Adsorption of yeast dextran on clinochlore surface and the implications for pyrite/clinochlore separation

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Abstract: Silicate minerals with a certain degree of flotability are often easy to mix into sulfide ore concentrate in mineral processing industry. In this paper, the adsorption of yeast dextran on clinochlore and its application in pyrite/clinochlore separation were investigated. The adsorbed amount and micro polarity measurement results displayed that the yeast dextran molecules selectively adsorbed onto clinochlore surface compared with pyrite. The adsorbed yeast dextran resulted in the increase in the surface polarity of clinochlore surface, and inhibited the further adsorption of xanthate, thus keep it hydrophilic and depressed. Quantum chemical computation results indicated that yeast dextran was mainly adsorbed on mineral surface by the chelation with the surface metal active sites, and the chelating strength of yeast dextran with three ions was in the sequence of $Fe^{3+} > Mg^{2+} > Fe^{2+}$. While Mg^{2+}, Fe^{2+} and Fe^{3+} are the main metal ions on the surface of clinochlore, and Fe^{2+} is the unique metal ions on pyrite surface. This is the reason of the selectivity of the yeast dextran depressant for pyrite/clinochlore flotation system. The flotation results demonstrated that yeast dextran was qualified to selectively depress clinochlore in pyrite flotation.

Keywords: clinochlore, pyrite, flotation, yeast dextran, adsorption

1. Introduction

Pyrite [FeS_2] is an important chemical raw material mainly used for sulfuric acid or sulfur manufacture. Its potential application refers to rubber, papermaking, construction and agriculture field etc (Yang et al., 2009). It is also the common carrier mineral for gold, silver, cobalt and selenium etc (Alam et al., 2019). The pyrite resources in south Sichuan province, China, has the first reserves in the country. In these deposits, clinochlore, a Mg-bearing silicate with stratified structure, is the main gangue mineral (Wei et al., 2012). Its Moh's hardness is low as 2-2.5, bringing about the problems of the production of slimes (fine particles) during grinding. The slimes may further bring about adverse effect to ore dressing process: easily transporting to flotation concentrates, and thus reducing concentrate grade (Chen et al., 2019). During smelting/roasting Mg-bearing minerals have great negative effect on melt flowing and furnace surroundings based on its refractory character, such as the case of pyrite roasting with clinochlore to produce sulfur oxide for sulphuric acid preparation (Tang et al., 2020). So they are the substances that must be rejected as much as possible in pyrite concentration, for providing a high-quality pyrite concentrate to smelting plant or sulphuric acid plant.

To achieve the concentration of pyrite, froth flotation is still the main method adopted, which utilizes the difference in surface physicochemical characteristics between valuable minerals and the gangue minerals (John et al., 2020). Clinochlore presents slightly lower hydrophobicity than pyrite mineral, so the flotation efficiency would be low, and commonly, a pyrite concentrate with high-content of clinochlore would be obtained if no depressant addition (Siddiqui et al., 2018; Xu et al., 2020). Based on the experience from other flotation systems of different minerals, effective depressant addition before

collector can improve the separation results. So the depressant development is also the important subject of clinochlore depression in corresponding valuable minerals' flotation. For instance, Guan et al found that xanthan gum had a selective depression ability for chlorite compared with arsenopyrite, and the arsenopyrite/chlorite separation could be achieved with xanthan gum in the pulp with reasonable pH value (Ming et al., 2020). For the flotation system of minerals with similar natural floatability, researchers often selectively regulate the gangue minerals' surface properties to strengthen its hydrophilic and thus depressing its flotation.

In microorganisms, plants and some animals dextran is widely found, and it is also called bacterial gum, mainly consists of high-molecular-mass hydro-colloidal polysaccharides (Thanardkit et al., 2002). Wide source and cheap price, therefore, are the superiorities of dextran. In some mineral systems it was considered to have the latent possibility of substituting starch, guar gum and CMC as the depressant. The sample investigated was a pyrite ore in which the main gangue was clinochlore mineral. Very few studies about flotation separation of pyrite from clinochlore and the mechanism have been reported. Therefore, it is of great theoretical and practical significance to use dextran as a possible depressant for pyrite/clinochlore flotation system.

The aim of this study was to investigate the mechanism of yeast dextran (YD) depressing clinochlore with the methods of adsorbed amount and micropolarity measurements and quantum chemistry calculation (QCC), and to verify its application for the separation of pyrite and clinochlore.

2.   Materials and methods

2.1. Minerals and reagents

From a pyrite mine in south Sichuan Province, China, pure clinochlore and pyrite samples were collected carefully. Then, they were dry ground, and screened to obtain −74+38 μm fractions for flotation, micropolarity and adsorbed amount tests, respectively. A part of -38 μm finer fractions were further comminuted to about -5 μm for FTIR determinations. Another part of -38 μm minerals was used for X-ray diffraction analysis. The XRD patterns obtained was shown in Fig. 1, together with their corresponding PDF cards extracted from Jade 6.0 package. Through intuitive comparison and integral computation the >96% purity of both minerals can be determined.

From Puripharm Co., Ltd., Zhejiang Province, China, the YD with ~30000 molecular weight and ~99% purity was purchased and used in the tests as the clinochlore depressant. The chemical structure of yeast dextran molecule is shown in Fig. 2 (Zhao et al., 2019). Its monomer is a six-member saturated heterocyclic with a O atom and five C atoms; every C atom bonds to a hydroxyl group. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used as the pH regulators. Technical pure sodium butyl xanthate (SBX) and analytically pure methyl isobutyl carbinol (MIBC) were used as the collector and frother, respectively. Distilled water (18.2 MΩ·cm) was used for all the tests.
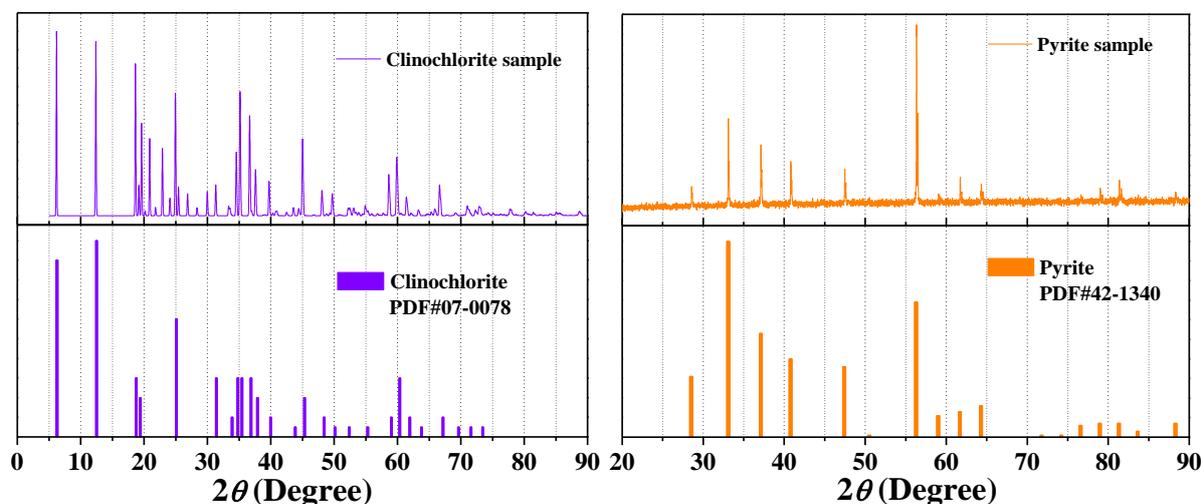

Fig. 1. XRD patterns of clinoclore and pyrite with the corresponding PDF cards
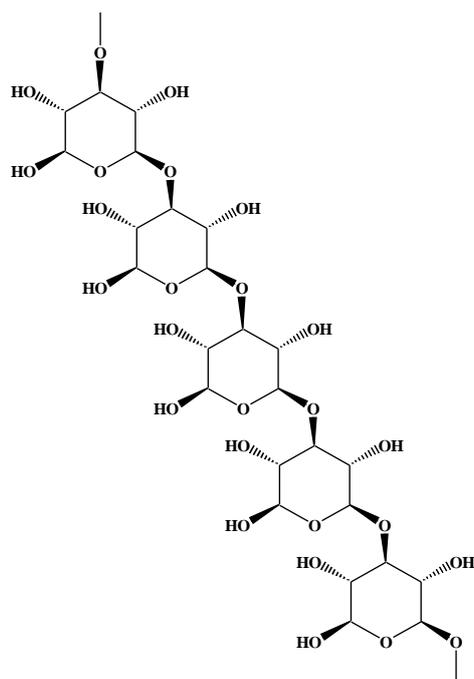
Fig. 2. Structural formula of YD with five monomers

2.2. Micropolarity detection

The pyrene was dissolved into hot water until saturation, then cooled to 25 °C and filtered out the excess undissolved pyrene to prepare its stock solution, of which the concentration of pyrene was measured as 6.52×10^{-7} M. Through mixing the stock solution with reagent(s) and mineral pulp, and conditioning for 1.5 h, the mineral samples used for measurement were prepared. Hitachi F-4500 fluorescence spectrophotometer was employed to obtained pyrene steady-state emission spectum, which commonly shows five peaks. I_1/I_3 (ratio between the 1st and 3rd peak intensity) is sensitive to the polarity of the micro-environmental located by the probe molecules. It changes with the polarity, and the values are common < 1.0 in nonpolar solvent, 1–1.2 in surfactant micelle or semi micelle, and 1.6–2 in water (Jiang et al., 2019). The standard deviations were given as error bars.

2.3. Adsorbed amount measurement

A 2.0 g sample was put into 60 mL distilled water to prepare a pulp; the desired reagent(s) was (were) added after the pH being adjusted to 8.5; the conditioned solution was stirred for 10 min to allow the reagent adsorption; it was then centrifuged for 15 min at 4,000 rpm using a high speed refrigerated centrifuge. The adsorbed amounts of SBX and YD on mineral were measured using an ultraviolet (UV-3100) spectrometer at the maximum absorption wavelength 301 nm and 545 nm, respectively. Adsorbed amounts of reagent on mineral powder were determined using solution depletion (Zhang et al., 2014). The standard deviations were given as error bars.

2.4. Quantum chemical calculation

The density functional theory calculations were conducted using the Gaussian 09 package. The popular exchange-correlation functional B3LYP (Becke, three-parameter, Lee-Yang-Parr), together with the 6-31G* basis set included in this package was used in the calculations (Stephens et al., 1994). Polarizable continuum model was employed for the water phase calculations (dielectric constant = 78.36, T=298 K) (Lyu et al., 2019). The B3LYP/6-31G* were performed for the determination of geometrical structure and the binding energy calculations.

2.5. Flotation tests

In a XFG^{II} type flotation machine equipped with a 60 mL flotation cell and produced by Jilin Exploration

Machinery Plant, China, the flotation performance of different reagent regimes on both minerals were investigated at the settled 1990 rpm impeller speed.

For single mineral system, 2.0 g of pyrite or clinochlore was put into the cell, then mixed with enough water to prepare a pulp. After starting the impeller, the desired pH value was regulated using the pH regulator under the monitoring of a pH meter, and conditioned the pulp for 2 min. Depressant YD (if needed), collector SBX and frother MIBC (fixed at 1×10^{-4} M) were successively added into the pulp with a 2.5 min interval. After that, 4.5 min of flotation was carried out to collect the floated fraction. Through weighing the dried non-floated and floated fractions, respectively, the mineral recovery was calculated based on mass balance. The average value of three tests under the same condition was reported. The standard deviations were given as error bars.

For artificial mixed minerals (total 2.0 g, 1:1 mass ratio of pyrite and clinochlore) tests the S recovery was calculated based on total solid yield and S grade of two products (Ityokumbul et al., 2000). The standard deviation were given also.

3.   Results and discussion

3.1. Variation of mineral surface micro polarity

Commonly, the flotation or depression of mineral in the pulp is relative to its surface hydrophobicity, and the hydrophobicity has a reverse correlation to the surface polarity (Wang et al., 2021). So the different depression of the YD on the two minerals may be attributed to the different variation of mineral surface polarity. In this study, we used the peculiarity of pyrene steady-state emission spectum that the ratio between the 1st and 3rd peak intensity (I_1/I_3) is sensitive to the polarity of the micro-environmental located by the probe molecules, to characterize the change of the mineral surface polarity and hydrophobicity. The results are displayed in Fig. 3.

Raw pyrite and clinochlore had the I_1/I_3 values between 1.6 and 1.8 in the tested pH range, illustrating the biggish polarity and poor hydrophobicity of them. After treatment using 6×10^{-5} M SBX, the values of both pyrite and clinochlore surface all located in the range of 1.2-1.6. This meant that the hydrophobicity became greater. Moreover, when the pH was lower than $\sim$ 9.7 the hydrophobicity of pyrite was better than clinochlore. When the minerals were treated with single 60 mg/L YD the polarity of the them became stronger. The value added of I_1/I_3 of pyrite was about 0.05 and that of clinochlore was a greater value of 0.2. Obviously, YD selectively resulted in the polarity enhancement (hydrophobicity decrease) of clinochlore.

When pyrite treated with YD was then interacted with SBX the hydrophobicity of pyrite surface was still increase dramatically, slightly lower than that pyrite directly acted with SBX, which suggested a weak depression of YD on SBX/pyrite interaction. While at the same conditions the hydrophobicity of clinochlore surface was slightly higher than that it directly acted with YD, and this showed that YD had a strong depression on SBX/clinochlore interaction. These phenomenon is similar as that found in other
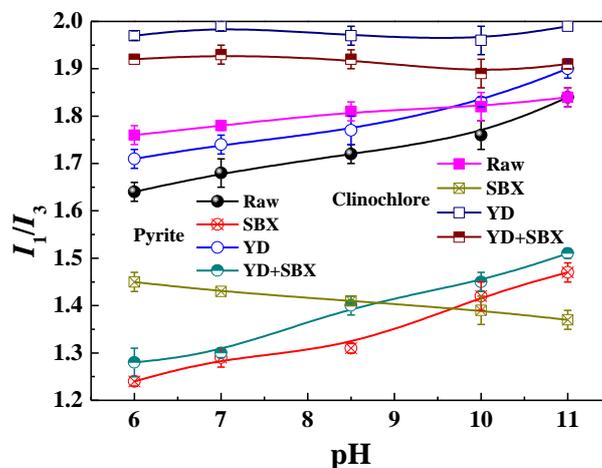

Fig. 3. I_1/I_3 as a function of pH for pyrite and clinochlore at different reagent conditions.(SBX: 6×10^{-5} M; YD: 60 mg/L)

paper studied depressant (Li et al., 2020). It is generally acknowledged that depressant selectively inhibits the adsorption of collector on gangue mineral (clinochlore here) compared with valuable mineral (pyrite here), manifesting its selectivity (Beattie et al., 2006).

3.2. Adsorption of reagents on mineral surface

The addition of YD selectively enhanced clinochlore surface polarity (Fig. 3), and this may be ascribed to the inhibition of YD on the adsorption of SBX with minerals. Macromolecular depressant adsorbed on mineral surface with its hydrophilic group orienting to the solution results in the polarity increase and hydrophobic decrease; moreover, it prevents the further adsorption of collector (Tohry et al., 2021). Here we present the results of the influence of YD dosage on the adsorption of SBX and YD on both minerals in Fig. 4, to further supports this deduction.

The adsorption of YD on clinochlore was greater than that on pyrite, and with the increasing YD dosage this difference had a tendency to expand. At 60 mg/L YD dosage the adsorption of YD on pyrite and clinochlore were 8.84×10^{-3} mg/g and 4.32×10^{-2} mg/g, respectively. This confirmed the phenomenon that the variation of the polarity of clinochlore was greater than that of pyrite with only YD treatment (Fig. 3). Without the pretreatment of YD, the adsorption of SBX on the two minerals were 8.47×10^{-7} mol/g and 6.29×10^{-7} mol/g, of little difference, which was consistent with the similar polarity between them with only SBX. With the increasing YD dosage the adsorption of SBX declined, but obviously that on clinochlore surface showed an even steeper decrease. The SBX adsorption on pyrite and clinochlore were 7.69×10^{-7} mol/g and 1.19×10^{-7} mol/g, respectively, with 60 mg/L YD pretreatment, of about 7 times different. These results revealed that the selectively pre-adsorbed YD on clinochlore surface resulted in the surface hydrophobicity decrease (Fig. 3) and inhibited the further adsorption of SBX.
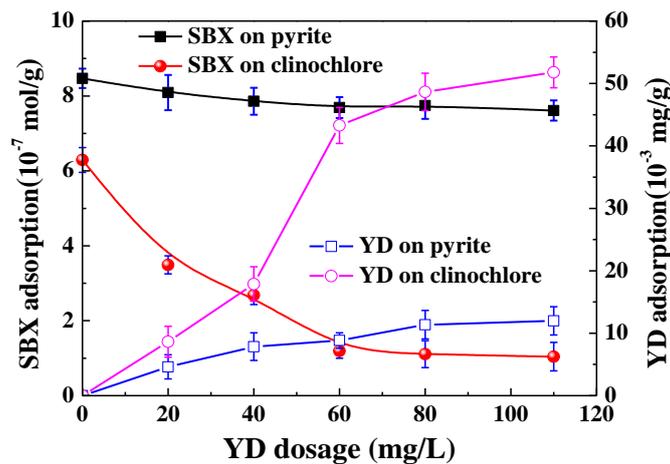

Fig. 4. Influence of YD dosage on the adsorption of SBX and YD on pyrite and clinochlore (pH: 8.5; SBX: 6×10^{-5} M; YD: 60 mg/L)

3.3. QCC results

Mg^{2+}, Fe^{2+} and Fe^{3+} are the main metal ions on the surface of clinochlore (Ferrage et al., 2003), and Fe^{2+} are the unique metal ions on pyrite surface. They can serve as the active sites for reagent adsorption. We have proved the selective adsorption of YD on clinochlore, so here the interaction mechanism between YD and these potential active sites on the molecular level was investigated by QCC method. The reagent energy, ion energy, and the total energy of the reagent-ion system were computed, respectively. The interaction energy is the difference between the total energy and the sum of reagent energy and ion energy. The smaller the value of the interaction energy is, the stronger this action is, and the greater the probability of reagent-ion interacting in this way (Lyu et al., 2019; Wang et al., 2020).

3.3.1. Interaction between Fe^{2+} and YD monomer

Fe^{2+} ions exist at both pyrite and clinochlore surface, so we investigated the interaction between Fe^{2+} and YD monomer first. Three possible coordinate forms of them, ortho-O-Fe^{2+}, meta-O-Fe^{2+} and ortho-

meta-O-chelate-Fe^{2+}, are shown in Fig. 5a-c. Here, the ortho- and meta- were relative to the O atoms in the six-membered ring. The energies of the three coordinate forms for Fe^{2+} and YD monomer are shown in Table 1. The interaction energies for ortho-O-Fe^{2+}, meta-O-Fe^{2+} and ortho-meta-O-chelate-Fe^{2+} systems were -125.522 kJ/mol, -191.152 kJ/mol and -328.570 kJ/mol, respectively. This showed that the interaction between YD monomer and Fe^{2+} was strongest when they combined with each other by the ortho-meta-O-chelate-Fe^{2+} form (Fig. 5c), and the probability of them interacting in this way was greatest. This was in consistent with the report that chelating collector usually has a better collection capacity (Zhang et al., 2021).
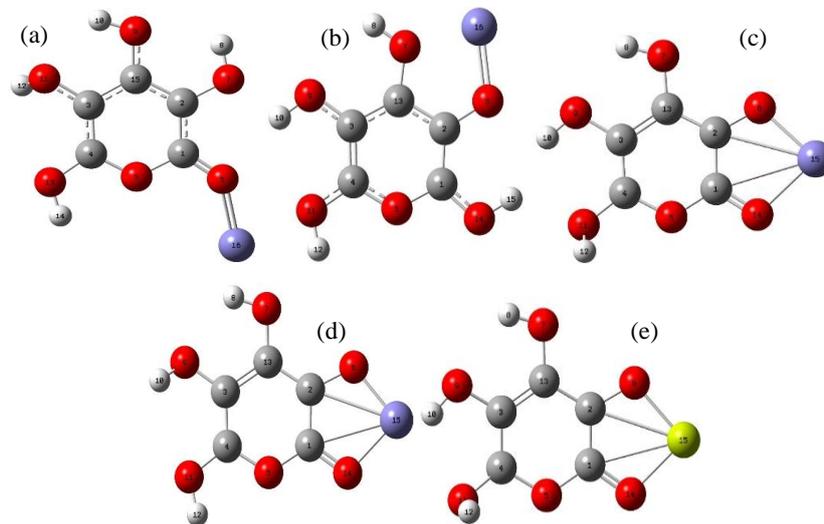

Fig. 5. Interaction of reagent-ion: (a) ortho-O-Fe^{2+}, (b) meta-O-Fe^{2+}, (c) chelate-Fe^{2+}, (d) chelate-Fe^{3+}, (e) chelate-Mg^{2+}

Table 1. The calculation of the interaction between Fe2+ and YD monomer

Ions	Coordinate form	Total energy (kJ/mol)	Reagent energy (kJ/mol)	Ions energy (kJ/mol)	Interaction energy (kJ/mol)
	Ortho-	-1691758.935	-1689983.975	-1649.438	-125.522
Fe^{2+}	Meta-	-1691787.357	-1689946.766	-1649.438	-191.152
	Chelate	-1690588.949	-1688610.941	-1649.438	-328.570

3.3.2. Chelation between YD monomer and three ions

Mg^{2+} and Fe^{3+} are also the considerable active sites for YD adsorption at clinochlore surface in pyrite/clinochlore flotation system. Here we comparatively investigated the chelation between YD monomer and Mg^{2+}, Fe^{3+} (Fig. 5d-e) and Fe^{2+}, and the results are shown in Table 2. The interaction energy of the chelation between Mg^{2+}, Fe^{3+}, Fe^{2+} and YD monomer were -742.673 kJ/mol, -1453.394 kJ/mol and -328.570 kJ/mol, respectively, showing a chelation strength in the sequence of $Fe^{3+} > Mg^{2+} > Fe^{2+}$. YD depressant can adsorb on clinochlore by the strong chelation with these ions (active sites) at mineral surface, and resulted in the mineral surface hydrophilic, inhibition of SBX adsorption. Moreover, it was clearly seen that the interaction energy of YD between Fe^{3+} and Mg^{2+} were ~2 times and ~4 times of that between Fe^{2+}, respectively. This is the reason of the selectivity of the YD depressant for pyrite/clinochlore flotation system, because of that Fe^{2+} is the only active sites on pyrite surface, and Fe^{3+}/Mg^{2+} are the main active sites on clinochlore surface for YD adsorption.

Fig. 6 shows the schematic diagram of the adsorption of YD on the clinochlore surface by the chelation with the Mg^{2+}, Fe^{2+} and Fe^{3+} active sites. The interaction of YD with the surface active sites is by the chelation with different strength. This results in the coverage of YD polymer molecules on clinochlore particle with its hydrophilic –OH orienting to the solution, among which for the chelation monomer the number of –OH is one and for the monomer not directly attached to the surface the

number is three. These hydrophilic –OH groups make the clinochore surface more hydrophilic and with high polarity; the adsorbed YD molecules prevent the SBX anions away from the clinochlore surface by the steric effect depending on them big size (Pugh and Tjus, 1990); moreover they also can inhibit the SBX adsorption by occupying the active sites (Kasomo et al., 2020).

Table 2. The calculation of the interaction between three ions and YD monomer by chelation

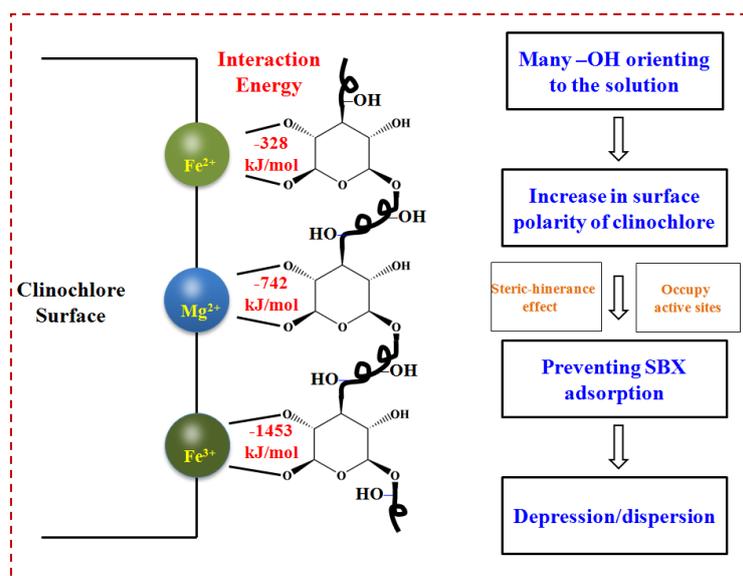| Ions	Coordinate form	Total energy (kJ/mol)	Reagent energy (kJ/mol)	Ions energy (kJ/mol)	Interaction energy (kJ/mol)
Fe^{2+}		-1690588.949	-1688610.941	-1649.438	-328.570
Fe^{3+}	Chelate	-2011480.992	-1688610.941	-321416.657	-1453.394
Mg^{2+}		-2011984.408	-1688610.941	-322630.794	-742.673

Fig. 6. Schematic diagram of the adsorption of YD on the clinochlore surface by the chelation with the Mg^{2+}, Fe^{2+} and Fe^{3+} active sites

3.4. Flotability of single mineral

Based on the above results, it is reasonable to believe that YD could selectively depress the flotation of clinochlore in pyrite/clinochlore system. Here we verified it by flotation experiments.

Pulp pH and reagent dosage are the main factors that influence the flotability of minerals. Here we investigated the responses of mineral recovery to the pulp pH and collector/depressant dosage through micro-flotation tests of the single mineral. The results are shown in Fig. 7. From Fig. 7a, it was seen that pyrite recovery declined with the increasing pulp pH, and when the pH > 9 the downward trend was more pronounced. The generation of metal hydroxide hydrophilic film on the mineral surface in strong alkaline solution, is commonly regarded as the reason of the poor flotability of sulfide mineral (Liu et al., 2019). The recovery of clinochlore rose slightly with the pH increase. With the increase of the SBX dosage, the flotabilities of pyrite and clinochlore were all improved, but it should be noted that the difference in the recovery of the two minerals was small and it was unable to be expanded significantly by increasing the collector dosage. Although some silicate minerals (e.g. serpentine) have been shown to float mainly by entrainment with sulfide minerals, but there's no denying that some silicate minerals with a certain degree of flotability (clinochlore here) can float on their own, in xanthate collector system.

The test results of the effect of YD dosage on the pyrite and clinochlore recovery are displayed in Fig. 7b. The addition of the YD showed some depression on pyrite flotation, and it (150 mg/L) can brought about 15% decrease in pyrite recovery at pH 8.5. While clinochlore recovery reduced quickly with the YD dosage increase to 60 mg/L, and further increasing the dosage of YD had little effect on clinochlore flotation. Compared with the results at pH 6, it was not hard to find that the YD showed more stronger depression on both minerals at pH 8.5. At this pH, with 60 mg/L YD the recovery of clinochlore declined

to 8.47%. This may be due to that at alkaline condition the alcoholic hydroxyl group in YD molecule is more stable; at acid solution, the alcoholic hydroxyl group may form unstable leaving group (Wu et al., 2015).
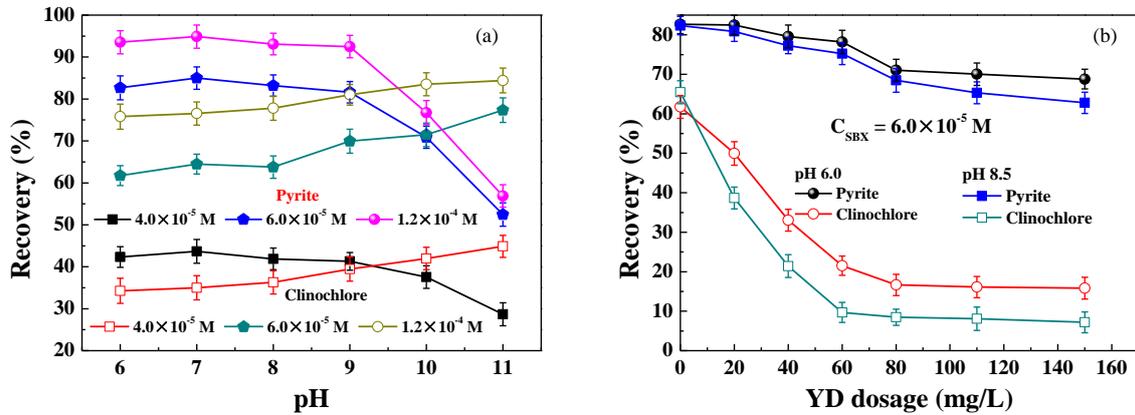

Fig. 7. Effects of (a) pH/SBX dosage, and (b) YD dosage on the flotation behavior of pyrite and clinochlore

3.5. Separation of artificial ore

In single mineral flotation tests, the new depressant YD was investigated its depression performance for clinochlore/pyrite flotation system. The results showed some possibility of using it for the flotation separation of pyrite from clinochlore. Here we further verified this performance through using it in the artificial ore system and comparing the depression effect with the traditional polysaccharide depressant starch (Rath et al., 2020). The results are exhibited in Table 3.

With 40 mg/L starch as the depressant, A concentrate containing 34.26% S was obtained from the artificial ore containing 26.72% S, and the S recovery is 83.67%. The high S recovery but low S grade suggested that the clinochlore had not been inhibited effectively thus entered the concentrate. When the dosage of starch increased to 60 mg/L the grade and recovery of S in the concentrate were 43.56% and 65.87%, respectively. This higher S grade but low S recovery meant that pyrite and clinochlore were suppressed simultaneously, i.e. starch did not exhibit good selectivity for the pyrite/clinochlore system at a higher dosage. With the same dosage (60 mg/L) of YD as the depressant, a concentrate with the flotation indexes of 49.03% S grade and 85.24% S recovery was obtained. The YD depressant showed stronger depression on clinochlore and had lesser negative effect on the flotation of pyrite, i.e. it presented good selectivity for the mineral system, like the single mineral system showed.

Table 3. The flotation results of artificial ore (C, concentrate; T, tailings; F, feed; STDEV, standard deviation)

Depressant	Products	Yield (%)	STDEV(%)	S grade (%)	STDEV(%)	S recovery (%)	STDEV (%)
Starch 40 mg/L	C	65.28	0.84	34.26	0.26	83.67	0.96
	T	34.72	0.97	12.57	0.37	16.33	1.08
	F	100.00	0.00	26.72	0.29	100.00	0.00
Starch 60 mg/L	C	40.42	1.23	43.56	0.31	65.87	1.49
	T	59.58	0.99	15.31	0.28	34.13	2.08
	F	100	0.00	26.72	0.29	100	0.00
YD 60 mg/L	C	46.46	1.08	49.03	0.25	85.24	1.24
	T	53.54	1.15	7.37	0.18	14.76	1.37
	F	100.00	0.00	26.72	0.29	100.00	0.00

Other conditions: Pulp pH: 8.5; SBX dosage: 6×10^{-5} M; MIBC dosage: 1×10^{-4} M

4. Conclusions

(I) For single reagent system, the adsorbed SBX results in the decrease in the surface polarity of two minerals, while YD is opposite; SBX has little adsorption selectivity on the two minerals, while YD is of great selectivity. A mass of pre-adsorbed YD molecules inhibit the further adsorption of SBX on

clinochlore surface, thus keep it hydrophilic and non-flotation.

(II) Chelating adsorption is the most strong coordinate forms of YD monomer and Fe^{2+} ion. The chelation strength of YD monomer with three ions is in the sequence of $Fe^{3+} > Mg^{2+} > Fe^{2+}$, which is the reason of the YD selectivity for pyrite/clinochlore flotation system.

(III) Clinochlore can also float well in xanthate system. Without depressant pyrite and clinochlore cannot be separated by flotation. Yeast dextran (YD) selectively depresses clinochlore in pyrite flotation, laying the foundation of their separation. YD shows better depression performance compared with starch: at optimum conditions, a concentrate of 49.03% S grade and 85.24% S recovery can be obtained.

Acknowledgments

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