

Research Article

Synthesis of N,N-Diethyldithiocarbamate Nitrile Ethyl and the Chelating Behaviors with Metal Ions

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The N,N-diethyldithiocarbamate nitrile ethyl (NND) was the nonionic polar collector, and it can synthesize the NND in dimethyl sulfoxide solvent. This method can effectively reduce the reaction intensity and the coefficient of the synthetic risk. The purity of NND which we synthesized is 94.23%, and the yield is 91.06%. UV analysis shows that the characteristic absorption peak wavelength of the NND is 276 nm, and its absorbance is 0.901. Based on the interaction of NND + Mⁿ⁺ (Mⁿ⁺ = Fe³⁺, Cu²⁺, Zn²⁺, Pb²⁺) and the quantum chemical calculation analysis of the NND and ethyl xanthate, we can conclude that the flotation performance of NND should be better than that of ethyl xanthate.

1. Introduction

With the continuous development and utilization of mineral resources, the mineral resources tend to be poor, fine, and complex, and it becomes difficult to sort the multimetal ore. This requires a higher concentration ratio. All of these demonstrate the importance of flotation reagent and also promote the great development of the scope of use, variety, and quantity [1]. At present, many countries in the world are researching more environmentally friendly flotation reagents with low toxicity or newly nontoxic flotation reagents dosage which has better performance and higher selectivity. There are many kinds of mineral processing reagents abroad with more widespread use of efficient flotation reagent. It can reduce the agent dosage because of high selectivity of the new flotation reagents. Generally, less dosage of the reagent can reduce the processing cost and the environment pollution [2].

The N,N-diethyldithiocarbamate nitrile ethyl (NND) is a nonionic polar collector and has strongly collected properties and good selectivity. Compared with the traditional xanthate collectors, the consumption of this collector can be greatly reduced, and it has foamed properties at the same time. Due to the good selectivity, it can greatly reduce the dosage of

inhibitors. So it can achieve a better recovery for the objective mineral, especially to the precious metals such as gold and silver, thus reducing the pollution. Therefore it has important practical significance to research on the synthesis process of the NND.

2. The Synthesis Process of the NND

There are two steps of halogenated substitution method and one step of unsaturated hydrocarbon additive method. One-step method needs less equipment, shorter flow, and lower cost. So this test adopts one step of unsaturated hydrocarbon additive method to synthesize the NND. One of the starting materials is the acrylonitrile (CH₂=CHC≡N) with a carbon-carbon double bond and cyano-conjugate in the structure of the acrylonitrile. The double bond is very active, and it can participate in many kinds of additional reaction. Another material is carbon bisulfide. The carbon atom with a partial positive charge can generate complex formation by reacting with many negative ions or unshared electron pair compounds.

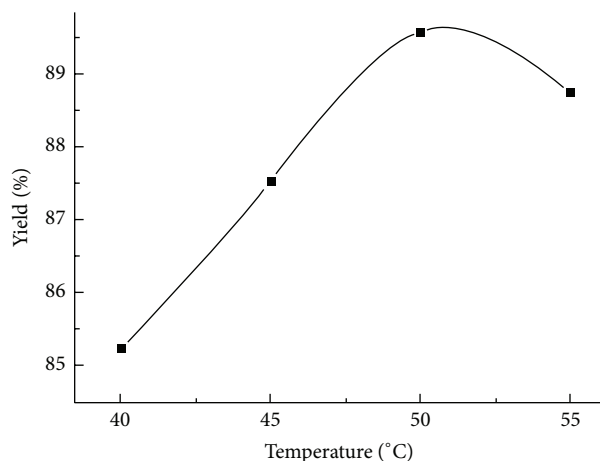
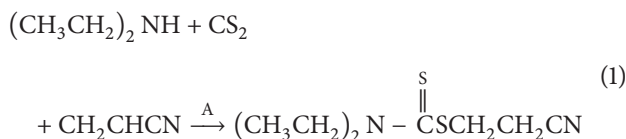


FIGURE 1: Effect of temperature on the synthesis.

Experiment was conducted in the aerator, and it was synthesized in a glass flask equipped with condenser. The rotary evaporation method was used to remove part of the outgrowth of acrylonitrile before synthesis. The flask was placed in a constant temperature bath with the constant magnetic stirring apparatus, and the materials took additional reaction in a phase. After the reaction was completed, the product was processed by vacuum distillation in a rotary evaporator to remove excess diethylamine and carbon bisulfide to get the pure NND.

The reaction equation is as follows:



We measured the amount of 10.5 mL (0.1 mol) of triethylamine and in accordance with the mass ratio of 1:1:1 measured a quantity of carbon bisulfide and acrylonitrile, slow mixing diethylamine, and carbon bisulfide in A phase at less than 20°C (A is a kind of important polar aprotic solvents which is the mixture of the two methyl sulfoxides and other sulfoxide organics. The mixture is not involved in the synthesis reaction, and it can be distilled from the mixed liquid composition and then isolated). Then we slowed addition of acrylonitrile after about 30 minutes. After exothermic reactions, we kept 1.5 h, respectively, at different temperatures to investigate effect of temperature on the synthesis of NND. The test results are shown in Figure 1. We study the yield in different proportions of compounds. The test results are shown in Figure 2.

Experiments show that it can get the maximum yield of NND when mass ratio of diethylamine, carbon bisulfide, and acrylonitrile is 1.15:1.2:1 and the optimum reaction temperature is 50°C because the diethylamine and carbon bisulfide belong to the volatile material. Material loss is more than normal temperature in the intense exothermic reaction; thus, it is reasonable to increase the amount of carbon bisulfide and triethylamine.

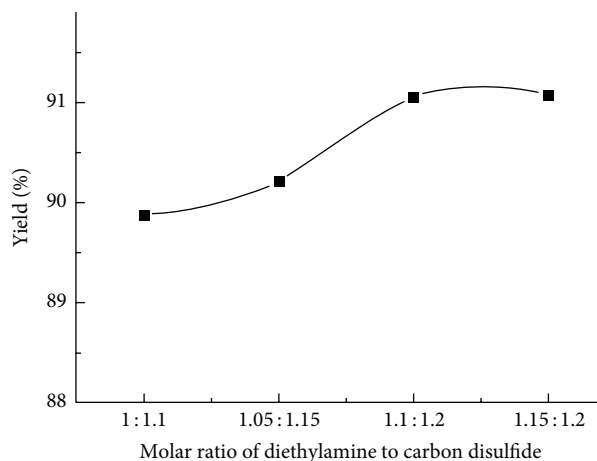


FIGURE 2: The yield in different proportions of compounds.

TABLE 1: Infrared spectrum analysis of synthetic NND.

The absorption peak position/cm ⁻¹	Absorption peak	
1205	Middle peaks	C=S
1271	Middle peaks	R-Ar-N-R'
2248	Middle peaks	-C≡N
2933	Strong peaks	C-H
2978	Strong peaks	C-H
3446	Strong peaks	R-NH ₂

Further test was done on reactive time in optimum conditions of the temperature and reactant mass ratio. We measured the amount of 10 mL of A and in accordance with the mass ratio of 1.15:1.2:1 measured a quantity of triethylamine, carbon bisulfide, and acrylonitrile. 50°C was kept, respectively, at different time to investigate the effects of reactive time on the synthesis of NND. The test results are shown in Figure 3.

Experiments show that the product yield almost has no change or even some decline after 90 minutes' reaction, which indicates that all NND has been fully synthesized after 90 minutes. If heating at higher temperature was conducted further, it could cause the decomposition or evaporate.

2.1. Infrared Spectral Analysis of NND. The NND which was obtained under optimal conditions in the laboratory was analyzed by infrared spectroscopy. The infrared spectrum test of NND is shown in Figure 4, and the infrared spectrum analysis is shown in Table 1.

2.2. The Physical Properties of NND. NND is dark brown oily liquid at room temperature. Its density is 1.08 g/mol, and there is a faint smell of fish. It cannot be soluble in water but in some organic solvents such as ethanol, ethyl ether, and carbon tetrachloride. The melting point of NND is about 23°C.

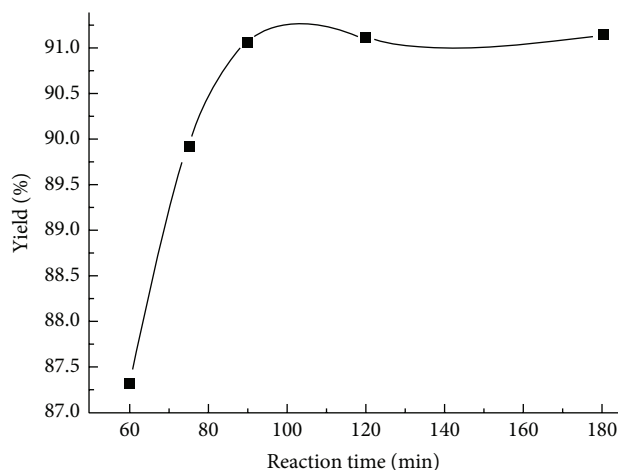


FIGURE 3: Effect of reaction time on the synthesis.

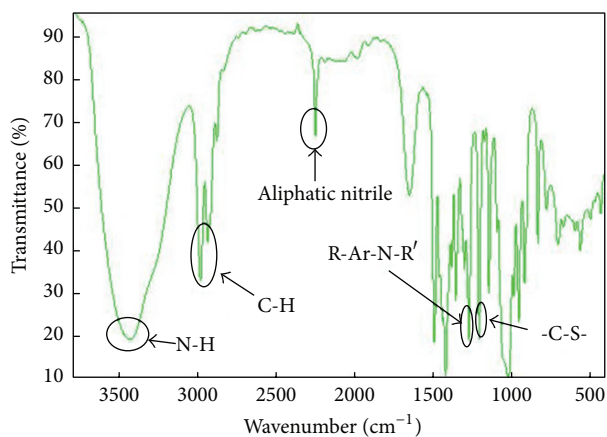


FIGURE 4: Infrared spectrum of synthetic NND.

2.3. UV Spectral Analysis of Reaction of NND and Some Metal Ions

2.3.1. UV Spectral Analysis of Reaction of NND. NND and ethanol were mixed into the solution, and then the solution is diluted that its molar concentration was 1×10^{-4} mol/L. The ultraviolet absorption spectrum of the diluted dilution is shown in Figure 5.

As can be seen from the graph, characteristic absorption peak wavelength of NND is 276 nm, and its absorbance is 0.901.

2.3.2. UV Spectral Analysis of Reaction of NND and NND + M^{n+} . The ultraviolet spectrum of NND and NND + M^{n+} is shown in Figure 5.

The UV trend is consistent with Figures 5(a) and 5(b), but the absorbance value of the maximum absorption peak has to some extent decreased. This shows that the NND + Fe^{3+} and NND + Cu^{2+} both have some interactions, and the NND + Fe^{3+} takes the most obvious interaction; we also can see that UV trend is consistent with Figures 5(c) and 5(d), but absorbance value of the maximum absorption peak has

no change. This shows that NND + Pb^{2+} and NND + Zn^{2+} both have no interaction.

2.4. Quantum Chemical Calculations and the Flotation Performance Interpretation of NND. Quantum chemical calculation of NND was calculated by Materials Studio software which was developed by the Accelrys Company. At the same time, we did quantum chemistry calculation of ethyl xanthate which is a flotation reagent of the traditional sulfide ore, and the calculation results were compared with the NND to theoretically evaluate and interpret the flotation performance.

The calculations are carried out by the DMol3 in Material Studio which is a first-principle pseudopotential method based on the density-functional theory (DFT). The exchange correlation functional is the generalized gradient approximation (GGA) which is developed by Perdew, Burke, and Ernzerhof (PBE). DFT calculations employing plane wave (PW) basis sets and ultrasoft pseudopotentials are performed. The interactions between valence electrons and ionic core are represented by ultrasoft pseudopotentials. The kinetic energy cut-off (310 eV) of the plane wave basis is used throughout the study. For self-consistent electronic minimization, the Pulay Density Mixing Method is employed with a convergence tolerance of 2.0×10^{-6} eV/atom. The energy tolerance is 2.0×10^{-5} eV/atom, the force tolerance is 0.05 eV/Å, and the displacement tolerance is 0.002 Å.

2.4.1. The Quantum Calculation Analysis of Optimization Molecular Structure of NND. The structure of NND molecules was optimized, and the space structure is shown in Figure 6(a). Due to the steric, N atoms connecting with 2 ethyl groups are not easy to interact with the ore. Each atom Mulliken charge distribution of optimization molecular structure of NND is shown in Table 2.

As the metal ions in the ore are positive ions, the larger the negative charges of Mulliken reagent molecules are, the more likely they are to react with metal iron in ores. In Table 2, it is obvious that S(12) (-0.524) is most likely to react with metal iron in ores.

Based on the above analysis, we constructed the model of NND + Cu^{2+} , through the optimization calculation, and got the effect of a stable model which is shown in Figure 6(b).

We can see that NND and metal ion together constitute rectangular and hexagonal ring from Figure 6(b), so it has the ability of collecting.

Mulliken charge distribution of each atom of NND interaction with copper ion is shown in Table 3.

By contrasting Table 3 with Table 2, we can see that S(5), S(12), and N(9) have a strong interaction with copper ions, and their Mulliken charge distributions have taken great changes between before interaction with copper ions and after interaction with copper ions.

2.4.2. Quantum Chemical Calculation and the Calculation Results of Ethyl Xanthate. Scholars put forward the hypothesis of molecular adsorption and ion adsorption hypothesis in a study of xanthate collection mechanism [3]. The former

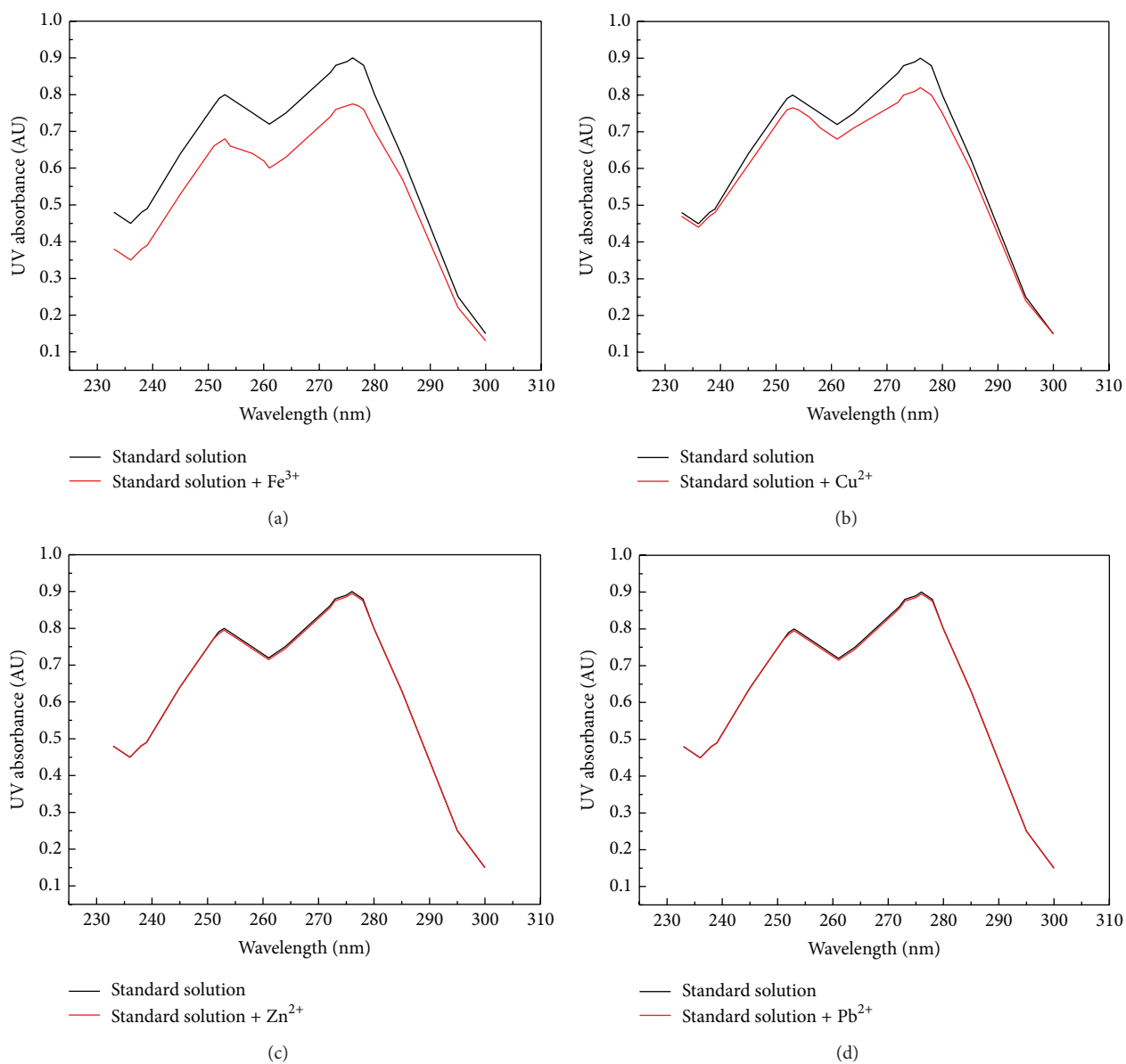


FIGURE 5: Ultraviolet spectrum of NND and NND + Mⁿ⁺ Mⁿ⁺ = Fe³⁺, Cu²⁺, Zn²⁺, Pb²⁺.

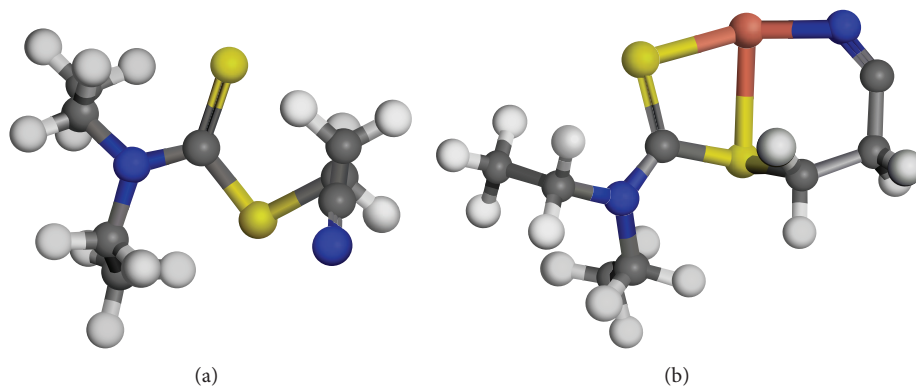


FIGURE 6: The molecular structure of NND and NND + Cu²⁺.

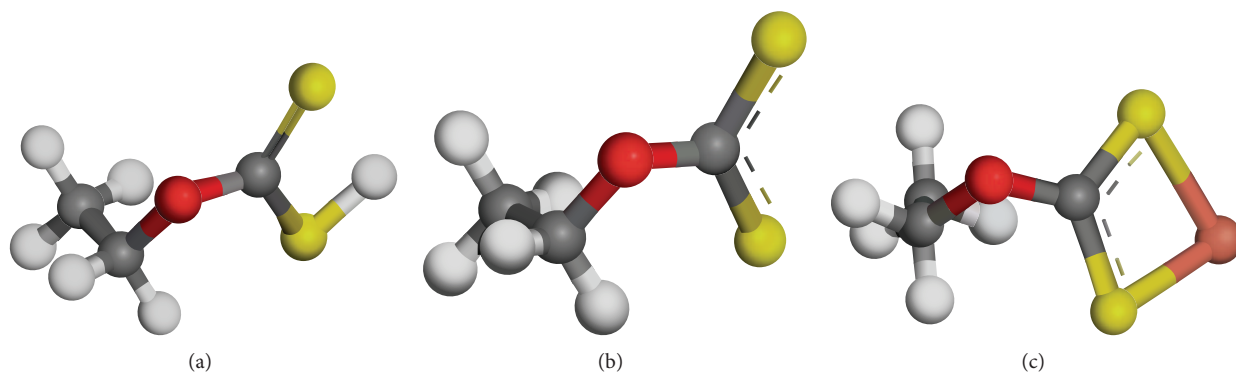


FIGURE 7: The spatial structure of ethyl xanthate molecules combined with metal ions.

TABLE 2: Each atom Mulliken charge distribution of optimization molecular structure of NND.

Atomic categories	C(1)	C(2)	N(3)	C(4)	S(5)	C(6)	C(7)	C(8)	N(9)
Electricity/ e	-0.322	-0.119	-0.243	0.412	-0.212	-0.207	-0.301	0.111	-0.205
Atomic categories	C(10)	C(11)	S(12)	H(13)	H(14)	H(15)	H(16)	H(17)	H(18)
Electricity/ e	-0.321	-0.155	-0.524	0.140	0.118	0.109	0.116	0.151	0.170
Atomic categories	H(19)	H(20)	H(21)	H(22)	H(23)	H(24)	H(25)		
Electricity/ e	0.155	0.191	0.168	0.123	0.135	0.121	0.157		

TABLE 3: Mulliken charge distribution of each atom of NND interaction with copper ion.

Atomic categories	C(1)	C(2)	N(3)	C(4)	S(5)	C(6)	C(7)	C(8)	N(9)
Electricity/ e	-0.312	-0.139	-0.215	0.268	-0.240	-0.214	-0.268	0.100	-0.268
Atomic categories	C(10)	C(11)	S(12)	H(13)	H(14)	H(15)	H(16)	H(17)	H(18)
Electricity/ e	-0.308	-0.130	-0.282	0.133	0.113	0.102	0.106	0.140	0.124
Atomic categories	H(19)	H(20)	H(21)	H(22)	H(23)	H(24)	H(25)	H(26)	Cu(27)
Electricity/ e	0.140	0.128	0.141	0.110	0.132	0.105	0.124	0.104	0.206

TABLE 4: Mulliken charge distribution of ethyl xanthate molecules.

Atomic categories	C(1)	C(2)	O(3)	C(4)	S(5)	S(6)	H(7)	H(8)	H(9)	H(10)	H(11)	H(12)
Electricity/ e	-0.309	-0.024	-0.307	0.385	-0.266	-0.279	0.106	0.125	0.119	0.109	0.115	0.125

TABLE 5: Mulliken charge distribution of optimization of ethyl xanthate anion.

Atomic categories	C(1)	C(2)	O(3)	C(4)	S(5)	S(6)	H(7)	H(8)	H(9)	H(10)	H(11)
Electricity/ e	-0.242	0.052	-0.354	0.390	-0.518	-0.516	-0.023	0.074	0.012	0.044	-0.019

believes that xanthan molecule is effective form of xanthate in the pulp, while the latter considers that it is xanthate anion. So it is necessary to study the structure of two kinds of collectors.

The spatial structure diagram of optimizing ethyl xanthate molecules is shown in Figure 7(a), and the spatial structure diagram of optimizing ethyl xanthate anion is shown in Figure 7(b). It can be seen from the chart that two-sulfur atom structure of ethyl xanthate anion is conjugate structure.

Mulliken charge distribution of ethyl xanthate molecules is shown in Table 4. Mulliken charge distribution of optimization of ethyl xanthate anion is shown in Table 5.

We determined the flotation characteristics by comparing Mulliken charge distribution of ethyl xanthate molecules

with Mulliken charge distribution of optimization of ethyl xanthate anion. As can be seen from the charts, Mulliken charge distributions of S(5) and S(6) in molecule are -0.266 and -0.279 , and Mulliken charge distributions of S(5) and S(6) in ion are -0.518 and -0.516 . It is obvious that the flotation effect of xanthate ion will be good. This is consistent with the actual. So we need to construct a better model.

Then, we constructed the model of the ethyl xanthate ion and the ethyl xanthate ion + Cu^{2+} through the optimization calculation, and the stable model of the ethyl xanthate ion + Cu^{2+} is shown in Figure 7(c). Mulliken charge distribution of ethyl xanthate ion and the ethyl xanthate ion + Cu^{2+} is shown in Table 6. It shows that two sulfurs interact with the Cu^{2+} .

TABLE 6: Mulliken charge distribution of ethyl xanthate ion and the ethyl xanthate ion + Cu²⁺.

Atomic categories	C(1)	C(2)	O(3)	C(4)	S(5)	S(6)	H(7)	H(8)	H(9)	H(10)	H(11)	Cu(12)
Electricity/e	-0.288	0.016	-0.351	0.302	-0.437	-0.416	0.009	0.106	0.047	0.055	0.004	-0.146

TABLE 7: Energy of NND and ethyl xanthate.

Energy	NND	NND + Cu ²⁺	Ethyl xanthate ion	Ethyl xanthate ion + Cu ²⁺
Binding energy	-4.66059 Ha	-5.02687 Ha	-2.10020 Ha	-2.27400 Ha
Total energy	-1212.84560 Ha	-2850.99734 Ha	-984.89550 Ha	-2622.85218 Ha

2.5. *Energy of NND, Ethyl Xanthate, and the Reactants with Copper Ions.* The energy of NND, ethyl xanthate, and the reactants with copper ions is shown in Table 7.

In the calculation process, we also calculated the binding energy and the total energy of the optimization system. The results are shown in Table 7.

With the thermodynamic theory, the bigger energy changes between the collector and Cu. The more easily the collector reacts with copper ore, the better the performance of the collector is.

The change value of combination energy of NND and Cu ion is -0.36628 Ha. The change value of its total energy is -1638.15174 Ha. The change value of combination energy of ethyl xanthate and Cu ion is -0.17380 Ha. The change value of its total energy is -1637.95668 Ha. The former change of the binding energy and the total energy is larger than the latter. Therefore, in theory, the flotation performance of NND should be better than that of ethyl xanthate.

3. Conclusion

- (1) The purity of NND which we use UV-Visible Spectrophotometry to measure is 94.23%, and the yield is 91.06%.
- (2) We know, according to the UV analysis, that the characteristic absorption peak wavelength of NND is 276 nm, and its absorbance is 0.901. NND + Fe³⁺ and NND + Cu²⁺ both have some interactions, and NND + Fe³⁺ takes the most obvious interaction; NND + Pb²⁺ and NND + Zn²⁺ both have no interaction.
- (3) Based on quantum chemical calculation analysis of NND and ethyl xanthate, the flotation performance of NND should be better than that of ethyl xanthate.

Conflict of Interests

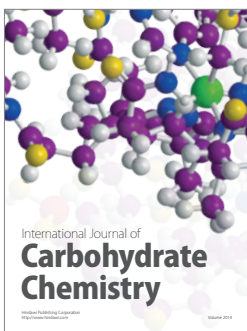
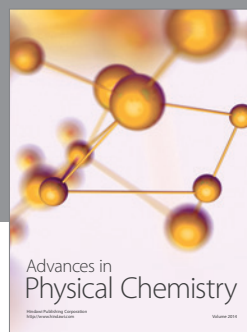
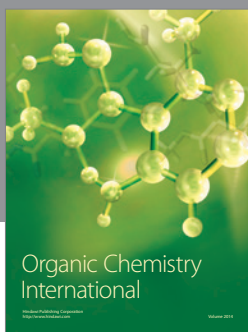
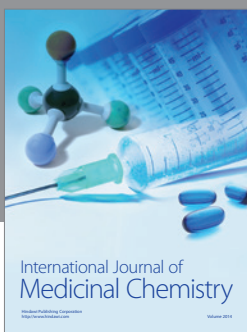
The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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