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Effect of sodium salt of N,N-dimethyldi-thiocarbamate on the flotation separation of marmatite from galena

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Abstract: An organic reagent, sodium salt of N,N-dimethyldi-thiocarbamate (DMDC) was investigated as a depressant for the separation of lead activated marmatite from galena in the presence of diethyldithiocarbamate (DDTC). The flotation tests of single mineral showed that lead-activated marmatite could be depressed efficiently using DMDC as the depressant. UV-vis spectroscopy and ICP study confirmed that DMDC had a stronger capacity of complexing with lead ions or hydroxy complexes of lead. FTIR and adsorption measurement showed that the adsorption of DMDC on galena and marmatite was chemisorption. In addition, after pre-treated with DMDC, DDTC could co-adsorb on the galena surface, however, less DDTC species adsorbed on the marmatite surfaces.

Keywords: DMDC, galena, marmatite, UV-vis spectroscopy, adsorption, ICP

1. Introduction

Marmatite is a major resource of zinc metal, which usually coexists with other sulfide minerals such as galena. The floatability of marmatite is poor since marmatite weakly interacts with short-chain thiol collector such as xanthate (Khmeleva et al., 2005; Chen and Yoon, 2000). However, in complex polymetallic sulphide ores, the floatability of marmatite can be increased significantly due to unintentional activation Pb^{2+} derived from galena dissolution (Morey et al., 2001; Trahar et al., 1997; Fornasiero and Ralston, 2006; Rashchi et al., 2004). Studies showed an activation mechanism where Pb^{2+} exchanges with Zn^{2+} in the zinc minerals lattice and reacts with collector to form Pb-X only in acidic solution. In addition, In the pH range of 7 to 10, the lead ions forms a Zn-O-Pb⁺ species through the adsorption of $Pb(OH)^+$ and produces the same Pb-X species with collector. At a higher pH, $Pb(OH)_2$ dominates and thus Pb^{2+} cannot activate zinc sulphide (Chandra and Gerson, 2009). Therefore, it is difficult to selectively separate the marmatite from galena after Pb^{2+} activation (Khmeleva et al., 2005). The inefficient flotation separation of Pb-Zn will have a detrimental effect on subsequent treatment process. Concerning this, both organic and inorganic regulators were used as depressants to improve the selectivity of the flotation separation of lead and zinc.

Inorganic reagents, include lime, cyanide, zinc sulfate and sodium sulfide were added to pulp for the differential flotation separation of Pb-Zn sulphides (Liu et al., 2018; Feng and Zhou, 2011; Seke and Pistorius, 2006). However, there are many practical problems in the application of inorganic depressants, such as the toxicity of cyanide, the high dosage of lime and the negative effects on the environment. Compared with inorganic depressants, organic depressants have the advantages of better selectivity and multiple structures, moreover, they are environmentally friendly. In recent years, organic depressants have gained increasing attention from many scholars. For example, the depression of azo organic on galena, jamesonite, marmatite, pyrite and chalcopyrite was proved and the depressing ability azo reagent was determined by their molecular structures (Chen et al., 2010); chitosan could be used as a depressant in Cu-Pb, Zn-Pb, and Pb-Fe separation and the mechanism was that chitosan specifically adsorbed on chalcopyrite, sphalerite, and pyrite surface but not on galena surface (Huang et al., 2011, 2012, 2013); Relevant studies also found that dextrin is a good depressant for pyrite in flotation

with xanthate collectors and the depressing effect of dextrin results from enveloping the dixanthogen which is a hydrophobic entity on the surface of pyrite reacted with xanthate, so dextrin can depress pyrite as efficiently as cyanide (Valdivieso et al., 2004); Sodium humate could depress galena in Cu-Pb separation (Liu et al., 2016; Wang et al., 2018). In addition, polymers are well-known depressants of both sulfide and non-sulfide minerals and have also been used to depress pyrite (Bogusz et al., 1997; Bolin and Laskowski, 1991).

In this study, sodium salt of N, N-dimethyldi-thiocarbamate (DMDC) was tested as a potential regulator in the differential flotation separation of Pb-Zn sulfides. It has been studied by many scholars and applied successfully in a number of fields, such as industry, chemistry, and agriculture, such as pesticides in agriculture, heavy metal precipitant in waste water remediation (Nitowski et al., 1997) and Terminator in Latex. In the mineral processing, DMDC was found to be a potential depressant in the differential flotation separation of Cu-Zn sulphides (Qin et al., 2013). Based on the previous study, the reagent was introduced into the flotation system of Pb-Zn separation as a depressant. In the present paper, the effect of sodium salt of N,N-Dimethyldi-Thiocarbamate on the flotation separation of marmatite from galena was studied in detail. Additional analytical techniques are employed in the current study to point out the mechanisms which are involved in the interaction of DMDC with sulfide minerals. Flotation test is designed to allow us to ascertain the degree of effectiveness of DMDC as a depressant and to optimize the conditioning parameters for the subsequent analysis. Meanwhile, solution chemistry, UV-visible spectroscopy of complex, ICP tests, Fourier transform infrared spectroscopy (FTIR) analysis and adsorption amount measurements were carried out to reveal the depressing mechanism.

2. Materials and methods

2.1 Materials and reagents

The pure galena and marmatite samples were obtained from Guangxi Province, China. The lumps of the galena and marmatite were firstly crushed and hand-picked to obtain high purity samples, and then ground in a laboratory porcelain mill with an agate ball. The -75+38 μ m size fractions were screened out and chosen for the pure mineral flotation tests. Part of the samples further ground to 5 μ m for FTIR analysis. The purity of minerals was determined through X-ray diffraction (Fig. 1) and chemical analysis (Table.1). The XRD spectrums showed that the samples were free from impurities. The chemical analysis results of the galena sample showed Pb 83.733%, S 11.55% and the marmatite sample contained 49.704 % Zn, 30.519 % S and 15.094% Fe. Based on the result of XRD and chemical analysis, it was determined that the purity of galena and marmatite meet the criteria for flotation.

Diethyldithiocarbamate (DDTC) and methyl isobutyl carbinol (MIBC) were used as collector and frother respectively in flotation tests, and they all analytical grade reagents supplied by Zhuzhou Flotation Reagents Factory in Hunan, China. DMDC, the structure of DMDC is $(\text{CH}_3)_2\text{NCSSNa}$, purchased from Zhuzhou fortune chemical industry CO., LTD, was used as depressant. Lead nitrate was supplied by Xilong Scientific CO., LTD. The dilute solutions of HCl and NaOH were used for pH regulator in the tests. The deionized water (resistivity=18.3 m Ω ·cm) was used in the flotation and measurements.

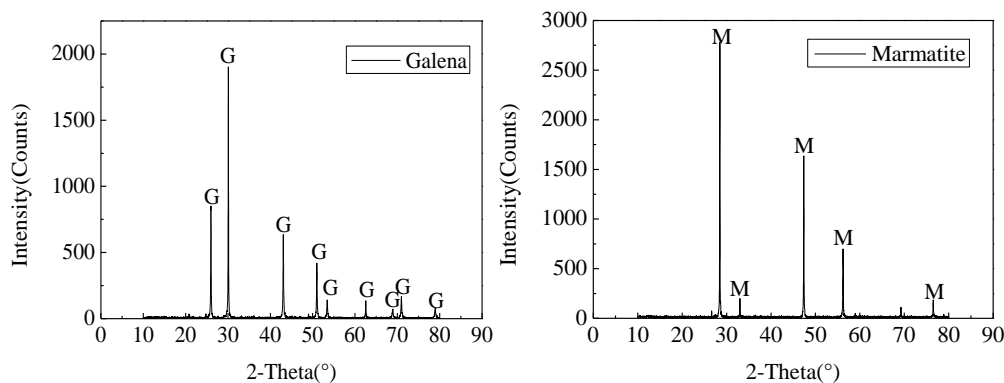


Fig. 1. XRD spectrums of the galena and marmatite samples used for flotation tests

Table 1. Main chemical composition of mineral samples

Minerals	Mass fraction/%								
	Pb	Fe	S	Zn	O	Mg	Al	Si	Ca
Galena	83.733	0.216	11.550	0.057	3.524	0.056	0.015	0.073	0.485
Marmatite	-	15.094	30.519	49.704	2.663	0.130	0.075	0.472	0.221

2.2 Flotation tests

Pure mineral flotation tests were conducted in a flotation machine with a 40 mL plexiglass cell, and the impeller speed was fixed at 1620 rpm. In each flotation test, 2.0 g of the -75+38 μ m samples were firstly cleaned by ultrasonic treatment prior to the test and then mixed with 40cm³ deionized water. After adjusting pH to appropriate value, conditioning was performed in the following order, depending on the number of reagents added: lead ions, depressants, collectors and frothers. For each reagent addition, the conditioning time was taken as 2 min, then concentrate samples were collected after flotation. The concentrate and tailing samples were filtered, dried, and weighted to calculate the flotation recovery by the following formula:

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

where m_1 and m_2 are the weights of the concentrate and tailing, respectively.

2.3 UV-visible spectroscopy of complex

UV-vis spectroscopy is employed to investigate the complexation of Pb²⁺ and Zn²⁺ with DMDC, respectively. The experiments were performed by UV-visible spectroscopy of complexUV-9100, Shimadzu of Japanese. The concentration of the ligand (DMDC) was fixed at 1.0 \times 10⁻⁵ mol/dm³, then different metal ions (Pb²⁺, Zn²⁺) with the concentration was 1.0 \times 10⁻⁵ mol/dm³ were mixed with ligand in buffer solution (pH 6.86), respectively. Subsequently, the solution was diluted to 50mL. The solution was put into quartz colorimetric utensil after standing for 10 min, and then the absorbance was determined. The scanning wavelength is from 200 to 700 nm.

2.4 ICP tests

The concentration of lead ions in flotation pulp was measured in the ICP (Inductively Coupled Plasma Atomic Emission Spectrometry). Each test, 2.0 g of the -75+38 μ m samples were conducted in a flotation machine with a 40 cm³ cell, and this was followed by the addition of a given amount of solutions with known lead ions concentration, either alone or in addition to DMDC. Then the flotation pulp was removed for centrifuging for 10 min after stirred for 20 min in the flotation machine. The supernatant was used to determine the equilibrium concentrations of the lead ions using the ICP.

2.5 FTIR tests

The infrared spectra of samples were recorded by NEXUS-470 spectrometer. Samples with size of 2 μ m were prepared in the same way used in flotation tests. 1.0g sample was settled in 20 cm³ reagents solution at pH 8 and then agitated for 30 min, filtrated, and washed 2 or 3 times using the corresponding pH buffer solution. The treated sample was dried in a vacuum desiccator for test. Each test, 1 mg sample of the dry precipitation and 30 mg potassium bromide powder were used for spectroscopy measurement and make sure the whole process was not contaminated.

2.6 Collector adsorption measurement

The adsorption of DDTC on galena and marmatite in the absence and presence DMDC was determined by UV-visible spectroscopy of complexUV-9100, Shimadzu of Japanese. First, the standard curve was measured and shown in Fig. 2. Then, the sample was prepared as the following order. Each test, 2.0g pure mineral sample of 38-74 μ m size fraction was cleaned by ultrasonic first, and then placed in a

plexiglass cell (40 cm³) filled with 35 cm³ of deionized water. After adjusting the pulp with HCl or NaOH to the desired pH values, a known concentration of reagent solution was introduced into the vessel and stirred until adsorption equilibrium was reached (Piao et al., 2013). At last, the pulp suspension was centrifuged in a centrifuge at 5000 rpm for 10 minutes and the supernatant was taken for adsorption amount measurement. The adsorption amount of DDTC on mineral surface was calculated from the difference between the original and residual concentrations and shown as the following equation.

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

where Q_e is the amount of DDTC adsorbed on mineral surface (mol/dm³), C_0 is the initial concentration of DDTC (mol/dm³), C is the equilibrium concentration of DDTC (mol/dm³), V is the volume(dm³), and M is the mass of minerals (g).

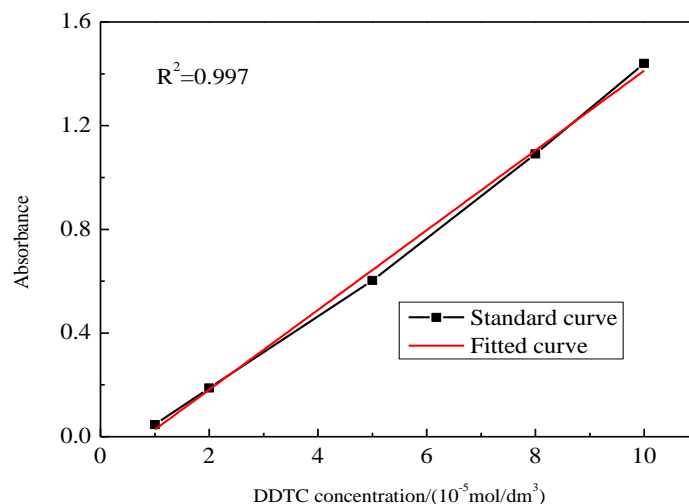


Fig. 2. Relationships between DDTC concentration and the absorbance

3. Results and discussion

3.1 Flotation tests of single mineral

Flotation is extremely sensitive to the pH value of the pulp. The surface and solution states of minerals, reagent and ions are all by the pH (Chen et al., 2017). Different hydroxy complexes of lead ions are presented in different pH regions due to the hydrolysis of Pb²⁺. These species play different roles in determining the flotation of the minerals. Fig. 3 shows the distribution diagram of Pb²⁺ species in aqueous solution at a Pb²⁺ concentration of 5×10⁻⁵mol/dm³, which is similar to previous reports (Liu et al., 2016; Li et al., 2016). We only discussed soluble species, and any other species have been omitted. It should be noticed that the dominant species is Pb²⁺ at pH<7. Over the pH range from 7 to 10, Pb(OH)⁺ becomes the dominant species. Moreover, Pb(OH)₃⁺ and Pb(OH)₂ are the predominated species at a higher pH value (pH>10), which have a slightly effect on activation of marmatite. Therefore, Pb²⁺ and Pb(OH)⁺ were the dominated species to activate marmatite, which in agreement with previous study(Chen et al., 2017).

The flotation recovery of galena and marmatite as a function of the pH in the presence and absence of Pb(NO₃)₂ with collector DDTC is shown in Fig. 4. In this experiment, the pH of the pulp was adjusted with NaOH or HCl, and the collector and frother used in the test were diethyldithiocarbamate (DDTC) and methyl isobutyl carbinol (MIBC), respectively. In addition, the Pb(NO₃)₂ was added to stimulate the accidental activation. As seen from Fig. 4, galena behaved excellent floatability with a high recovery of more than 90% at a wide pH value range, and that for marmatite showed a poor floatability without Pb(NO₃)₂ addition, especially at pH>7.5, the flotation recovery of marmatite is less than 10%. With Pb²⁺ as the activator, the flotation recovery of marmatite increases sharply from below 10% to above 50% at pH<8. Just as depicted in Fig. 3, this is contributed to the activation effect of Pb²⁺ and Pb(OH)⁺. Therefore, it is difficult to selectively separate the marmatite from galena after Pb²⁺ activation at low pH.

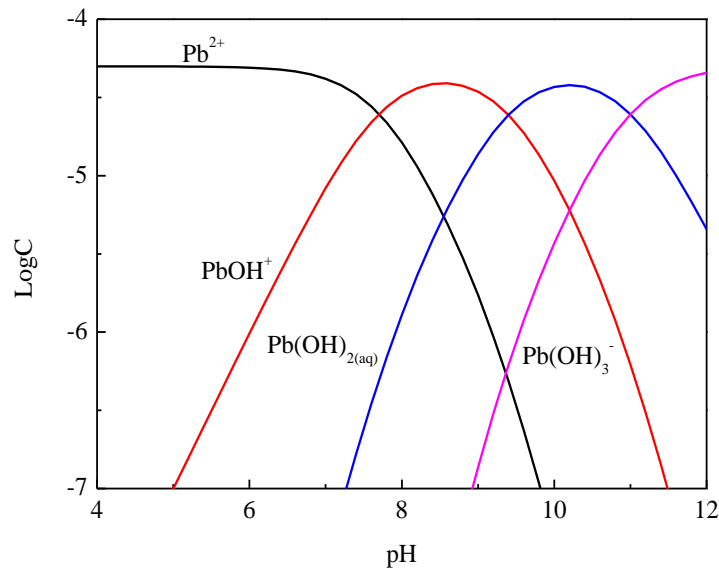
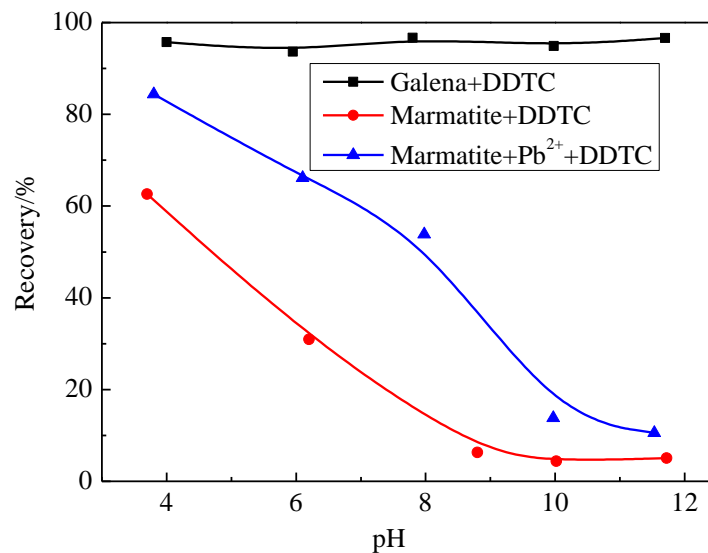
Fig. 3. Species distribution diagram of the Pb^{2+} - H_2O systemFig. 4. Flotation recovery of galena and marmatite as a function of the pH without depressant ($c(DDTC)=5 \times 10^{-5} \text{ mol/dm}^3$, $c(Pb^{2+})=5 \times 10^{-5} \text{ mol/dm}^3$, $\rho(MIBC)=10 \text{ mg/dm}^3$)

Fig. 5 shows the effects of DMDC concentration on the flotation of galena and marmatite at pH 8. Obviously, the flotation recovery of galena was almost unchanged and stable above 90% in the whole pH. However, when the DMDC was added, marmatite became more hydrophilic. As the concentration of DMDC increased from 10^{-5} mol/dm^3 to 10^{-4} mol/dm^3 , the flotation recovery of marmatite drastically reduces from 56.7% to 8.7%. When the concentration of DMDC is 10^{-4} mol/dm^3 , the recovery of marmatite reaches a minimum and remains constant with the further increase of DMDC concentration. At this point, the recovery difference between galena and marmatite is about 80%, so it is possible to separate marmatite from galena. (The difference of flotation recovery is more than 50% that could separation efficiently).

The effects of DMDC on the flotation recovery of galena and marmatite in the presence $Pb(NO_3)_2$ with collector DDTC in Fig. 6. It is shown that the flotation recovery of galena is basically stable about 90% in the range of pH 4-10 after DMDC addition, illustrating that the galena is less sensitive to DMDC at $pH < 10$ and maintains a high recovery, but the recovery of galena decreases sharply as the pH increasing, this is mainly attributed to a large number of hydroxyl ions existing in alkaline solution, leading to the production of lead hydroxide for galena. However, the recovery of marmatite decreases

from about 50% to below 10%, indicating that marmatite is effectively depressed by DMDC. The single mineral flotation results indicated that the floatability of galena much high than that of marmatite at a wide pH value range. Therefore, it is possible to selectively separate the lead-activated marmatite from galena in the presence of DMDC and DDTC. The preferable pH for separating the marmatite from galena was approximately at 7-9 where the recoveries of galena and marmatite were about 90% and 10%, respectively.

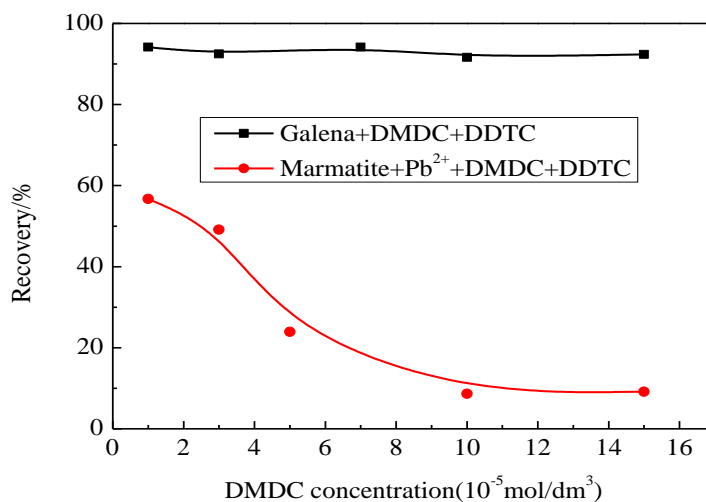


Fig. 5. Effects of DMDC on the flotation recovery of galena and marmatite as a function of DMDC concentration (pH=8, $c(\text{DDTC})=5 \times 10^{-5}$ mol/dm³, $c(\text{Pb}^{2+})=5 \times 10^{-5}$ mol/dm³, $c(\text{DMDC})=10^{-4}$ mol/dm³ $\rho(\text{MIBC})=10$ mg/dm³)

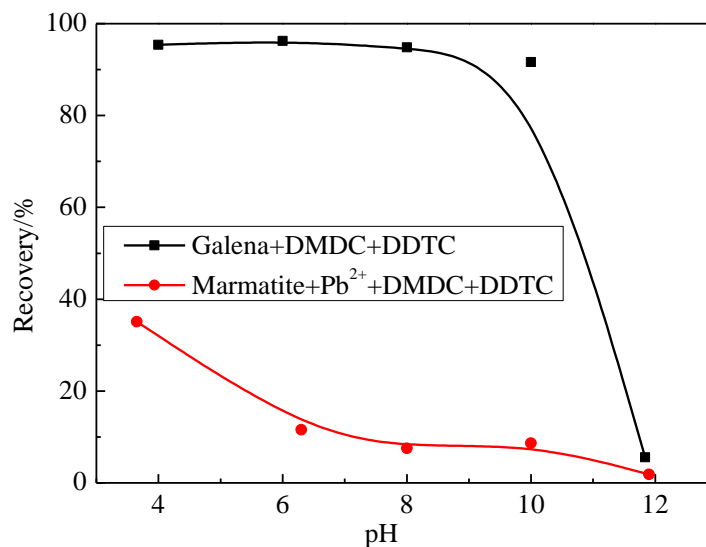


Fig. 6. Effects of DMDC on the flotation recovery of galena and marmatite as a function of the pH ($c(\text{DDTC})=5 \times 10^{-5}$ mol/dm³, $c(\text{Pb}^{2+})=5 \times 10^{-5}$ mol/dm³, $c(\text{DMDC})=10^{-4}$ mol/dm³ $\rho(\text{MIBC})=10$ mg/dm³)

3.2 UV-visible spectroscopy analysis

The complexation between DMDC and Pb^{2+} , Zn^{2+} was studied by UV-vis spectroscopy, and the results were shown in Fig. 7. It could be seen that there are three maximum adsorption peaks appeared in 208nm, 252 nm and 278.5 nm for DMDC. The peak in 208nm is the π - π^* transition of alkyl group. In 252 nm, the peak is the π - π^* transition of $\text{N} \cdots \text{C} \cdots \text{S}$, and the peak in 278.5nm is the transition from non-bonding electron in sulfur atom of group $\text{S} \cdots \text{C} \cdots \text{S}$ to n - π^* of conjugated system (Ma et al., 2016). It is noted that, the adsorption peaks have no significant change after the addition of Zn^{2+} , however, in terms of Pb^{2+} , there are two maximum peaks disappeared in 252 nm and 278.5 nm, illustrating that DMDC has the higher affinities and stronger capacity to lead ions or hydroxy complexes of lead.

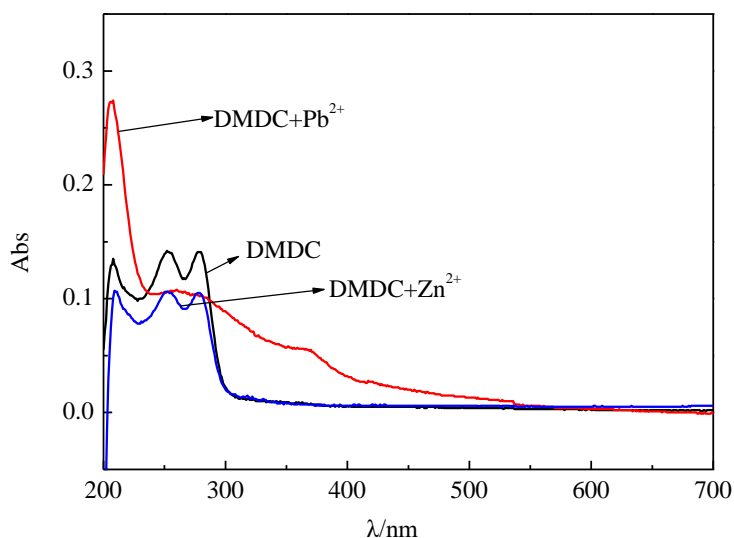


Fig. 7. Spectrophotometric adsorptions of the ligand of DMDC and its complexes with Pb^{2+} and Zn^{2+}

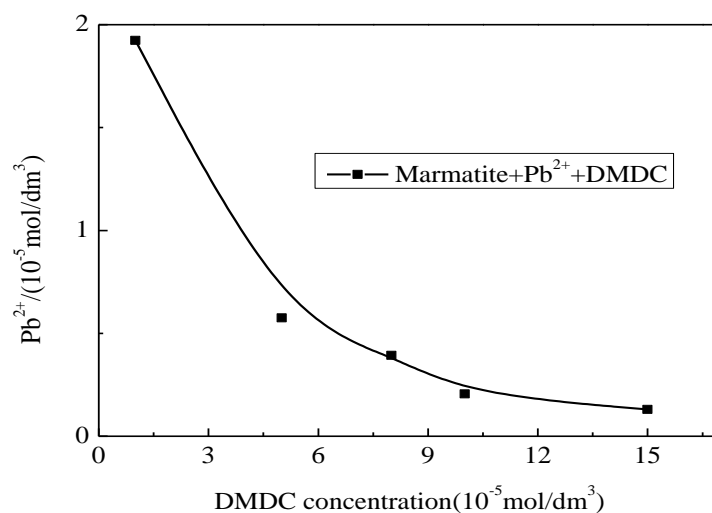


Fig. 8. The content of Pb^{2+} in flotation pulp as a function of DMDC concentration (pH=7-9, $c(Pb^{2+})=5 \times 10^{-5} \text{ mol/dm}^3$)

3.3 ICP analysis

UV-visible spectroscopy indicated that DMDC has a stronger capacity of complex with lead ions or hydroxy complexes of lead. In order to better study the complexation ability of DMDC in flotation, ICP was carried out to test the content of Pb^{2+} in flotation pulp. Fig. 8 shows the content of Pb^{2+} in pulp as a function of DMDC concentration. We can see from Fig. 8, with the concentration of DMDC increased from 10^{-5} mol/dm^3 to 10^{-4} mol/dm^3 , the content of Pb^{2+} in pulp dropped sharply from $2 \times 10^{-5} \text{ mol/dm}^3$ to $2 \times 10^{-6} \text{ mol/dm}^3$ and reached a minimum value. After that, the content of Pb^{2+} remains constant with the further increase of DMDC concentration. This trend could be attributed to the complex react between Pb^{2+} and DMDC. The results had good correlations with flotation test (Fig. 6).

Fig. 9 presents the content of Pb^{2+} in flotation pulp as a function of pH. It can be seen from that the content of Pb^{2+} decreases rapidly with increasing of pH, which could be attributed to the formation of hydroxyl compounds. In the previous studies, we have illustrated that $Pb(OH)^+$ became the dominant species in solution at $pH > 7$. In addition, the content of Pb^{2+} decreases rapidly at a wide pH value range compared with no DMDC addition, illustrating that the formation of the complex between DMDC and Pb^{2+} . This could greatly reduce the content of Pb^{2+} in the pulp, thereby reducing the activation of marmatite.

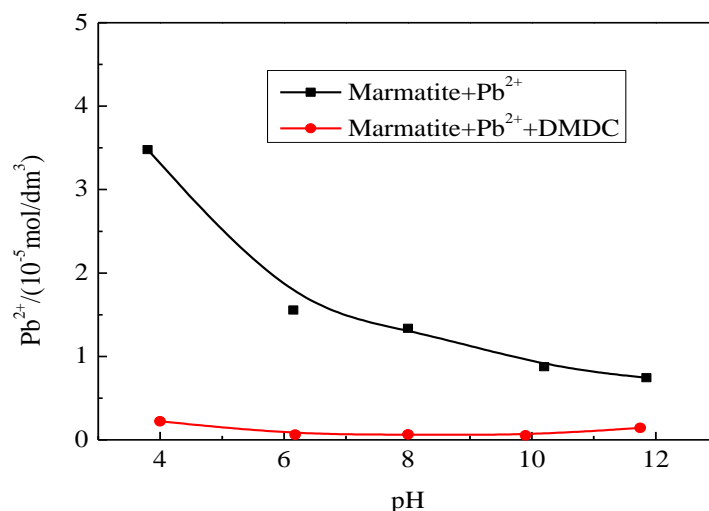


Fig. 9. The content of Pb^{2+} in flotation pulp as a function of pH ($c(Pb^{2+})=5 \times 10^{-5} \text{ mol/dm}^3$, $c(DMDC)=10^{-4} \text{ mol/dm}^3$)

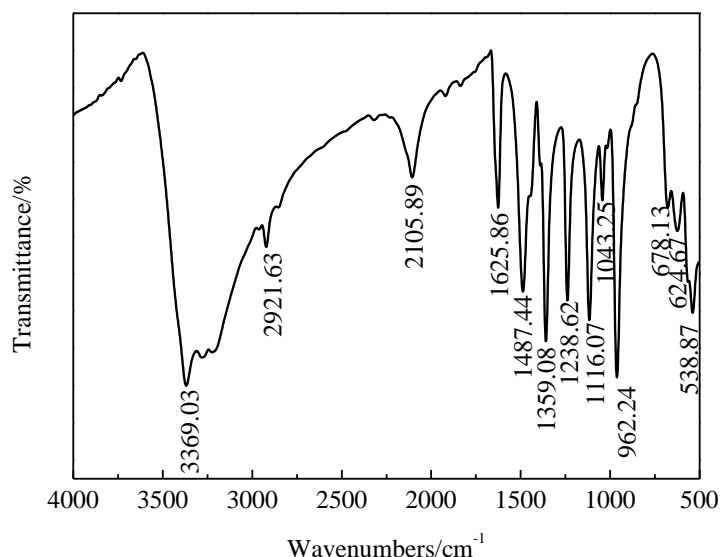


Fig. 10. Infrared spectrum of DMDC

3.4 FTIR

Infrared spectroscopy was used to identify the adsorption mechanism of the DMDC on the mineral surface, and the FTIR spectrums of minerals before and after treating with DMDC were carried out. The infrared spectrum only shows the 600-4000 cm^{-1} , since this area includes most of the characteristic bands of DMDC. The results are presented in Fig. 9. As for the DMDC spectra shown in Fig. 10, the band at 1625.86, 1116.07, 1043.25 and 962.24 cm^{-1} were attributed to $-NH_2$ bend vibration (Qin et al., 2013) C-N stretching vibration, C=S stretching vibration and C-S stretching vibration (Ma, et al., 2016), respectively. Additionally, the bands at 1487.44, 1359.08 and 1238.62 cm^{-1} were due to the N-C=S stretching vibration (Sun et al., 2006). The band at 2921.63 cm^{-1} was attributed to the C-H stretching vibration of the $-CH_3$ groups (Chen et al., 2017).

Fig. 11 shows the spectra obtained from galena. The characteristic bands of DMDC at 2923.56, 1504.20, 1245.06 and 970.02 cm^{-1} were observed when galena was conditioned with DMDC, which are assigned to the $-C-H$ -, $-N-C=S$ and $-NH_2$ groups in DMDC, indicating DMDC is chemically adsorbed on the galena surface. The spectra of marmatite interaction with reagent are shown in Fig. 12. From curve a we can see that new peaks appear at 1390.2 and 1243.76 cm^{-1} after treating marmatite with DMDC, which is contributed by $-N-C=S$ stretching vibration in DMDC.

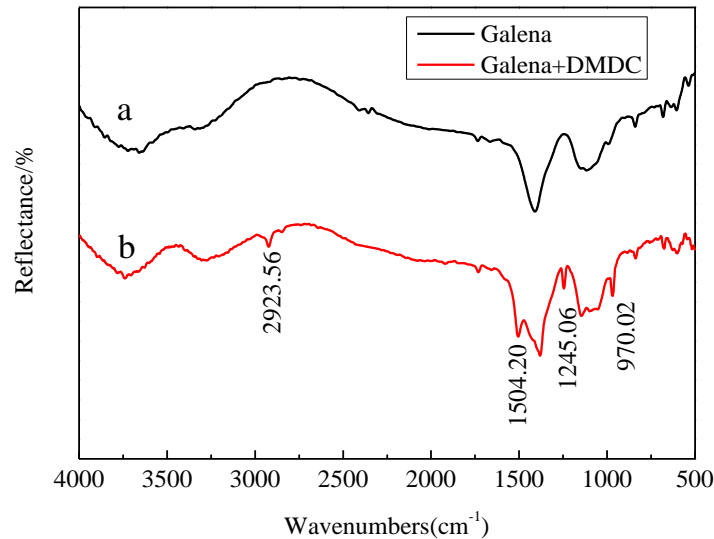


Fig. 11. Infrared spectrum of galena: a) galena, b) galena + DMDC

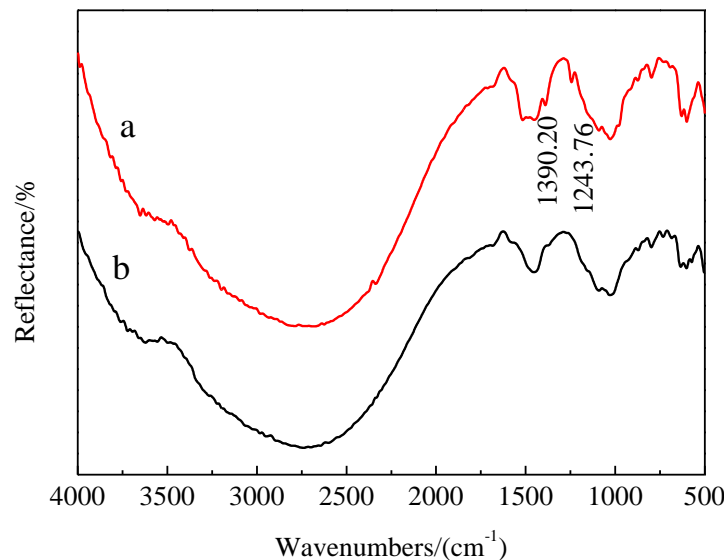


Fig. 12. Infrared spectrum of marmatite: a) marmatite+ DMDC, b) marmatite

3.5 Adsorption amount of collector

The adsorption amount of collector is closely related to the floatability of mineral. To characterize the effects of DMDC on the adsorption of DDTC, the adsorption amount of DDTC on galena and marmatite in the presence and absence DMDC was investigated, and the results are shown in Fig. 13. It can be seen from Fig. 13(a), the adsorption amount of reagents on galena surface is almost unchanged after adding of DMDC throughout the pH tested, indicating that DMDC has little effect on the adsorption of DDTC galena surface and it can co-adsorb with DDTC on galena surface, which corresponds well to the flotation results in Fig. 6. Fig. 13 (b) shows that the amounts of DDTC adsorbed on the marmatite surface, after the addition of lead ions, the adsorption curve of marmatite increases at the entire pH range compared to Fig. 13(a) , illustrating the activation effect of lead ions. The result is consistent with the flotation tests in Fig. 3. In the presence of DMDC, the adsorption amount of reagents adsorbed on the surface of marmatite decreases at the pH range tested. The decrease in the amount of reagents adsorbed on the surface of marmatite reflected that there is a competitive adsorption between DMDC and DDTC and less DDTC adsorb on marmatite surface in the presence of DMDC. Therefore, the flotation recovery of marmatite decreases with the addition of DMDC. The adsorption amount measurement corresponds well to the flotation results.

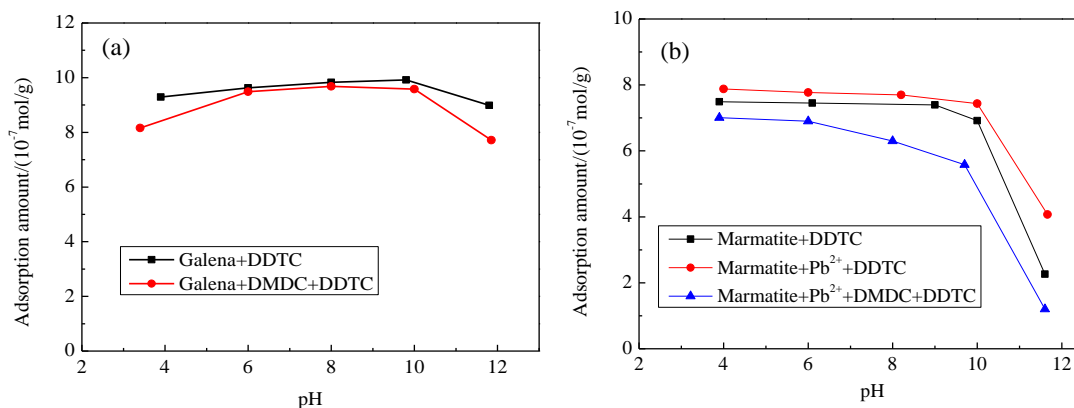


Fig. 13. Adsorption amount of DDTC on galena(a) and marmatite (b) surface as a function of pH

4. Conclusions

The flotation result shows that DMDC could sharply decrease the recovery of Pb-activated marmatite but has small effect on galena using DDTC as collector. Therefore, DMDC was a promising organic depressant in selectivity flotation of galena–marmatite in the presence of DDTC.

From the results of UV–vis spectroscopy test and ICP study, DMDC has a stronger capacity of complexing with lead ions or hydroxy complexes of lead, which indicated that DMDC is effective in preventing lead activation of marmatite, which in turn results in depression.

Infrared adsorption spectra demonstrate that DMDC is absorbed on the two mineral surfaces chemically. In addition, according to collector adsorption test, DMDC could reduce the DDTC adsorption of marmatite surface, but it could co-adsorb on the galena surface.

From above study, it can be concluded that DMDC could reduce the activation of Pb-contaminated marmatite, and the complex adsorbed on two minerals surface, which has an effect on collector adsorption. Therefore, DMDC can be used as an efficient and environmentally friendly reagent for marmatite depressant in mineral processing.

Acknowledgments

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