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Effect of iodine value of sodium fatty acids on flotation of collophanite

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Abstract: The sodium fatty acids were firstly prepared by fatty acids with different iodine values which were from surfactant extraction using soybean oil fatty acid as raw material in this study. Effects of iodine value of sodium fatty acids on the flotation of collophanite were then investigated by flotation tests, contact angle measurements, adsorption tests, Krafft point measurements, foaming ability tests, and the resistance to the hard water measurements. Results show that the final flotation recovery was directly proportional to the iodine value of sodium fatty acid. Sodium fatty acid with higher iodine value has higher solubility and dispersity in the solutions, and stronger foaming ability and resistance to hard water. After interacting with collophanite, sodium fatty acid with higher iodine value made the mineral more hydrophobic, thus contributing to better flotation performances.

Keywords: flotation, vcollophanite, fatty acid, iodine value

1. Introduction

The phosphate ore has been considered as the basic material for the production of phosphate fertilizers and other chemicals (Chen, 2018; Zafar, 1995). Due to the non-substitutability and non-recyclability during the applications in agriculture, phosphate ores are becoming increasingly valuable (Liu, 2017; Lu,1998). In industry, the phosphate resources mainly come from crystalline fluorapatite (component of igneous rocks) and cryptocrystalline francolite (component of sedimentary rocks) (Hernáinz, F, 2004; Guimarães, 2004). Flotation is the most widely and commercially used method in recovering and concentrating phosphate (Sis, 2003; Liu, 2017).

In phosphate ore flotation, the fatty acids and their derivatives are the main collectors due to their low cost and high recovery efficiency (Sis, 2003; Nanthakumar, 2009). Industrial sodium oleate is one of the most commonly and traditionally used anionic collector. It derives from the vegetable oil. The fatty acids in the vegetable oil is found to be oil-dependent (Hui, 1996). In common vegetable oil, such as soybean oil, corn oil, peanut oil, canola oil, sunflower seed oil, and olive oil, the content of 16 and 18-carbon fatty acids (i.e., palmitic acid (saturated), stearic acid (saturated), oleic acid (monounsaturated, cis), linoleic acid (diunsaturated, cis, cis), linolenic acid (polyunsaturated, cis, cis, cis)) in the oil account for more than 95% (Hui, 1996). The fatty acid molecular curvature, area of cross section, and solubility increase with the increase of unsaturation (Brandao, 1982). Many researches have been done about oxidized minerals flotation using fatty acids with different saturation as collectors, especially in phosphate ores flotation. Brandao et al. (Brandao, 1994) found that under basic pH the linoleic acid was the best collector for apatite, followed by linolenic acid and oleic acid in micro-flotation process. Because of the low solubility of sodium stearate, the apatite would be poorly floated at room temperature. Cao et al. (Cao, 2015) proposed an ideal mixed collector composition for phosphate ores flotation of 54 wt.% oleic acid, 36 wt.% linoleic acid and 10 wt.% linolenic acid by batch flotation tests. For the natural

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vegetable oil, an equivalent recovery could be achieved only when the fatty acid composition of the vegetable oil was similar to that of the ideal mixed collector. Li et al. (Li, 2013) presented that the higher content of linoleic acid and linolenic acid in collectors, the better flotation performance could be achieved in reverse flotation of phosphate ores. However, the stearic acid almost showed no efficiency. Brando et al. found that the efficiency of the 18-carbon fatty acids in magnesite flotation was in the order of elaidic acid > oleic acid > linoleic acid > linolenic acid (Brandao, 1982). The reproducible and comparable results could not be achieved because the solubility of sodium stearic acid was very low at room temperature. The refined tall oil behaved as an intermediate collector, comparing with linoleic acid and oleic acid which were the two main components of the oil.

Based on the above-mentioned findings, it was observed that saturation of fatty acid has significant influences on minerals flotation. As well known, mixed fatty acid with different saturation could be obtained by fatty acid extraction technology. The iodine value generally was applied to present the saturation of fatty acid. In this paper, the fatty acid with different iodine values from soybean oil were prepared by surfactant extraction. The collophanite flotation behaviors using sodium fatty acids with different iodine values as collectors were explored.

Accordingly, the main objectives of this work are to: i) compare the flotation behaviors of collophanite using the sodium fatty acids with different iodine values as collectors, ii) find the mechanisms and regular patterns for the different flotation behaviors by surface and solution chemistry researches, which would provide some suggestions in developing high performance collophanite collectors.

2. Materials and methods

2.1. Materials

The soybean oil fatty acid was purchased from Jiangxi Tianyuan Environmental Protection Co.,Ltd., located in Jiangxi, China. The fatty acid was saponified by NaOH, and the sodium fatty acid was used as collector. Other chemicals were analytical grade, including $MgSO_4$, sodium dodecyl sulfate (SDS), HCl, NaOH. The high-purity deionized water with a resistivity of 18 MΩ was used in all experiments. The pure collophanite was provided by Yunnan Phosphate Chemical Group Co.Ltd, Kunming City, Yunnan Province. The XRD results of the collophanite were shown in Figure 1. The elements analysis results of collophanite were shown in table. 1. The sample was drily grounded in an agate grinder and screened through 74μm sieve, the particle size distribution was shown in Figure 2 (measured by laser particle sizer). The -74μm fraction with a specific surface area 0.5373 m^2/g (measured by BET method), was used for micro-flotation tests, and adsorption tests.

2.2. Methods

2.2.1. The measurement method of the iodine value

The iodine value was measured according to the standard of ISO 3961:1996.

2.2.2. The preparation of fatty acids with different iodine values

100g soybean oil fatty acid was added to 500 mL beaker, heating the fatty acid until all of the fatty acid fused, then cooled the fatty acid to the extraction temperature. Under stirring and extraction temperature, 100 mL SDS (1wt. %) and 50mL $MgSO_4$ (1wt. %) solutions were added to the beaker, then the mixed solution was stirred for 1h. Afterwards, the mixed solution was moved to centrifuge tube for centrifugation at 5000 rpm for 5 min. After centrifugation, the upper oil layer was fatty acid with high iodine value, and the lower layer contained the low iodine value fatty acid and water. Heating the lower layer to 80°C, the low iodine value fatty acid at the upper layer was gotten.

Table 1. Elements analysis result of collophanite

	P_2O_5	MgO	Fe_2O_3	Al_2O_3	SiO_2	K_2O	Na_2O
Content (%)	40.13	0.05	0.12	0.06	0.26	0	0.1

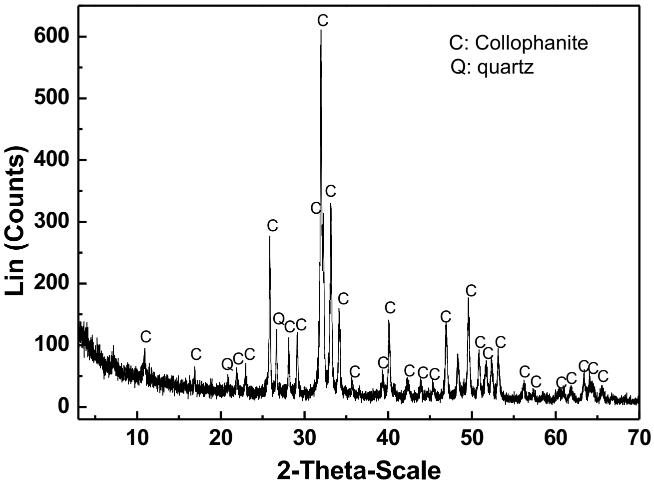

Fig. 1. XRD pattern of collophanite sample

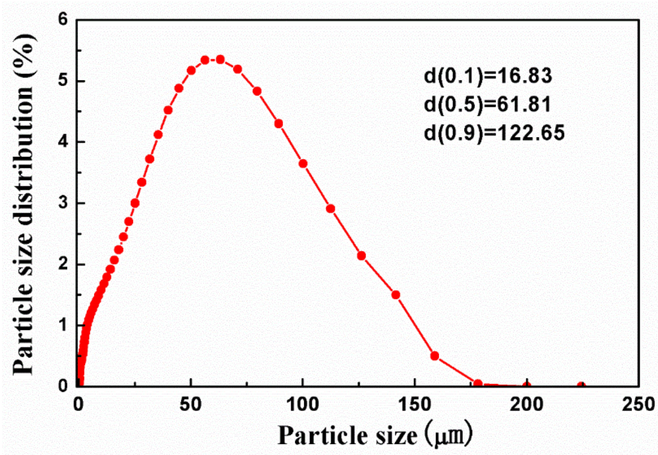

Fig. 2. The particle size distribution of collophanite

2.2.3. Flotation tests

Single mineral flotation tests were carried out in a XFG flotation machine with a 40mL flotation cell at agitating speed of 2500 rpm. 2.0 g collophanite was added to 38 mL water to form the mineral pulp, and NaOH or HCl solution was used to adjust pH value. The sodium fatty acid solution (2 mL, 4×10^{-3} M) was added and agitated for 2 min, then the pH of the pulp was recorded. In this case, the concentration of sodium fatty acid was 2×10^{-4} M. The flotation was conducted for 3 min, and then the flotated and unflotated particles were collected, filtered and dried. The flotation recovery was calculated based on the solid weight distribution of the two products. The flotation machine is shown in Figure 3, and the flotation flowsheet is shown in Figure 4.

Fig. 3. Flotation cell

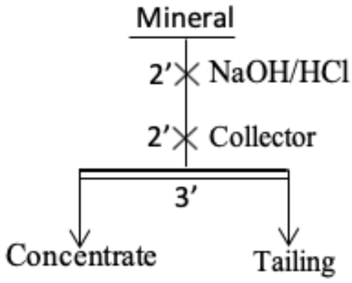

Fig. 4. Flotation flowsheet

2.2.4. Contact angle measurements

The contact angle measurements were conducted by sessile drop method using a Digidrop goniometer (GBX, Isere, France). The collophanite block was embedded in the resin, then the mineral surface was ground by diamond grinding wheels of roughness 100μm, 40μm, 9μm, 1μm to obtain a flat surface. After grinding, the crystal was successively polished with 0.3 and 0.05 μm alumina powder solution on a ''Selected Silk'' polishing cloth. For the measurements of mineral contact angle in the presence of sodium fatty acid, the prepared sample was immersed in the solution with sodium fatty acid for 10 min (the sodium fatty acid concentration is 2×10^{-4} M) at pH 10. Next the surface was washed by deionized water and then air dried. One drop of deionized water (about 3mm diameter) was generated on the collophanite surface by the syringe pump. The profile of the free drop on collophanite surface was monitored by a video camera connected to computer. The images were analyzed for measuring the contact angle.

2.2.5. Adsorption density measurements

According to the flotation test procedures, the different sodium fatty acid was added into the pulp. After 6 min stirring, the mineral suspension was centrifuged at 9000rpm for 15 min. The supernatant in the centrifugation tube was pipetted out for concentration determination of the sodium fatty acid by SHIMADZU TOC-L total carbon analyzer.

2.2.6. The krafft point measurements

40 mL, 15g/L sodium fatty acid solution was transferred to 50 mL colorimetric tube with stopper. Then the colorimetric tube was immersed in the constant temperature water tank. After the water temperature increased 1°C, the temperature was kept for 1h. The krafft point temperature was recorded when the solution was clear and transparent.

2.2.7. potentiometric titration

40 mL sodium fatty acid solution (2×10^{-4} mol/L) was prepared, and the solution pH was adjusted to 10 by NaOH. The Ca^{2+} electrode was selected for measuring the saltation of reaction potential, and the $CaCl_2$ solution was used as titration standard solution. The reaction end point was measured by potentiometric titration using 905 titrando potentiometric titrator.

3. Results and discussions

3.1. The preparation of fatty acids with different iodine values

Fatty acids with different iodine values were prepared by surfactant extraction at extraction temperature of 12°C, 20°C, 30°C respectively. The results were shown in table 2. It was observed that fatty acids with different iodine values were prepared by surfactant extraction using the soybean oil fatty acid (iodine value = 125 gI/100g) as raw material. Under the different extraction temperature, 6 kinds of fatty acids with different iodine values were prepared. The iodine values of the above fatty acid were 163 gI/100g, 152 gI/100g, 136 gI/100g, 84 gI/100g, 55 gI/100g, 18 gI/100g respectively. With the increase of extraction temperature, the iodine value of fatty acid with high iodine value and low iodine value decreased, and the yield of fatty acid with high iodine value increased, the yield of fatty acids with low iodine value decreased

Table 2. Surfactant extraction results

Extraction temperature (°C)	Yield of high iodine value fatty acid (%)	the iodine value of high iodine value fatty acid (gI/100g)	Yield of low iodine value fatty acid (%)	the iodine value of low iodine value fatty acid (gI/100g)
12	51.90	163	48.10	84
20	72.16	152	17.84	55
30	90.68	136	9.32	18

3.2. Effect of iodine value of sodium fatty acid on the flotation of collophanite

Figure 5 presents the comparative flotation results of collophanite using sodium fatty acid with different iodine values as collector. As shown in Figure 5, the recovery of collophanite was highly dependent on the pH value and the iodine value of sodium fatty acid. Little collophanite could be floated in acidic pH. When pH increased from 7 to 10, the flotation recovery increased sharply, above pH 10, the flotation recovery keep constant using the four sodium fatty acid with higher iodine value. But the collophanite could not be floated effectively using the two sodium fatty acid with lower the iodine value at selected pH range. The flotation performance order of the 6 kinds of collector is as following when pH>7: iodine value = 163 sodium fatty acid > iodine value = 152 sodium fatty acid > iodine value = 125 sodium fatty acid (raw material) > iodine value = 84 sodium fatty acid > iodine value = 52 sodium fatty acid > iodine value =18 sodium fatty acid.

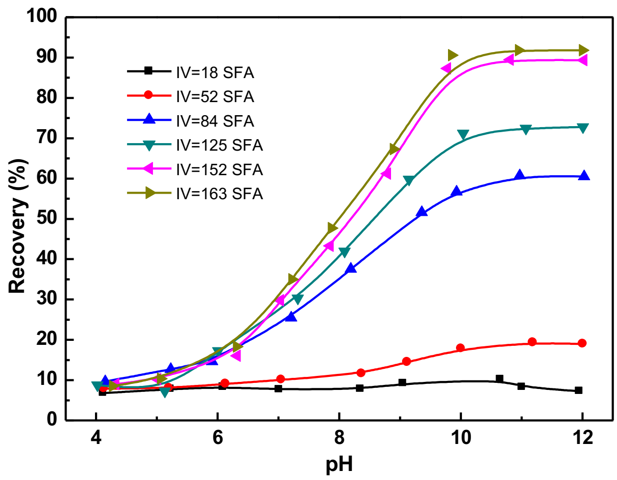

Fig. 5. Recovery of collophanite using different sodium fatty acids as collectors at different pH, $C_{\text{sodium fatty acid}}=2\times10^{-4}$ M, 25°C

3.3. Effect of iodine value of sodium fatty acid on the contact angle of collophanite

Because of the extraction yield of the iodine value =163 gI/100g sodium fatty acid was much lower than that of the iodine value =152 gI/100g sodium fatty acid, and the flotation recovery was very close using the two sodium fatty acid as collector respectively, only the researches about the iodine value =152, 125, 84, 52, 18 gI/100g sodium fatty acid were done respectively in the next researches. The contact angle measurement experiment results were shown in figure 6. As shown in figure 6, after the collophanite reacted with the different sodium fatty acids, the final contact angle values of mineral increased apparently with the iodine value increase of sodium fatty acid. Contact angle value is a good indicator of mineral hydrophobicity, which suggests the sodium fatty acid with higher iodine value shall result in better flotation performance. The results shown in Fig.6 are consistent with that in section 3.2.

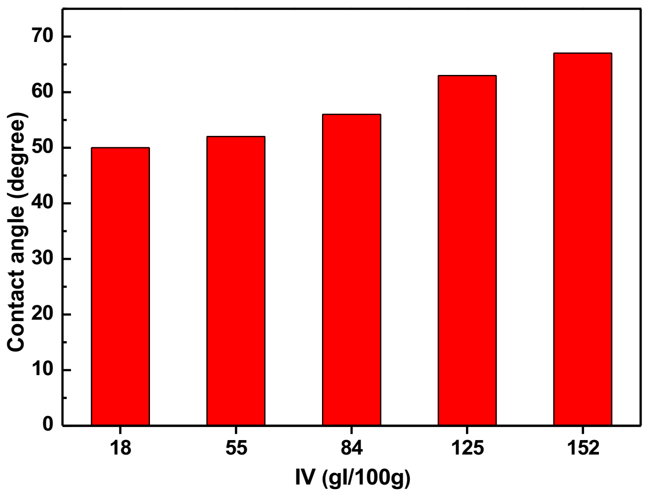

Fig. 6. Contact angle of collophanite after reacting with different sodium fatty acids, $C_{\text{sodium fatty acid}}=2\times10^{-4}$ M, pH=10, 25℃

3.4. Effect of iodine value on the adsorption density of sodium fatty acid

To further reveal the flotation phenomena, the adsorption density of the five sodium fatty acids on collophanite surface was also investigated respectively. Figure 7 shows the adsorption density of the five sodium fatty acid at 25℃. It was observed that the adsorption density increased with the iodine value increase of sodium fatty acid. Higher collector adsorption benefits higher flotation recovery. The results of adsorption density measurements confirm that sodium fatty acid with high iodine value are more helpful in achieving improved flotation performance.

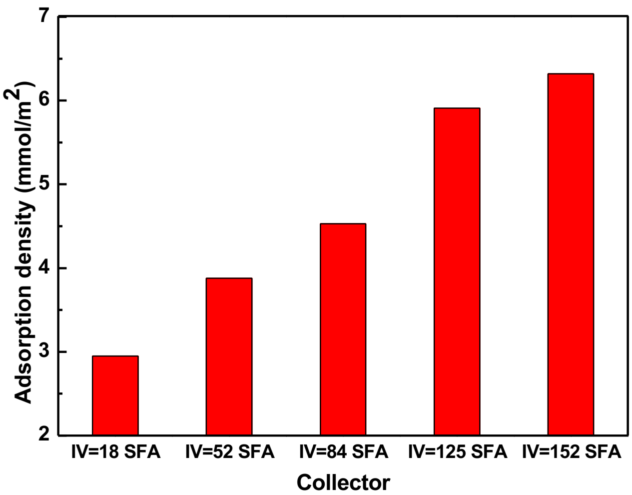

Fig. 7. Adsorption density of different sodium fatty acid on collophanite surface, pH=10, $C_{\text{sodium fatty acid}}=2\times10^{-4}$ M, 25℃

3.5. The effect of iodine value on krafft point of sodium fatty acid

The Krafft point is a critical indicator of anion surfactant, which is associated with solubility and dispersity of surfactant (Fekarcha, 2012). The krafft point measurement results were shown in table 3. It was observed that the Krafft point of sodium fatty acid decreased with the increase of the iodine value, indicating that the sodium fatty acid with higher krafft point had the higher solubility and dispersity. And the sodium fatty acid with higher iodine value was easy to interact with collophanite which promoted the higher flotation recovery.

Table. 3. The effect of the iodine value on the Krafft point of sodium fatty acid

Iodine value of sodium fatty acid(gI/100g)	18	52	84	125	152
Krafft point(℃)	62	56	49	34	22

3.6. Effect of iodine value on foaming ability of sodium fatty acid

When sodium fatty acid is used as collector, generally it works as both collector and frother (Atrafi, 2012). So the foaming ability of sodium atty acid is also critical to the final flotation performance. The foaming ability of sodium fatty acid was measured in accordance with the method of reference (Gu, 2013). The measurement results were show in figure 8. As shown in figure 8, the foaming ability of sodium fatty acid increased with the increase of the iodine value, that was to say, the maximum foam height and the foam half-life time of the sodium fatty acid were directly proportional to its iodine value. The sodium fatty acid with higher iodine value had better solubility and dispersity which promoted the rapidly dispersity of the sodium fatty acid on gas-liquid interface. The rapid dispersion of sodium fatty acid with higher iodine value on the gas-liquid interfacial could induce the decrease of interfacial tension and keep the liquid film thickness of foam which made the sodium fatty acid with higher iodine value has stronger foaming ability. Meanwhile, the stronger foaming ability of sodium fatty acid with higher iodine value also promoted its outstanding flotation performance.

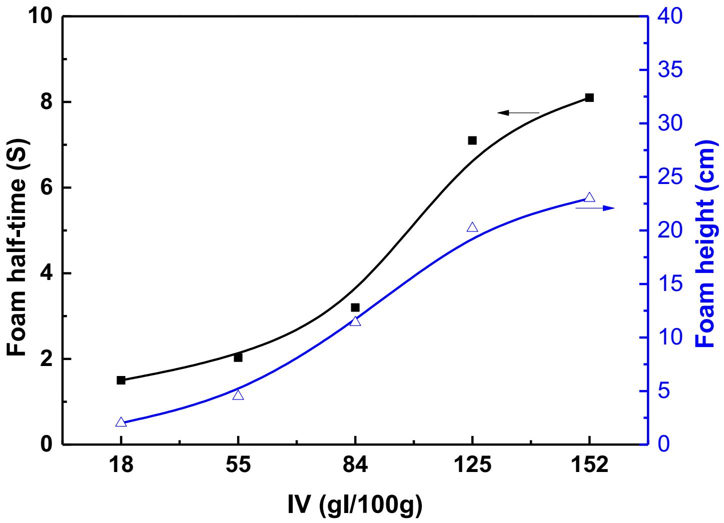

Fig. 8. The foaming ability of different sodium fatty acids, pH=10, C $_{\text{sodium fatty acid}}$=2×10^{-4} M, 25℃

3.7. Effect of iodine value on the resistance to hard water of sodium fatty acid

It's well known that some polyvalent metal ions (e.g., Ca^{2+}, Mg^{2+}) deteriorate flotation by reacting with collectors, and led to the excessive consumption of collector and poor selectivity of flotation (Ejtemaei, 2012; Dos santos, 2010). Therefore, the resistance to hard water is an important index for evaluating collector performance.

Table 4 shows the potentiometric titration reaction ratio of sodium fatty acid using $CaCl_2$ solution as standard solution. It was observed that the reaction ratio of sodium fatty acid decreased with the increase of the iodine value. The phenomenon suggested that more calcium fatty acids generated in sodium fatty acid solution with lower iodine value. In other words, the resistance to hard water of sodium fatty acid with higher iodine value was better than that of low iodine value sodium fatty acid, which played an important role in enhancing the flotation of the collophanite as shown in figure 5.

Table. 4. Resistance to hard water of different sodium fatty acids（$C_{Ca^{2+}}=8\times10^{-3}$ M）

Iodine value of sodium fatty acid (gI/100g)	$C_{sodium\ fatty\ acid}$ （M）	End point $V_{Ca^{2+}}$ （mL）	Reaction ratio of sodium fatty acid （%）
152	2*10-4	0.3117	62.35
125	2*10-4	0.3523	70.46
84	2*10-4	0.4136	82.72
52	2*10-4	0.4673	93.46
18	2*10-4	0.4819	96.38

4. Conclusions

The fatty acids with different iodine values had been prepared successfully by surfactant extraction using soybean oil fatty acids as raw materials. Then, the flotation of collophanite using the sodium fatty acids with different iodine values as collectors were investigated. Results shown that sodium fatty acid with higher iodine value contributes to better flotation performance. The sodium fatty acid with higher iodine value could enhance the surface hydrophobicity of collophanite more effectively, and had better solubility and dispersity, as well as stronger foaming ability and resistance to hard water, which might be the main contributing reasons for the improved flotation performance.

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