation and surface tension measurement. The different adsorption behavior and adsorption mechanism of BHMDC to hematite and quartz were analyzed by zeta potential measurements, X-ray photoelectron spectroscopy (XPS) analysis, and Fourier transforms infrared (FTIR) spectroscopy tests. The application of BHMDC in the reverse flotation of hematite ore was also studied by the flotation of single minerals, artificially mixed mineral, and actual ore, respectively.

2. Experiments

2.1. Materials

The samples of hematite and quartz were obtained from Ansteel Mining (Anshan, China). The hand-picked high-purity hematite and quartz ores were ground and purified to get the high pure samples. The samples of hematite and quartz were respectively analyzed by the chemical composition and X-ray diffraction, which suggests that the purity of samples was above 99.0%. The main chemical compositions of quartz were SiO_2 (99.72%), Fe_2O_3 (0.15%), MgO (0.02%), CaO (0.01%), Al_2O_3 (0.08%), K_2O (0.01%), and P_2O_5 (0.01%), and those of hematite were Fe_2O_3 (99.02%), SiO_2 (0.93%), MgO (0.01%), CaO (0.01%), Al_2O_3 (0.02%), and P_2O_5 (0.01%). The sample components with the particle size of −74.0 + 15.0 μm were applied for the flotation tests. The sample components with the particle size of −5.0 μm were used for the measurements of zeta potential, FTIR spectroscopy, and XPS. Ore samples with a Fe grade of about 42.0% were prepared by mixing hematite and pure quartz minerals in a mass ratio of 6:4 for the separation tests of artificially mixed minerals. The actual flotation samples were taken from the feed ore before the flotation in Qidashan Iron Mine, and their Fe grade was 50.53%.

2.2. Reagents

A novel quaternary ammonium salt collector was screened for the reverse flotation of hematite. With the aid of DFT, BHMDC was evaluated to have better flotation performance than DDA in the reverse flotation of hematite. The novel quaternary ammonium salt collector (BHMDC, its purity about 99.0%) was purchased from Shanghai Baika Chemical Technology Co., LTD. BHMDC with a suitable concentration prepared by deionized water was applied into the flotation performance and mechanism. Analytical-grade of dodecylamine (DDA, collector), hydrochloric acid (pH regulator), sodium hydroxide (pH regulator), potassium bromide, potassium chloride, and acetic acid were purchased from Sinopharm. Starch obtained from Qidashan Iron Mine was regarded as the depressant, and starch solutions were freshly prepared to use in the tests. Deionized water was applied in all experiments.

2.3. Computational details

All the collectors were drawn in the Gaussian View. Based on DFT, the quantum chemistry calculations were conducted by the software of Gaussian 09 and Materials Studio 8.0 (MS). Firstly, the structures of the collectors were conducted with optimization and frequency to get the global minima construction of the collectors with no imaginary frequencies. All the calculations were performed using the B3LYP method 6-311G+ (d, p) basis. The solvation effect was considered, and the solvation model of IEF-PCM (integral equation formalism for the polarizable continuum model) was chosen. The water was chosen as the solvent, whose dielectric constant was 78.39 (Patra et al., 2018). Then, the optimized constructions of the collectors were introduced into the MS software. Physicochemical parameters of the collectors were analyzed using the DMol3 package. The calculations of the electron exchange and correlation interaction adopted GGA-PBEsol (the generalized gradient approximation in the Perdew-Burke-Ernzerhof solid functional scheme). The fine quality of an orbital cutoff and a double numerical plus polarization basis set were chosen. In the calculation, the DNP (double numerical with d and p polarization) basis set was chosen, corresponding to a 6-31G (d, p) Gaussian-type basis set (Liu et al., 2018). Integration accuracy and SCF tolerance were chosen fine. All electron was used for the core treatment. Global was used in the orbital cutoff scheme, and the global orbital cutoff was 4.5 Å. Conductor-like Screening Model (COSMO) was used to study the effect of solvation, and water (dielectric constant=78.54) was chosen as the solvent (Liu et al., 2019d).

2.4. Surface tension measurements

The surface tension measurement is usually considered as a common method to study the flotation performance of reagents. Surface tensions of DDA and BHMDC were measured by platinum sheet method on JK99B automatic tensiometer (Shanghai Zhongchen Digital Instrument Co., Ltd.). JK99B automatic tensiometer was calibrated with deionized water. The reported surface tension values were obtained by the averages of three measurements (experimental error $< 2.0\%$). All the tests were conducted at about 25.0 ± 2.0°C. The relationships between the collector concentration and surface tension in the neutral pH (pH about 6.5-7.5) were plotted. The critical micelle concentration (CMC) value was calculated to evaluate the surface activity.

2.5. Zeta potential measurements

The zeta potential of hematite and quartz treated with or without BHDMC were measured using a Nano-ZS90 laser particle analyzer (Malvern Instruments, UK). The pulp pH of the samples was adjusted using hydrochloric acid or sodium hydroxide. 0.05 g pure sample with the particle size of −5.0 µm and 50.0 mL KCl solution with the concentration of 1.0×10^{-3} mol/L were agitated for fifteen minutes and held for ten minutes to obtain the supernatant. The supernatants were conducted at about 25.0 ± 2.0°C. The presented zeta potential values were obtained by the averages of three measurements (measurement tolerance: ± 2.0 mV).

2.6. FTIR measurements

FTIR spectroscopy is often applied to explore the adsorption behavior and mechanism of the collector on the mineral surface. FTIR analyses of samples untreated or treated with the collector were conducted in a Nicolet 740 FTIR spectrometer (Thermo Fisher Scientific, USA) using KBr pellets. The preparation method of the sample to be measured was similar to that of the flotation test. 1.0 g of pure samples with the particle size of −5.0 μm and 30.0 mL of deionized water with or without BHMDC in the neutral pH (about 7.5) of the slurry was agitated for thirty minutes. And then, the samples were filtered, washed, and dried in a vacuum oven (35.0 ± 2.0°C). The dried samples mixed with KBr were pressed into tablets for FTIR measurements. The wavenumbers ranging from 400 to 4000 cm^{-1} of the samples were measured and analyzed.

2.7. XPS measurements

XPS measurements of samples with or without BHMDC in the natural pulp pH were measured by Thermo Scientific Escalab 250Xi (ThermoFisher Scientific, USA). The preparation method of the samples in XPS measurements was similar with that of the FTIR samples. All elements in the samples were measured by survey scan, and high-resolution XPS spectra of the target elements (C, N, O, and Si) were recorded. The C1s spectrum at a binding energy of 284.8 eV was used to calibrate all the spectra, and the high-resolution spectra of these elements were quantified and fitted by Thermo Scientific Advantage software (Li et al., 2019).

2.8. Flotation tests

Flotation tests were conducted according to the flowsheet shown in Fig. 1. 5.0 g of mineral samples were used to the flotation of the single mineral and artificially mixed mineral by an XFGII5 type laboratory flotation machine (Jilin Exploration Machinery Plant, Changchun, China). 200.0 g of mineral samples were used for the flotation of actual iron ore by an XFD-0.5L single cell laboratory flotation machine (Jilin Exploration Machinery Plant, Changchun, China). The flotation temperature was at room temperature (20.0 ± 2.0°C), and the agitation speed was fixed at 1920.0 rpm. The reported values of flotation tests were the average of the three experiments.

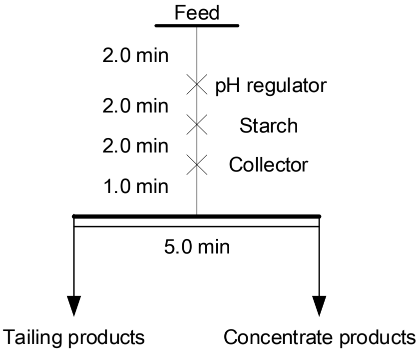

Fig. 1. The flowsheet of flotation tests

3. Results and discussion

3.1 Characterization of BHMDC

The optimized geometry of BHMDC is shown in Fig. 2. From Fig. 2, compared with the common cationic collector DDA, one methyl and two ethanol group were introduced, which could increase the number of the active sites (O atom) and the geometric size of the polar group, and then affect the related flotation performances (Deng et al., 2016). In order to evaluate the performance of BHMDC, the physicochemical parameters of the optimized DDA$^+$ and BHMDC were calculated, and the results are shown in Table 1.

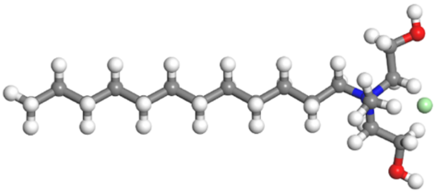

Fig. 2. Optimized geometry of BHMDC at the B3LYP/6-311G + (d, p) level. (N=blue, O=red, Cl=palegreen, C=gray, H=white)

Table 1. Physicochemical parameters of the optimized DDA^+ and BHMDC

Parameter	DDA^+	BHMDC	Quartz	Hematite
Charge/e	N −0.298	N −0.400	-	-
	-	O −0.518	-	-
Group charge/e	0.838	0.678	-	-
Polar group cross-section size/ nm^2	0.019	0.289	-	-
Polar group height/ nm	0.085	0.412	-	-
E_{HOMO}/eV	−0.2622	−0.2471	−0.3026	−0.1907
E_{LUMO}/eV	0.0032	−0.0058	−0.0743	−0.1794
Reagents with quartz ΔE_1/eV	0.3058	0.2968	-	-
Reagents with hematite ΔE_1/eV	0.1939	0.1849	-	-
Reagents with quartz ΔE_2/eV	0.1879	0.1728	-	-
Reagents with hematite ΔE_2/eV	0.0828	0.0667	-	-

*$\Delta E_1 = E_{LUMO(reagent)} - E_{HOMO(mineral)}$, $\Delta E_2 = E_{LUMO(mineral)} - E_{HOMO(reagent)}$

It can be seen from Table 1 that the charge of N atom (−0.298 e) in DDA was higher than those of N atom (−0.400 e) and O atom (−0.518 e) in BHMDC, which could form the hydrogen bond with the exposed electronegative atom (O) on the mineral surfaces. The charge of the polar group in the DDA (0.838 e) was higher than that of BHMDC (0.678 e). It can be known that the cationic collector usually adsorbs on the mineral surface via electrostatic attraction and hydrogen bonding, and the strong electrostatic adsorption has no selectivity (Pattanaik and Venugopal, 2018). Hence, the polar group containing the relatively weak charge would provide weak electrostatic adsorption between the cationic collector and the mineral surface, which might increase the adsorption difference of minerals and enhance the selectivity. Meanwhile, the geometric size was represented by the cross-section size and height of the polar group. It can be noted that the cross-section size and height of the polar group in DDA were smaller than those of BHMDC. For the cationic collector, the large geometric size of the polar group would enhance the steric hindrance effect and indicate better selectivity (Liu et al., 2019c). Frontier molecular orbital theory as a common method for qualitatively predicting chemical-reactivity characteristics are often used to evaluate the reactivity of a surfactant and guide its application in the flotation (Deng et al., 2016). The HOMO energy and LUMO energy characterize the donating and receiving ability of electron, respectively. It can be noted that the HOMO energy of BHMDC (−0.2471 eV) was higher than that of DDA (−0.2622 eV), while the LUMO energy of BHMDC (−0.0058 eV) was slightly lower than that of DDA (0.0032 eV). Hence, compared with DDA, BHMDC was easier to donate its electrons to the unoccupied orbitals of the other atoms, and the difference between BHMDC and DDA in the receiving electron abilities was smaller. It can be inferred that BHMDC might have a better affinity for the mineral surface. The smaller the energy difference between HOMO and LUMO, the stronger the interaction between minerals and reagents is. Table 1 also shows that all the ΔE_2 values were smaller than the ΔE_1 values, indicating that the interaction involving the electron transfer mainly occurred between LUMO of minerals and HOMO of collectors. Compared with DDA, the ΔE_2 values of BHMDC to quartz and hematite were slightly smaller, indicating that BHMDC had a better performance to the minerals. For BHMDC, the ΔE_2 value to hematite was smaller than that to quartz. It indicates that BHMDC might have a better performance to hematite, which contradicted the above conclusions (Zhang et al., 2017a). The reason for this phenomenon might be that the iron atoms contained d-orbital electrons, and the electrostatic interaction hardly involved the electron transfer. Hence, the charge and size of polar groups should be given priority.

At the same time, surface tension measurement was carried out to study the surface activity of BHMDC. The surface tension measurement results of DDA and BHMDC are shown in Fig. 3. As can be seen from Fig. 3, BHMDC was more efficient than DDA in reducing surface tension. It also can be obtained that the CMC value of BHMDC (3.24×10^{-3} mol/L) and its corresponding surface tension values (24.78 mN/m) were smaller than those of DDA (CMC 1.12×10^{-2} mol/L, 25.28 mN/m). It suggests that BHMDC had better hydrophobicity than DDA.

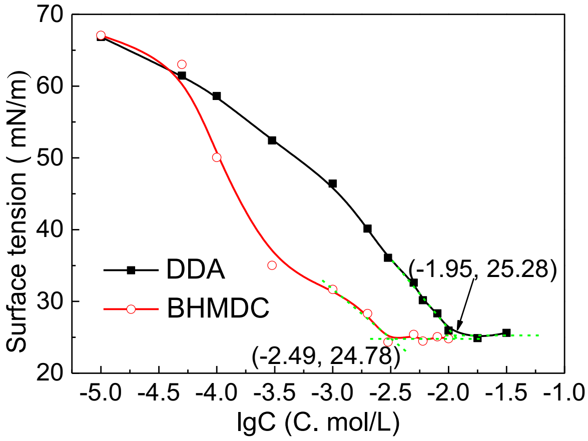

Fig. 3. The surface tension of DDA and BHMDC

reagent and mineral in the flotation. The zeta potentials of quartz and hematite untreated and treated with 20.0 mg/L of BHDMC, as the function of the pulp pH value, were measured respectively. The results are shown in Fig. 4. It shows that the isoelectric point (IEP) of quartz and hematite were 2.01 and 5.46, respectively, which was agreed well with the previously reported study (Feng et al., 2018; Zhang et al., 2017b). After the introduction of BHMDC, the zeta potential values of quartz and hematite became more positive, especially in the pH value range of 4.0-12.0. Meanwhile, the isoelectric points (IEP) of quartz and hematite respectively moved to 5.55 and 7.62. It can be suggested that BHMDC could adsorb on the negative surface of hematite and quartz via electrostatic interaction, and the positive surface of the minerals via hydrogen bonding (Liu et al., 2017; Liu et al., 2016; Pattanaik and Venugopal, 2018). The different change of the zeta potential occurred in the quartz and hematite. After treating with BHMDC, the zeta potential variation in quartz and hematite was obvious in the pH value range of 4.0-12.0, and that changes in quartz were greater than that in hematite. It can be inferred that BHMDC could interact with the quartz and hematite, and the collecting ability of quartz was greater than that of hematite, especially in the pH value range of 4.0-12.0.

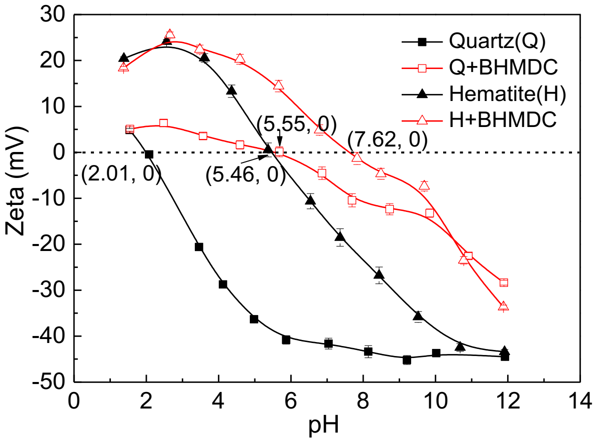

Fig. 4. Zeta potentials of quartz and hematite as a function of pH (BHMDC 20.0 mg/L)

3.3. FTIR analyses

FTIR spectra of BHMDC, quartz, and hematite before and after treating with BHMDC in the prestine pulp pH value (about 7.5) are shown in Fig. 5. All the spectra at the range of 3400-3500 cm^{-1} corresponded to the -OH stretching vibration from water in the air or the sample surfaces. In the spectra of BHMDC, the bands at 2959, 2923, and 2853 cm^{-1} were assigned to the -CH$_3$ symmetric and asymmetric stretching vibrations, and the -CH$_2$- asymmetric stretching vibration, respectively. The band around 1465 cm^{-1} was assigned to the -CH$_3$ asymmetric bending vibration, and the band around

722 cm^{-1} was assigned to the -(CH$_2$)$_n$- bending vibration. While, the band around 1086 cm^{-1} was related to the C-O stretching vibration from the alcohol hydroxyl, and the band around 1051 cm^{-1} was assigned to the C-N stretching vibration (Deng et al., 2016; Liu et al., 2016). For the spectra of quartz and hematite, the bands around 1620-1640 cm^{-1} were assigned to the -OH bending vibration from the surface-bound water of minerals. The bands (400 to 1200 cm^{-1}) were regarded as the characteristic peaks of quartz, and the bands (400 to 1100 cm^{-1}) were regarded as the characteristic peaks of hematite (Kar et al., 2013). After treating with BHMDC, there were the bands around 2958, 2923, and 2851 cm^{-1} in the quartz spectra, and the weak bands around 2923 and 2852 cm^{-1} in the hematite spectra, which was corresponded to the vibration peaks of the alkanes from BHMDC. It indicates that BHMDC adsorbed on the surfaces of quartz and hematite. There were no new peaks on the surfaces of quartz and hematite except for the peaks from BHMDC. At the same time, the peak (the Si-OH bending vibration) around 1633 cm^{-1} and the peak (the Si-O-Si symmetrical bending vibration) around 692 cm^{-1} in the spectra of quartz respectively moved to low frequency to 1628 cm^{-1} (−5 cm^{-1}) and 668 cm^{-1} (−4 cm^{-1}), while the peak (the Fe-O vibration) around 556 cm^{-1} in the spectra of quartz also slightly moved to low frequency to 554 cm^{-1} (−2 cm^{-1}). The results imply that there was no chemical interaction between BHMDC and quartz and hematite, and the groups (the Si-OH and Si-O-Si groups from quartz, the Fe-O group from the hematite) were involved in the adsorption between BHMDC and the minerals (quartz and hematite). It can be inferred that BHMDC might adsorb on the surfaces of minerals via electrostatic interaction and hydrogen bonding (Liu et al., 2017; Liu et al., 2019a).

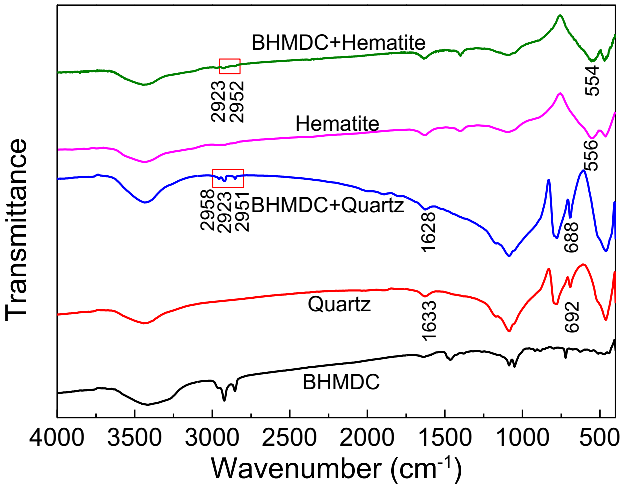

Fig. 5. FTIR spectra of BHMDC, quartz, and hematite before and after treating with BHMDC

3.4. XPS measurements

In order to further study the adsorption mechanism of quartz with BHMDC, the XPS spectra of quartz untreated and treated with 20.0 mg/L BHMDC were measured and analyzed. These results are shown in Table 2 and Figs. S1-4. It can be seen that compare with the pure quartz, the atomic concentration of C 1s increased, indicating that the -CN- and -CO- group of BHMDC adsorbed on the quartz surface (Liu et al., 2016). Meanwhile, N 1s corresponding to the protonated N (-N$^+$-) from BHMDC appeared on the surface of quartz treated with BHMDC, which could also demonstrate that BHMDC adsorbed on the quartz surface. However, the atomic concentration of Si 2p and O 1s obviously decreased, which could be explained by the reason that BHMDC adsorbing on the quartz surface covered up the exposed Si and O atoms on its surface. The high-resolution XPS spectra of Si and O atoms were further fitted, the results show that the atomic concentration of Si 2p components at approximately 102.92 eV (Si atom from Si-OH) obviously increased, compared with those of others Si 2p and O 1s components (Liu et al., 2017). It can be inferred that BHMDC adsorbed on the surface of quartz. The binding energy of Si 2p component was almost no deviation, suggesting that the chemical environment of Si 2p atoms on the surface did not change. For O 1s components on the quartz surface, all the atomic concentration of O 1s components obviously decreased, meanwhile the binding energies at about 531.41 and 532.13 eV obviously shifted to the low frequency. It can be inferred that BHMDC adsorbed on the quartz surface, and changed the chemical environment of O 1s atoms on the surface. The O 1s from Si-O⁻ (531.41 eV) and Si-OH (532.13 eV) took part in the adsorption between BHMDC and the quartz surface, which was mainly by the electrostatic force and hydrogen bonding (Liu et al., 2019b).

Table 2. XPS characterization of reference compounds in the samples

Element	Quartz		Quartz with BHMDC		Difference
	B.E. /eV	A.C. /%	B.E. /eV	A.C. /%	A.C./% (B.E./eV)
N1s	-	-	402.55	1.03	+1.03(-)
C 1s	284.80	23.02	284.80	23.19	+0.17(-)
	-	-	286.42	2.65	+2.65(-)
Si 2p	102.44	4.94	102.43	3.17	−1.77(−0.01)
	102.99	14.09	102.92	19.78	+5.69(−0.07)
	103.54	7.47	103.58	2.28	−5.19(+0.04)
O 1s	531.69	10.28	531.41	4.96	−5.32(−0.28)
	532.39	19.49	532.13	10.31	−9.18(−0.26)
	532.89	6.42	532.84	28.37	−21.95(−0.05)
	533.79	14.29	533.77	4.26	−10.03(−0.02)

*BE-binding energy, AC-Atomic concentration, "-" Denotes none

3.5. Flotation tests

To verify the flotation performance of BHMDC and explore the application of BHMDC in the flotation of hematite ore, the flotation of a single mineral, artificially mixed minerals, and actual ores were conducted with BHMDC as the collector.

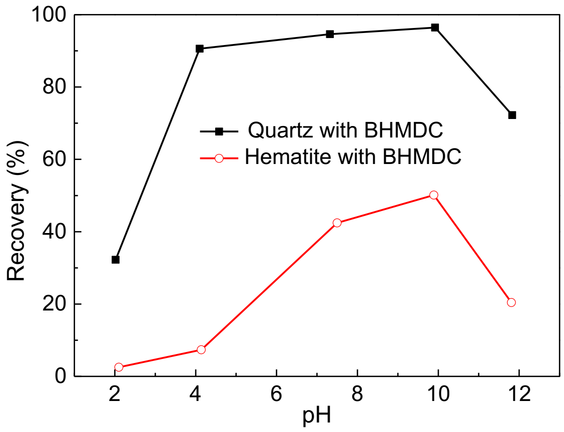

Fig. 6. Effects of the pulp pH value on the flotation behaviors of quartz and hematite with 25.0 mg/L of BHMDC

Fig. 6 reveals the effects of pulp pH value on the flotation behaviors of hematite and quartz with 25.0 mg/L of BHMDC. In Fig. 6, the flotation recoveries of hematite and quartz exhibited a trend of first increasing and then decreasing with the increase of pulp pH value, and the recovery of quartz was higher than that of hematite at the same pulp pH value. For quartz, the recovery increased to more than 90.0% in the pulp pH value of 4.0, and slowly increased with increasing pulp pH value, and then it slowly decreased pH value above 10.0. However, when the pulp pH value was up to 10.0, the highest recovery of hematite (less than 55.0%) was obtained. There was a significant difference in the flotation behavior to hematite and quartz in the tested pH value range. It can be inferred that BHMDC had better selective performance and might contribute to realize the flotation separation of quartz and hematite, especially in the pulp pH value range of 4.0-10.0. These phenomena were in agreement with those of the zeta potential tests. Although the difference in the flotation behavior to hematite and quartz under acid condition was the biggest, the recovery of quartz was low and the equipment would be corroded. So, the natural pulp pH condition (pH_{Quartz}=7.32, $pH_{Hematite}$=7.50), which had a significant difference in the flotation behavior to hematite and quartz, was chosen for the follow-up tests.

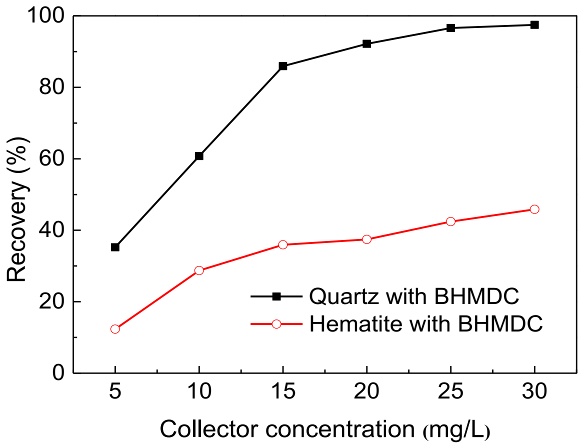

Fig. 7. Effects of BHMDC concentration on the flotation behaviors of quartz and hematite in natural pulp pH value (pH_{Quartz} 7.32, $pH_{Hematite}$ 7.50)

Fig. 7 reveals the effects of BHMDC concentration on the flotation behaviors of hematite and quartz in the natural pulp pH value (pH_{Quartz}=7.32, $pH_{Hematite}$=7.50). As shown in Fig.7, the recoveries of quartz and hematite increased with increasing BHMDC concentration. The recovery of quartz was above 95.0% as the BHMDC concentration increased to above 25.0 mg/L, and then increased slowly. While the recovery of hematite increased slowly, and the highest recovery of hematite was less than 46.0% at the tested BHMDC concentration, which was far less than the recovery of quartz. Hence, BHMDC displayed the strong collecting ability to quartz and the weak collecting ability to hematite at low concentration, which could illustrate the better selectivity of BHMDC.

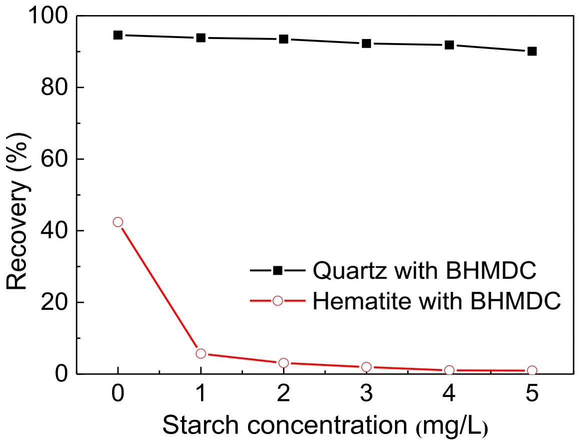

Fig. 8. Effect of starch concentration on flotation behaviors of quartz and hematite in the natural pulp pH value with 25.0 mg/L of BHMDC (pH_{Quartz} 7.32, $pH_{Hematite}$ 7.50)

Fig. 8 reveals the effects of starch concentration on the flotation behaviors of hematite and quartz in the natural pulp pH value with 25.0 mg/L of BHMDC. As shown in Fig. 8, as the starch concentration increased from 0 to 5.0 mg/L, the recovery of quartz slowly decreased to 90.08%, while the recovery of hematite quickly decreased to 0.98%. In particular, when starch concentration was only 1.0 mg/L, the recovery of hematite reduced to less than 6.0%. These results show that starch had little effect on the flotation of quartz and could significantly affect the flotation of hematite with BHMDC as the collector. When BHMDC concentration was 25.0 mg/L with 4.0 mg/L of starch in the natural pulp pH value of 7.5, the recovery of quartz was 91.84%, and the recovery of hematite was 1.02%. Hence, it can be known that BHMDC could realize the separation of hematite and quartz in the pulp pH value from 4.0 to10.0 with the addition of low dosage of starch.

The flotation of artificially mixed mineral, and actual ores with BHMDC as the collector were tested to study the separation performance and the application of BHMDC in the floatation of hematite ores. The results are illustrated in Figs.9-10.

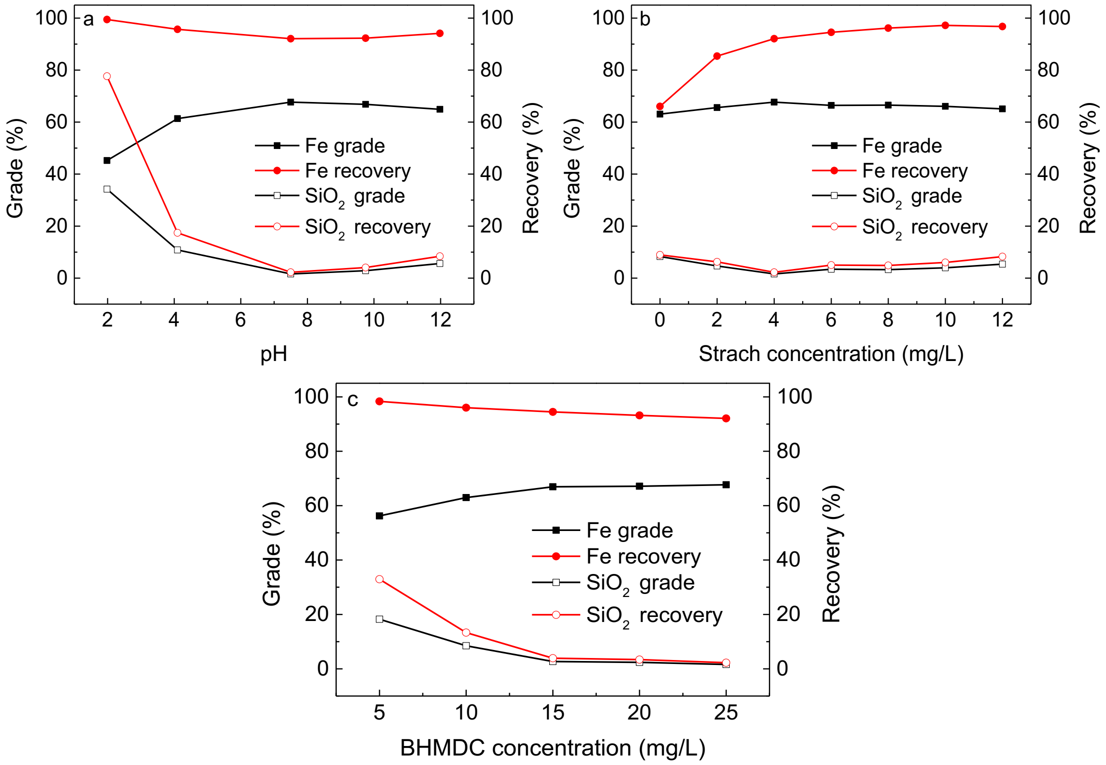

Fig. 9. Flotation results of artificially mixed mineral. (a) Effect of slurry pH value (collector 25.0 mg/L, starch 4.0 mg/L). (b) Effect of starch concentration (collector 25.0 mg/L, pH 7.50). (c) Effect of BHMDC concentration (starch 4.0 mg/L, pH 7.50)

Figs. 9a-c respectively show the effects of the pulp pH value, BHMDC concentration, and starch concentration on the separation behaviors of quartz and hematite with starch as the depressant and BHMDC as the collector. As shown in Fig. 9a, with 25.0 mg/L of BHMDC and 4.0 mg/L of starch, the Fe recovery in the concentrate was above 92.0% in the studied pulp pH value range, while the Fe grade in the concentrate increased firstly and then decreased as the pulp pH value from 2.0 to 10.0. When the pulp pH value was in the range from 4.0 to 12.0, the Fe grade in the concentrate was above 61.0%, and the Fe recovery in the concentrate was above 92.0%. Meanwhile, the SiO_2 grade in the concentrate was less than 11.0%, especially under the condition of natural pulp pH value, the SiO_2 grade in the concentrate was only 1.60%. It can be inferred that BHMDC could realize the separation of hematite and quartz in a wide pulp pH value range. As shown in Fig. 9b, in the natural pulp pH, with 25.0 mg/L of BHMDC, the concentrate with Fe recovery of 66.02% and Fe grade of 63.08% were obtained. With the addition of starch, the Fe recovery in the concentrate gradually increased to 90.0%, the Fe grade increased and then fluctuated around 66.0%, while the grade and recovery of SiO_2 in the concentrate firstly decreased and then increased, which were less than 9.0%. It can be known that BHMDC had excellent selectivity to separate quartz and hematite. As shown in Fig. 9c, in the natural pulp pH of 7.50, with 4.0 mg/L of starch, the Fe recovery in the concentrate gradually decreased to 92.0%, the Fe grade increased and fluctuated around 67.0%, the grade and recovery of SiO_2 in the concentrate gradually decreased, as the increase of BHDMC concentration from 5.0 to 25.0 mg/L. Hence, the natural pulp pH value with 15.0 mg/L of BHMDC and 4.0 mg/L of starch was chosen as the optimized separation condition of artificially mixed minerals, and then, the grade and recovery of Fe in the concentrate were 66.94% and 94.45%, respectively. When DDA was used as the collector, under the same flotation condition, the grade and recovery of Fe in the concentrate were 59.32% and 88.37%, respectively. It also can be known that BHMDC had excellent flotation performance to separate quartz and hematite, which could obtain the qualified concentrate products with the low concentrations of BHMDC and starch, compared with other cationic collectors.

Fig. 10 shows the flotation results of actual ores with DDA or BHMDC in the natural pulp pH of 7.34 with 100.0 g/t of starch. It shows that with the same dosage of the collector (150.0 g/t), the grade (65.37%) and recovery (88.92%) of Fe in the concentrate with BHMDC as the collector were higher than those with DDA as the collector, in which the grade and recovery of Fe in the concentrate were respectively 58.38% and 78.58%. It can be concluded that BHMDC had a greater flotation performance compared with DDA. The flotation results also show that BHMDC had greater flotation performance, especially in selectivity, which could be in agreement with the above forecasting results. It is generally known that the cationic collectors adsorbed on the surfaces of minerals mainly via electrostatic interaction and hydrogen bonding, which were also in good agreement with the adsorption mechanism of BHMDC on the mineral surface. So, the flotation performance of BHMDC was greater than that of DDA, which could be explained by the weaker charge and larger size of polar groups in BHMDC. Meanwhile, the new introduced active sites (O atoms) could also enhance the flotation performance of BHMDC. Therefore, BHMDC, a high surface-active and water-soluble quaternary ammonium salt, was a potential excellent collector with great industrial application potential in the reverse flotation of hematite ores due to its good selectivity. Meanwhile, the novel efficient quaternary ammonium salt with the weaker charge, and larger size of polar groups could be introduced in the flotation to enrich the cationic collector system and improve the comprehensive utilization of resources.

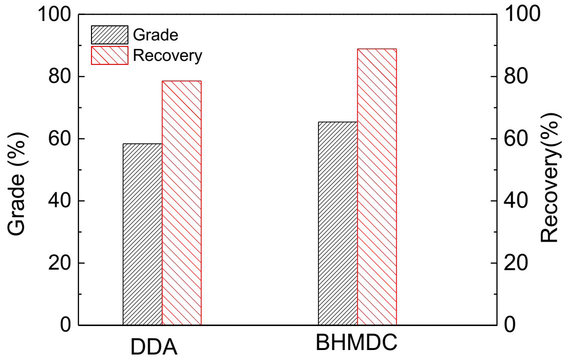

Fig.10. Flotation results of actual ores with DDA or BHMDC. (pH 7.34, starch 100.0 g/t, collector 150.0 g/t)

4. Conclusions

In this paper, a high surface-active and water-soluble quaternary ammonium salt was screened and firstly introduced in the reverse flotation of hematite ores by DFT calculation. The results of DFT calculation and surface tension measurement indicated that BHMDC had higher selectivity and hydrophobicity than DDA. The analyses of FTIR, zeta potential, and XPS demonstrated that BHMDC adsorbed on the surfaces of mineral mainly via electrostatic interaction and hydrogen bonding. It also demonstrated that the interaction of BHMDC with quartz was stronger than that with hematite. The higher number of active sites (O atoms), and the weaker charge and larger size of polar groups in BHMDC could analyze that the performance of BHMDC was better than that of DDA, especially in selectivity. The flotation of single mineral and artificially mixed mineral showed that BHMDC could make a notable difference in the flotation of hematite and quartz, and realize the efficient separation of hematite and quartz in a wide pH value range (4.0-10.0), which were agreed with the results of DFT calculation and zeta potential tests. In the pulp natural pH value of 7.50 with 15.0 mg/L of BHMDC and 4.0 mg/L of starch, the grade and recovery of Fe in the concentrate were respectively 66.94% and 94.45%. The flotation of actual ores showed that in the pulp natural pH value of 7.34 with 150.0 g/t of collector and 100.0 g/t of starch, the grade (65.37%) and recovery (88.92%) of Fe in the concentrate with BHMDC as the collector were higher than those with DDA, which also indicated that BHMDC was an excellent collector and had great industrial application potential in the reverse flotation of hematite ores.

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Supplementary data

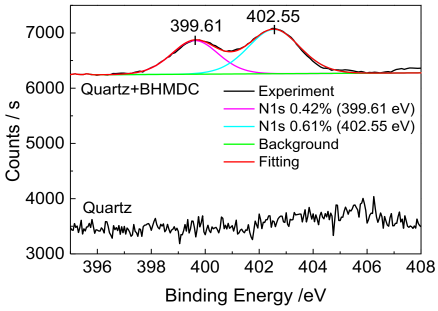

Fig. S1. XPS N 1s spectra of quartz and quartz treated with BHMDC

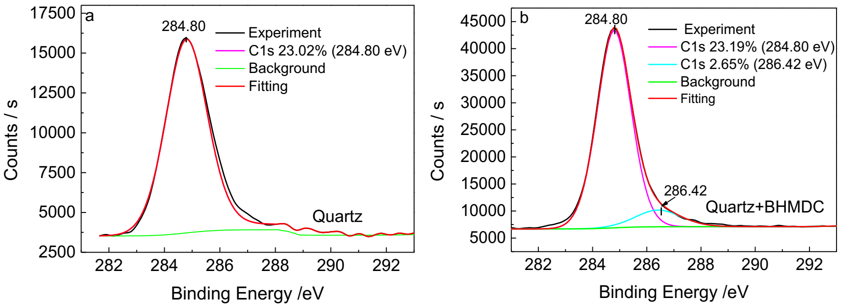

Fig. S2. XPS C 1s spectra of quartz and quartz treated with BHMDC

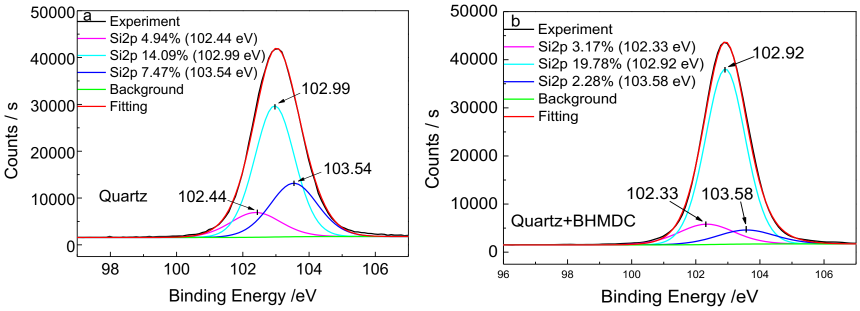

Fig. S3. XPS Si 2p spectra of quartz (a) and quartz treated with BHMDC (b)

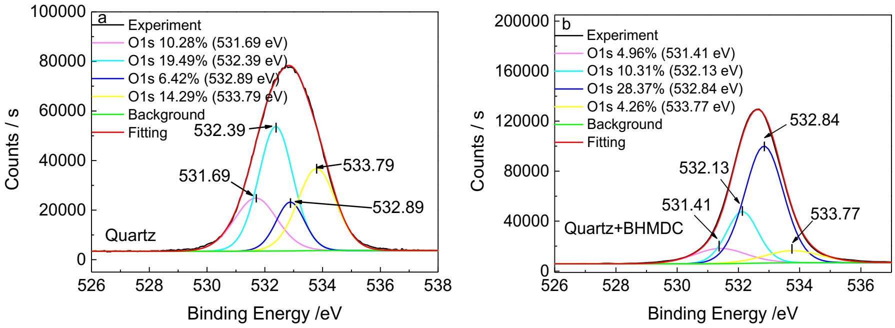

Fig. S4. XPS O 1s spectra of quartz (a) and quartz treated with BHMDC (b)

References

ARAUJO, A.C., VIANA, P.R.M., PERES, A.E.C., 2005. *Reagents in iron ores flotation*. Miner. Eng. 18, 219-224.

DAI, C.L., LI, W.T., CUI, Y., SUN, Y.P., WU, W.J., XU, Z.L., LIU, Y.F., YANG, Z., WU, X.P., 2016. *The effect of functional groups on the sphere-to-wormlike micellar transition in quaternary ammonium surfactant solutions*. Colloid. Surfaces. A. 500, 32-39.

DENG, L.Q., ZHAO, G., ZHPNG, H., WANG, S., LIU, G.Y., 2016. *Investigation on the selectivity of N-((hydroxyamino)-alkyl) alkylamide surfactants for scheelite/calcite flotation separation*. J. Ind. Eng. Chem. 33, 131-141.

FENG, Q.C., WEN, S.M., ZHAO, W.J., CHEN, Y., 2018. *Effect of calcium ions on adsorption of sodium oleate onto cassiterite and quartz surfaces and implications for their flotation separation.* Sep. Purif. Technol. 200, 300-306.

FILIPPOV, L.O., SEVEROV, V.V., FILIPPOVA, I.V., 2014. *An overview of the beneficiation of iron ores via reverse cationic flotation*. Int. J. Miner. Process. 127, 62-69.

HU, Y.H., YANG, F., SUN, W., 2011. *The flotation separation of scheelite from calcite using a quaternary ammonium salt as collector*. Miner. Eng. 24, 82-84.

JORDAN, D., TAN, E., HEGH, D., 2012. *Synthesis, Characterization and Conductivity of Quaternary Nitrogen Surfactants Modified by the Addition of a Hydroxymethyl Substructure on the Head Group*. J. Surfactants. Deterg. 15, 587-592.

KAR, B., SAHOO, H., RATH, S.S., DAS, B., 2013. *Investigations on different starches as depressants for iron ore flotation*. Miner. Eng. 49, 1-6.

LI, Y.L., LI, Q.X., ZHI, L.F., ZHANG, M.H., 2011. *Synthesis, Characterization and Surface-Activity of Hydroxyethyl Group-Containing Quaternary Ammonium Surfactants*. J. Surfactants. Deterg. 14, 529-533.

LI, Z.H., HAN, Y.X., ZUO, K.S., 2019. *Surface-charging and particles aggregation behavior of ascharite.* Physicochem. Probl. Mi. 55, 991-1001.

LIU, W.B., LIU, W.G., WANG, B.Y., DUAN, H., PENG, X.Y., CHEN, X.D., ZHAO, Q., 2019a. *Novel hydroxy polyamine surfactant N-(2-hydroxyethyl)-N-dodecyl-ethanediamine: Its synthesis and flotation performance study to quartz*. Miner. Eng. 142.

LIU, W.B., LIU, W.G., WANG, B.Y., ZHAO, Q., DUAN, H., CHEN, X.D., 2019b. *Molecular-level insights into the adsorption of a hydroxy-containing tertiary amine collector on the surface of magnesite ore*. Powder. Technol. 355, 700-707.

LIU, W.B., LIU, W.G., WEI, D.Z., LI, M.Y., ZHAO, Q., XU, S.C., 2017. *Synthesis of N,N-Bis(2-hydroxypropyl)laurylamine and its flotation on quartz*. Chem. Eng. J. 309, 63-69.

LIU, W.B., LIU, W.G., ZHAO, Q., PENG, X.Y., WANG, B.Y., ZHOU, S.J., ZHAO, L., 2019c. *Investigating the performance of a novel polyamine derivative for separation of quartz and hematite based on theoretical prediction and experiment*. Sep. Purif. Technol. 116370. https://doi.org/10.1016/j.seppur.2019.116370.

LIU, W.B., PENG, X.Y., LIU, W.G., WANG, X.Y., ZHAO, Q., WANG, B.Y., 2019d. *Effect mechanism of the iso-propanol substituent on amine collectors in the flotation of quartz and magnesite*. Powder. Technol.. https://doi.org/10.1016/j.powtec.2019.10.060.

LIU, W.G., LIU, W.B., DAI, S.J., WANG, B.Y., 2018. *Adsorption of bis(2-hydroxy-3-chloropropyl) dodecylamine on quartz surface and its implication on flotation*. Results. Phys. 9, 1096-1101.

LIU, W.G., LIU, W.B., WANG, X.Y., WEI, D.Z., WANG, B.Y., 2016. *Utilization of novel surfactant N-dodecyl-isopropanolamine as collector for efficient separation of quartz from hematite.* Sep. Purif. Technol. 162, 188-194.

LUO, X.M., WANG, Y.F., MA, M.Z., SONG, S.X., ZHANG, Y., DENG, J.S., LIU, J., 2017. *Role of dissolved mineral species in quartz flotation and siderite solubility simulation*. Physicochem. Probl. Mi. 53, 1241-1254.

MEDEIROS, A.R.S.D., BALTAR, C.A.M., 2018. *Importance of collector chain length in flotation of fine particles*. Miner. Eng. 122, 179-184.

MOWLA, D., KARIMI, G., OSTADNEZHAD, K., 2008. *Removal of hematite from silica sand ore by reverse flotation technique*. Sep. Purif. Technol. 58, 419-423.

PAPINI, R.M., BRANDAO, P.R.G., PERES, A.E.C., 2001. *Cationic flotation of iron ores: amine characterization and performance*. Miner. Metall. Proc. 18, 5-9.

PATRA, A.S., NULAKANI, N.V.R., KUMAR, P. Y., SUBRAMANIAN, V., DASH, J., Mukherjee, A.K., 2018. *Design and synthesis of novel polyamine collector to recover iron values from iron ore slimes*. Powder. Technol. 325, 180-191.

PATTANAIK, A., RAYASAM, V., 2018. *Analysis of reverse cationic iron ore fines flotation using RSM-D-optimal design – An approach towards sustainability*. Adv. Powder. Technol. 29, 3404-3414.

PATTANAIK, A., VENUGOPALl, R., 2018. *Investigation of Adsorption Mechanism of Reagents (Surfactants) System and its Applicability in Iron Ore Flotation – An Overview*. Colloid. Interface. Sci. 25, 41-65.

RODRIGUES, O.M.S., PERES, A.E.C., MARTINS, A.H., PEREIRA, C.A., 2013. *Kaolinite and hematite flotation separation using etheramine and ammonium quaternary salts*. Miner. Eng. 40, 12-15.

SAHOO, H., RATH, S.S., JENA, S.K., MISHRA, B.K., DAS, B., 2015. *Aliquat-336 as a novel collector for quartz flotation*. Adv. Powder. Technol. 26, 511-518.

TANG, Z.D., GAO, P., SUN, Y.S., HAN, Y.X., LI, E.L., CHEN, J., ZHANG, Y.H., 2019. *Studies on the fluidization performance of a novel fluidized bed reactor for iron ore suspension roasting.* Powder. Technol. https://doi.org/10.1016/j.powtec.2019.09.092.

WANH, Y. H., REN, J.W., 2005. *The flotation of quartz from iron minerals with a combined quaternary ammonium salt*. Int. J. Miner. Process. 77, 116-122.

WEI, X.L., PING, A.L., DU, P.P., LIU, J., SUN, D.Z., ZHANG, Q.F., HAO, H.G., YU, H.J., 2013. Formation and properties of wormlike micelles in solutions of a cationic surfactant with a 2-hydroxypropoxy insertion group. Soft. Matter. 9, 8454-8463.

WEMG, X.Q., MEI, G.J., ZHAO, T.T., ZHU, Y., 2013. *Utilization of novel ester-containing quaternary ammonium surfactant as cationic collector for iron ore flotation*. Sep. Purif. Technol. 103, 187-194.

XIA, L.Y., ZHONG, H., LIU, G.Y., HUANG, Z.Q., CHANG, Q.W., 2009. *Flotation separation of the aluminosilicates from diaspore by a Gemini cationic collector*. Int. J. Miner. Process. 92, 74-83.

YANG, F., SUN, W., HU, Y.H., LONG, S.S., 2015. *Cationic flotation of scheelite from calcite using quaternary ammonium salts as collector: Adsorption behavior and mechanism*. Miner. Eng. 81, 18-28.

ZHANG, C., LI, L.X., YUAN, Z.T., XU, X.Y., SONG, Z.G., ZHANG, Y.R., 2019. *Probing the effect of particle imperfections on the sliming of siderite in carbonate-bearing iron ore*. Miner. Eng. 143, 106014.

ZHANG, X.L., GU, X.T., HAN, Y.X. PARRA-ALVAREZ, N., CLAREMBOUX, V., KAWATRA, S.K. 2019. *Flotation of Iron Ores: A Review*. Min. Proc. Ext. Met. Rev. https://doi.org/10.1080/08827508.2019.1689494.

ZHANG, X.R., QIAN, Z.B., ZHENG, G.B., ZHU, Y.G., WU, W.G., 2017a. *The design of a macromolecular depressant for galena based on DFT studies and its application*. Miner. Eng. 112, 50-56.

ZHANG, X.R., ZHU, Y.G., XIE, Y., SHANG, Y.B., ZHENG, G.B., 2017b. *A novel macromolecular depressant for reverse flotation: Synthesis and depressing mechanism in the separation of hematite and quartz*. Sep. Purif. Technol. 186, 175-181.