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Sodium N-Lauroylsarcosinate (SNLS) as a Selective Collector for Calcareous Phosphate Beneficiation

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Abstract: Sodium N-lauroylsarcosinate (SNLS) was employed as a selective flotation collector for dolomite–apatite separation. The influence of pH, condition time, and collector dose on the flotation performance of both apatite and dolomite minerals was investigated using single mineral and binary mixed mineral flotation experiments. The performance of SNLS was compared to sodium oleate (NaOL), as a standard collector. In this study, the adsorption mechanism of SNLS on both minerals was studied using zeta-potential and FT-IR measurements. The results showed that SNLS prefers to adsorb on the dolomite mineral. The maximum difference in floatability was 83% for single dolomite and apatite minerals at pH 10 in the presence of 0.05 mmol/L SNLS. Binary mixtures of dolomite and apatite minerals of different ratios were applied, to evaluate their separation efficiency. The SNLS could separate dolomite from its mixtures with apatite minerals. Using 0.2 mmol/L of SNLS at pH 10, a concentrate of 30.9% P_2O_5 and 0.79% MgO was obtained from a natural phosphate ore having 25.8% P_2O_5 and 5.16% MgO.

Keywords: apatite; dolomite; SNLS collector; flotation; selective adsorption

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1. Introduction

Phosphorous is one of the most common elements on Earth and is the main component of plants, making it one of the most important industrial raw materials [1,2]. It is utilized in a variety of industrial applications, such as fertilizers, detergents, pharmaceuticals, effluents, and cement. It is found in the Earth's crust as a valuable mineral, in the form of apatite. Apatite is a naturally occurring mineral in phosphate deposits, such as fluorapatite, and is accompanied by gangue minerals such as dolomite, calcite, and silicate [3,4]. Fluorapatite is more abundant in igneous phosphate deposits in crystalline form than in nature. It contains a variety of phosphate minerals, including hydroxyapatite and chlorapatite, which are rare in nature. Its structure always results from the transformation of existing sedimentary phosphate rocks under different ionic substitutions. Sedimentary phosphates have great industrial importance, since they account for the majority of world phosphorus production [5–7].

Carbonates are typically connected with the apatite structure. Dolomite mineral ($CaMg(CO_3)_2$) is the most common gangue mineral and the most troublesome impurity in phosphate ores [8]. The presence of dolomite is linked to apatite. Several problems arise during the manufacture of phosphoric acids; such as using too much sulfuric acid, and decreasing filtration capacity by raising viscosity. In addition, it reduces the quality of concentrates of phosphate products. The latter reduces the filtration rate, so it is vital to remove it from the phosphate concentrate [9]. Although froth flotation is one of the most commonly used approaches to this problem, it has limitations, due to the comparable surface behavior of dolomite and apatite minerals. Dolomite is difficult to separate. As a result, it has played a vital role in the development of reagents. This is regarded as the most crucial part of achieving an optimum separation and efficiency throughout the flotation process [10].

Fatty acids such as sodium oleate (NaOL) have been used as collectors for flotation separation of apatite from carbonate minerals, because of their low cost and poor selectivity. The chemisorption mechanism of using fatty acids to separate dolomite-bearing phosphate has been revealed. However, it is difficult to use only a fatty acid in the separation process, due to the similarity of surface properties between the two minerals, so it is necessary to develop novel flotation reagents to achieve economic recovery and improve the efficiency of low-grade phosphate ore via reverse flotation [11]. Although, fatty acid is used as a collector, depressants have been widely used to improve the separation of dolomite from apatite mineral, and sodium pyrophosphate (NaPP) has been used as a depressant in separating apatite from dolomite through reverse flotation. This may promote the selective separation of apatite from dolomite by preventing the adsorption of NaOL onto the apatite surface and also improving NaOL reactivity on the dolomite surface [12]. Conventional depressants such as sulfuric acid, phosphoric acid, cellulose enzyme, and b-naphthyl sulfonate formaldehyde condensate have been used to separate apatite from dolomite [13,14]. They have a number of drawbacks, including a negative environmental effect, a large dosage, low selectivity, high toxicity, and a high price.

As a result, a new depressant has been developed that is both effective and safe for the environment. Acrylic acid-2-acrylamide-2-methylpropane sulfonic acid copolymer [P (AA-AMPS)] has a strong interaction with magnesium ions on the dolomite surface, which reduces the NaOL adsorption on the dolomite surface, while the NaOL can still be significantly adsorbed on the apatite surface [15]. Furthermore, all previous studies revealed that [P (AA-AMPS)] is a critical part in the selective adsorption of dolomite rather than apatite and, thus, a strong dolomite depressant. There is a stronger interaction of [P (AA-AMPS)] with magnesium sites than with calcium sites. Thus, it is considered an eco-friendly and strong depressant for dolomite. Due to its limited ability to aggregate and low separation efficiency [15,16], in recent years, many studies have been conducted to improve the separation efficiency of apatite from carbonate minerals; and it has been reported that sodium dodecyl benzene sulfonate (SDBS) has a significant collector impact on apatite flotation, but has no effect on dolomite adsorption characteristics. SDBS was discovered to interact with Ca active sites on the apatite surface through chemical bonding. SDBS was used as a collector, to separate dolomite from apatite. Sodium N-lauroylsarcosinate (SNLS) is a carboxyl and amide-based amino acid surfactant with strong reactivity, good biodegradability, and safe application in biomedicine, electro-plating, dyeing, agriculture, and environment-friendly and low-cost applications. The goal of this research was to evaluate the role of the SNLS as a novel collector for efficiently separating dolomite and apatite minerals from phosphate ores. Furthermore, to enhance separation, pH and condition time were investigated.

2. Materials and Methods

2.1. Materials

The Egyptian Mineral Resources Authority (EMRA) contributed two samples of high-purity apatite and dolomite minerals. The sample was ground to less than 0.105 mm. Desliming was used to remove fine fractions (−0.075 mm). NaOL and SNLS (Figure 1), with a purity of over 95%, were supplied by Shanghai Macklin Biochemical Co., Ltd, Shanghai, China. All other chemicals, such as NaOH or HCl from Sigma-Aldrich (Burlington, MA, USA), were of analytical grade and were used to make 0.1 M solutions or served as pH regulators.

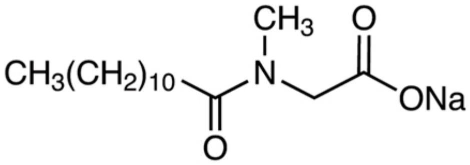

Figure 1. Chemical structure of sodium N-lauroylsarcosinate (SNLS).

2.2. Experimental Techniques

2.2.1. Chemical Composition and X-ray Diffraction

X-ray diffraction (XRD) was used to detect the mineral phases on a Philips (Andover, MA, USA) type 1710 XRD unit with Ni filter Cu radiation (K = 1.5446) at 40 kV and 20 mA at a scan rate of one theta degree per minute. X-ray fluorescence (Rigakusuper Mini 200, Rigaku, Akishima, Japan) was used to determine the chemical analysis of the apatite and dolomite rocks. Using Fluxana PR-25N (Fluxana, Bedburg-Hau, Germany), the mixture was pressed into a pellet at a pressure of 15 ton/cm^3 for 25 s.

2.2.2. Zeta-Potential Measurements

The zeta-potential was determined using a laser Zeta Meter Malvern Instruments Model Zeta Seizer Nano ZS (Malvern, Paoli, PA, USA). Then, 0.05 g of the sample was added to 50 mL 2×10^{-2} M KCl solution and interacted with the known collector concentration, after which it was conditioned for 5 min at room temperature to the required pH. The measurements of each test were repeated at least three times as a function of pH and the zeta potential was calculated.

2.2.3. FT-IR Measurements

The solid samples were filtered, air dried, and the FT-IR spectra were taken after contact with the collector. The spectra were obtained of KBr pellets prepared with a solid sample and analytical grade KBr from Merck. The FT-IR investigation was carried out using a Perkin Elmer Spectrum 2000 spectrometer. The spectrum was recorded in the wave number range from 400 to 4000 cm^{-1}.

2.2.4. Flotation Experiments

In a bench-scale flotation experiment, a 100 mL flotation column was used. One gram of mineral was prepared at different specific pH, collector concentrations, and interaction times. At a rate of 0.65 cm^3/min of air, flotation was performed for 5 min. The sink and floating fractions were weighed after being collected and dried. To evaluate apatite grade and determine recovery, the concentrate and tailing were weighed and subjected to binary mixed mineral tests. Each experiment was carried out three times, and the average and standard deviation of each grade and recovery were calculated.

3. Results and Discussion

3.1. Characterization of Pure Minerals and Natural Ore

The chemical analysis of the apatite mineral in Table 1 showed that it is composed of 56.97% CaO, 34.58% P_2O_5, 4.50% CO_2, and 3.90% F. The dolomite mineral contains 30.37% CaO, 21.69% MgO, and 47.85% CO_2. The natural phosphate ore is mainly composed of apatite and dolomite. It is composed of 50.36% CaO, 25.41% P_2O_5, 15.38% CO_2, 5.48% MgO, and 2.92% F. The impurities such as silica and iron are less than 0.4%. The X-ray diffraction pattern of each mineral contains only its characteristic peaks, without significant peaks from impurities (Figure 2). On the other hand, the pattern of phosphate ore contains only the characteristic peaks of dolomite and apatite minerals.

Table 1. Chemical composition of the pure minerals and natural phosphate ore.

Item	Weight %		
	Dolomite	**Apatite**	**Natural Ore**
P_2O_5	0.002	34.58	25.41
CaO	30.37	56.97	50.36
MgO	21.69	0.005	5.48
Fe_2O_3	0.016	0.001	0.013
SiO_2	0.012	0.003	0.378
Al_2O_3	0.028	0.016	0.026
K_2O	0.016	0.012	0.013
Na_2O	0.015	0.018	0.021
CO_2	47.85	4.498	15.38
F	0.001	3.897	2.92
Total	100	100	100

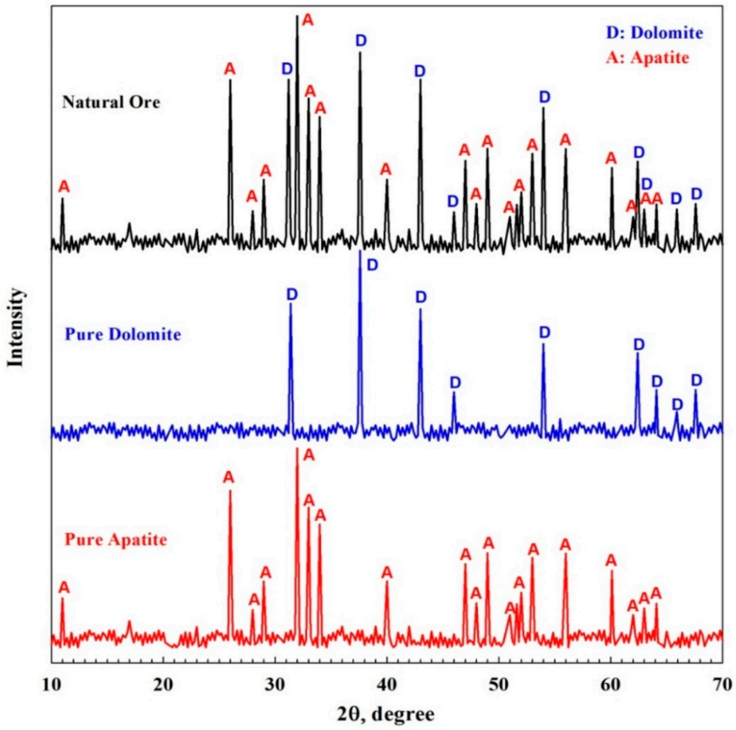

Figure 2. X-ray diffraction patterns of natural phosphate rock ore and pure minerals.

The chemical analysis of apatite mineral, which has a chemical formula [Ca_5 $(PO_4)_3(OH,F,Cl)$], confirmed its high purity as a pure phosphate mineral and matched the theoretical composition. The dolomite composition [$CaMg(CO_3)_2$] confirmed its high purity. The XRD and chemical analysis showed that the phosphate ore was mainly composed of apatite and dolomite.

3.2. Flotation of Single Minerals with NSLS or NaOL

Single mineral flotation tests using single mineral and binary mixed minerals were performed, to evaluate the effects of pH, condition time, and collector dosage on the flotation behavior of apatite and dolomite minerals. SNLS or NaOL was used as a collector, and the flotation test results of a single mineral are shown in Figures 3–8 for pH, collector dosage, and conditioning time.

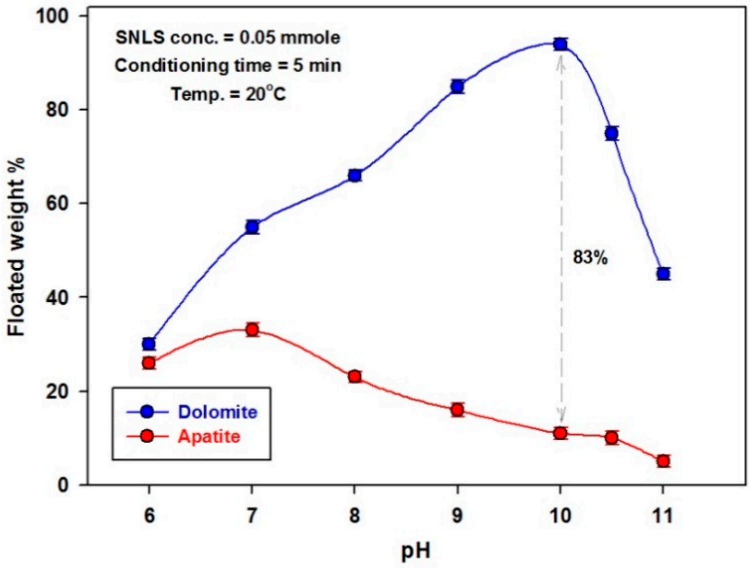

Figure 3. Effects of pH on the floatability of single minerals in the presence of SNLS.

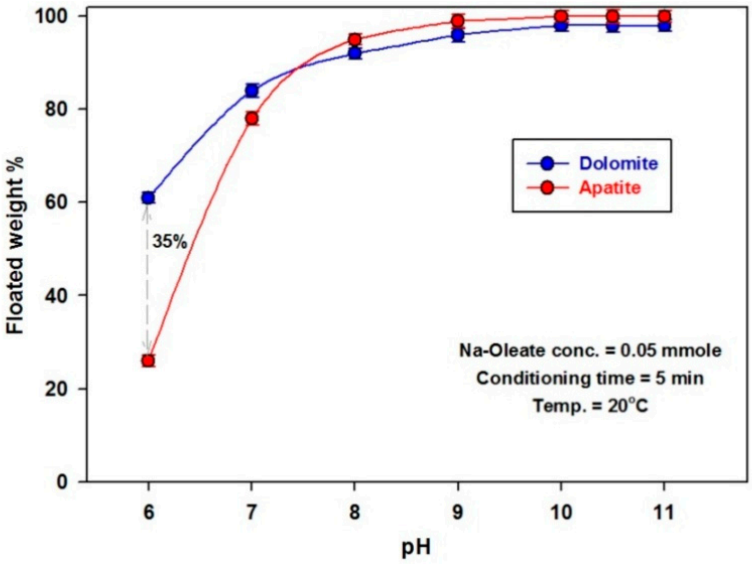

Figure 4. Effects of pH on the floatability of single minerals in the presence of NaOL.

3.2.1. Effect of pH

Figure 3 shows that increasing the pH from 6 to 10 improved the flotation of dolomite mineral in the presence of 0.05 mmol/L SNLS, and then declined. The floatability of apatite minerals increased until pH 7, after which it decreased. The maximum floatability difference (83%) was achieved at pH 10. In comparison, with NaOL as a collector in the same pH range, the difference in recovery never exceeded 35%, as depicted in Figure 4, which strongly indicates that SNLS has a higher selectivity than the commonly used NaOL for flotation of dolomite mineral from apatite mineral. Therefore, pH 10 was chosen for the subsequent tests.

3.2.2. Effect of Collector Dose

Figures 5 and 6 demonstrate that increasing the SNLS or NaOL dose improved the recovery of dolomite and apatite minerals. However, when using SNLS as a collector, the difference in flotation recoveries between the two minerals was roughly 83%, and when using NaOL as a collector, it was about 37%.

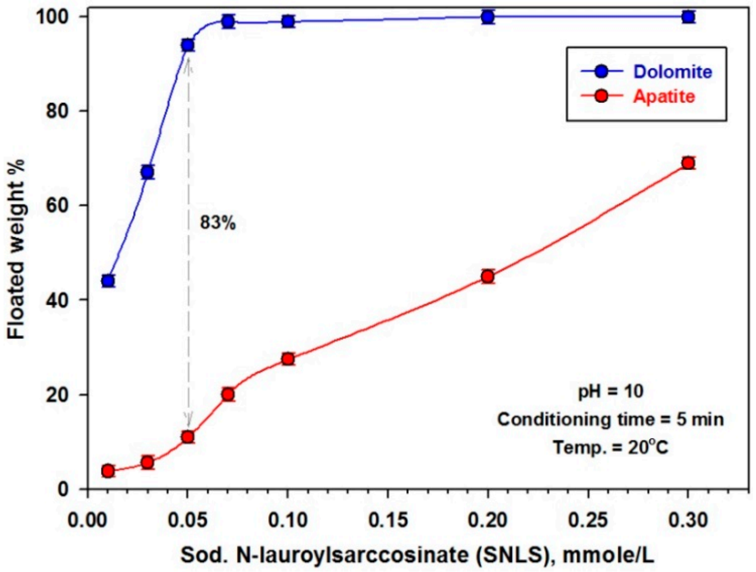

Figure 5. Effects of SNLS concentration on the floatability of single minerals.

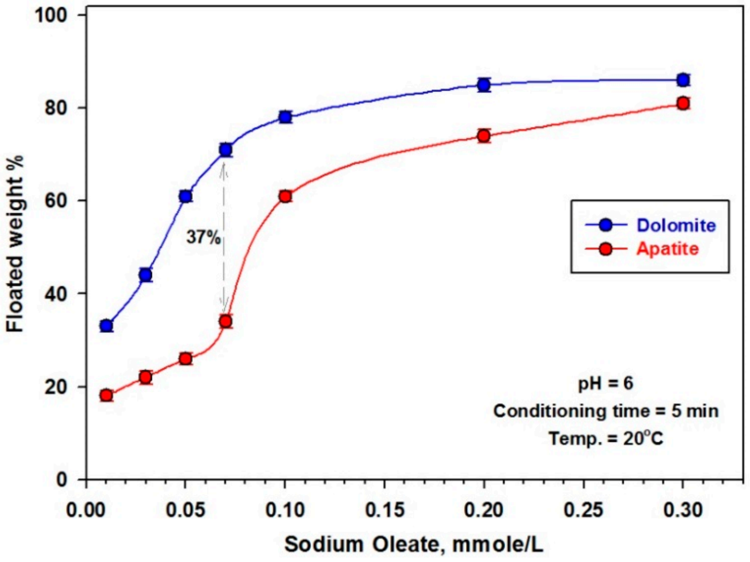

Figure 6. Effects of NaOL concentration on the floatability of single minerals.

3.2.3. Effect of Conditioning Time

Figures 7 and 8 indicate that increasing the conditioning time improved the recovery of dolomite mineral substantially up to 5 min, after which it became nearly constant in the presence of SNLS or NaOL. While increasing the conditioning time increased the recovery of apatite mineral up to 10 min, in the presence of SNLS or NaOL, it was only minimally increased. This finding suggests that the optimum separation of dolomite from apatite was achieved by conditioning the minerals with 0.05 mmol/L SNLS for 5 min at pH 10.

3.3. Flotation of Different Binary Mixed Minerals

Binary mixed mineral flotation experiments were performed in a flotation column, to simulate the actual mineral flotation process. The flotation test results are presented in Table 2 for binary mixed minerals with an SNLS dosage of 0.05 mmol/L at pH 10. As the apatite content increased from 50 to 75%, the recovery of apatite increased from 85 to 95%, and furthermore, the content of P_2O_5 rose from 17 to 30%. The dosage effect of SNLS as a collector at the same pH was also evaluated, to discover the effect of degree of concentration of different binary mixed minerals. This was also conducted to simulate the different compositions of phosphate ores.

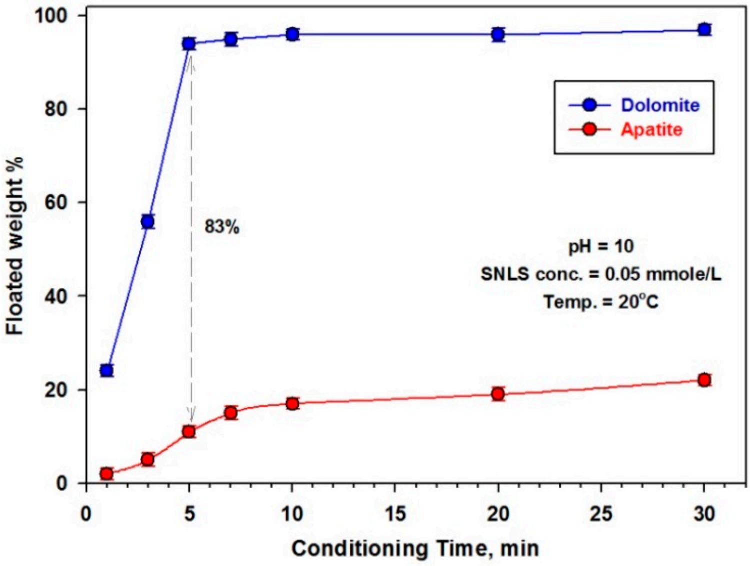

Figure 7. Effects of conditioning time on the floatability of single minerals in the presence of SNLS.

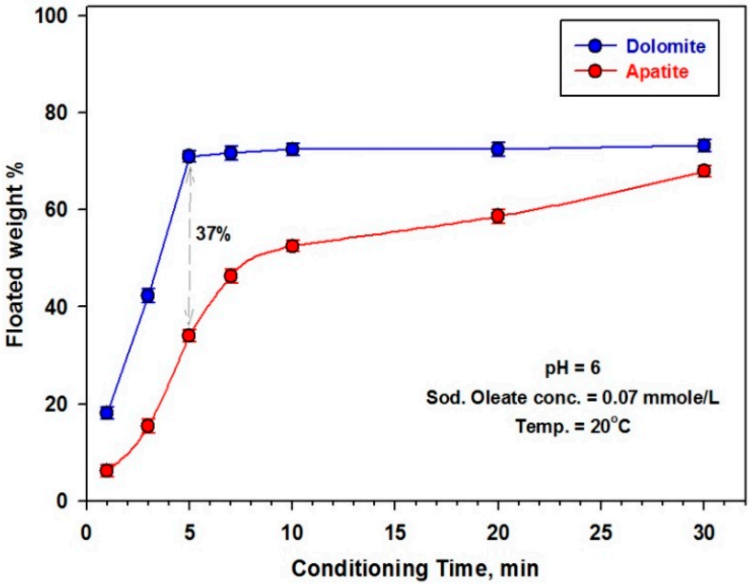

Figure 8. Effects of conditioning time on the floatability of single minerals in the presence of NaOL.

Table 2. Flotation of binary mixed minerals of different ratios, using 0.05 mmol/L at pH 10.

Mix	Feed (Mixture)				Concentrate			
	Weight (g)		%		Weight %		%	
	Apatite	Dolomite	P_2O_5	MgO	Float	Sink	Rec.	P_2O_5
1	1.0	1.0	16.5	10.8	16	84	85.5	16.8
2	1.2	0.8	19.8	8.7	26	74	88.2	23.6
3	1.5	0.5	24.7	5.4	21	79	95.6	29.9

Flotation of a binary mixture containing 50% apatite (16.5% P_2O_5 and 10.8% MgO). Figure 9 shows that as the SNLS dosage increased from 0.001 to 0.05 mmol/L, the apatite recovery of the concentrate decreased gradually, from 100 to 85.5%, but increased to 89.2%

with 0.2 mmol. When the SNLS dosage was increased from 0.001 to 0.2 mmol/L, the grade of apatite increased from 16.5 to 22.3%, while the MgO concentration decreased from 10.8 to 5.2%.

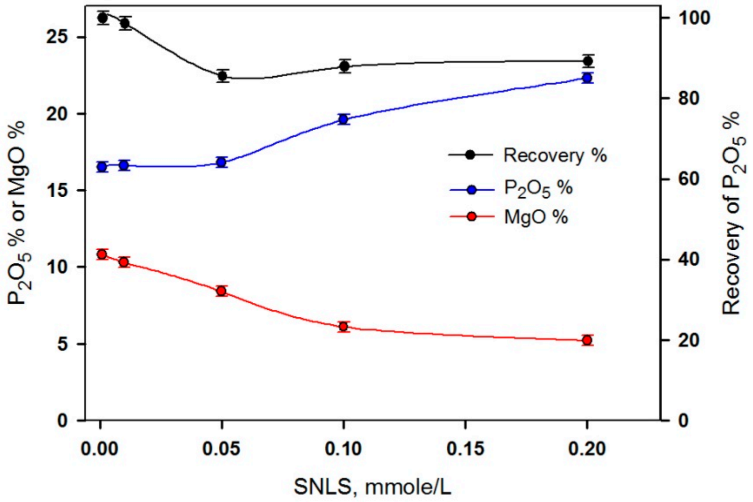

Figure 9. Effects of SNLS dose at pH 10 on P_2O_5% recovery and grade and the MgO content of the concentrate of binary mixed minerals (1.0/1.0).

A binary mixture containing 60% apatite (19.8% P_2O_5 and 10.8%% MgO) was floated. Figure 10 shows that as the SNLS dosage increased from 0.001 to 0.05 mmol/L, the recovery of apatite decreased gradually from 99.4 to 88.2%, while it increased to 92.8% with 0.2 mmol/L. The grade of apatite increased from 20.5 to 28.7% when increasing the SNLS dosage from 0.001 up to 0.2 mmol/L and the MgO content reduced from 8.3 to 2.5%.

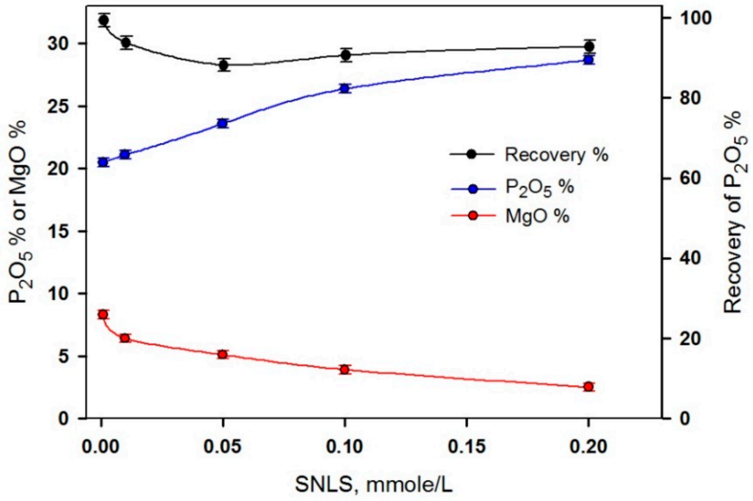

Figure 10. Effects of SNLS dose at pH 10 on P_2O_5% recovery and grade and MgO content of the concentrate of binary mixed minerals (1.2/0.8).

For a binary mixture containing 75% apatite (24.7% P_2O_5) in Figure 11, as the SNLS dosage increased from 0.05 mmol/L, the recovery increased from 93.5 to 95.6%, whereas it decreased to 79.8% with 0.2 mmol/L. The P_2O_5% increased from about 25 to 31.8% when increasing the SNLS dosage, whereas the MgO% reduced from 4.7 to 0.7%.

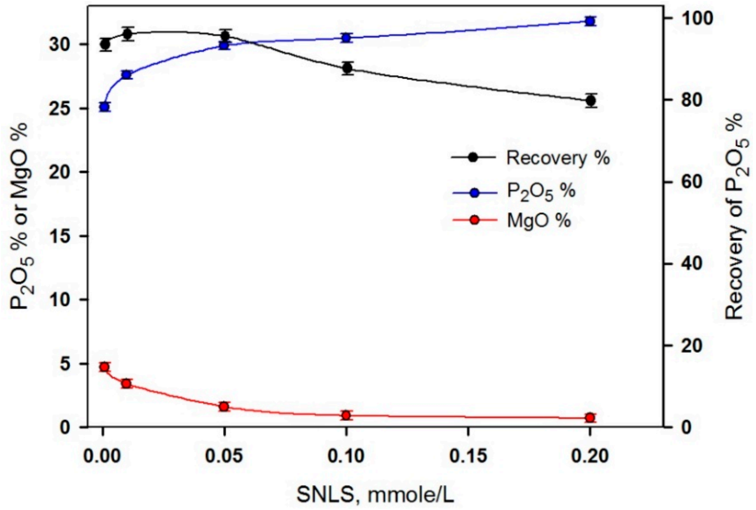

Figure 11. Effects of SNLS dose at pH 10 on P_2O_5% recovery and grade and MgO content of the concentrate of binary mixed minerals (1.5/0.5).

3.4. Application of the Natural Phosphate Ore

Table 3 shows that as the SNLS dosage was increased, the recovery decreased from 97.5 to 81.5%, while the MgO content decreased from 5.16 to 0.79%. The P_2O_5 content, on the other hand, rose from 25.8% to almost 31%. These findings suggest that even at low dosages of 0.05–0.2 mmol/L, the new collector SNLS has a high selectivity for dolomite over apatite.

Table 3. Results of natural phosphate ore flotation.

SNLS (mmol/L)	**Concentrate**			
	Weight %	**Rec. %**	**P_2O_5 %**	**MgO %**
0.001	96	97.5	25.8	5.16
0.010	83	90.2	27.6	3.24
0.050	77	87.0	28.7	1.56
0.100	74	85.9	29.5	0.89
0.200	67	81.5	30.9	0.79
Head	100	100	25.4	5.48

3.5. Surface Behavior of Treated Mineral

3.5.1. Zeta-potential Measurements

The zeta potential measurements of apatite and dolomite were studied with varied pH values, to determine the underlying chemical interaction between reagent and mineral, in order to understand the adsorption behavior of SNLS. The results of zeta potential are shown in Figure 12. The zeta potentials of apatite are positive within the pH range of 3–5.2, but negative at pH values higher than 5.2. The addition of SNLS causes a slight positive shift in the zeta potential of apatite in the pH range of 3–11, as well as a slight shift in the point of zero charges from 5.2 to 5.3, indicating a weak interaction between SNLS and the apatite surface [17,18].

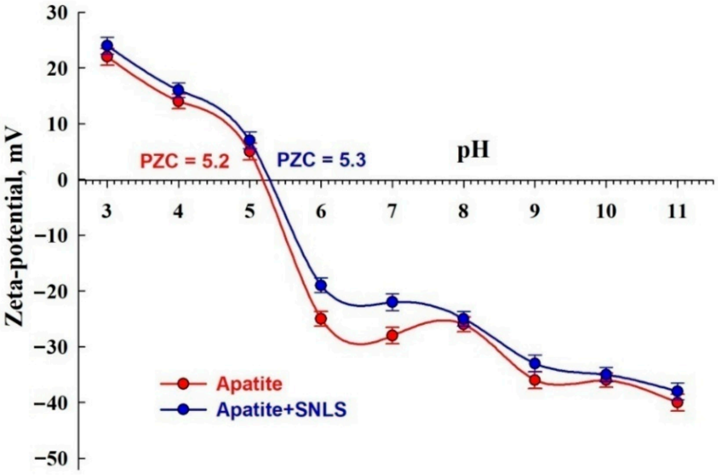

Figure 12. Zeta potential of apatite before and after treatment with SNLS as a function of pH.

The decrease in the zeta potential of dolomite was significant when SNLS was added in the pH range of 7–10, indicating a strong interaction between SNLS and the dolomite surface (Figure 13). The zeta potential of apatite remained nearly unaltered (1 mV) after SNLS treatment at pH 10, meanwhile the zeta potential of dolomite reduced by 13 mV and the point of zero charge changed from 6.2 to 5.5. These results indicate a stronger adsorption of SNLS on dolomite than that on apatite and agree well with the flotation results.

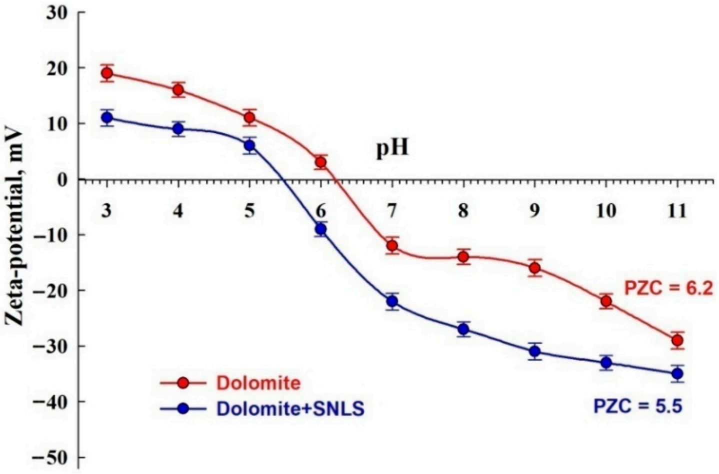

Figure 13. Zeta potential of dolomite before and after treatment with SNLS as a function of pH.

3.5.2. FT-IR Measurements

FT-IR measurements were performed on dolomite and apatite minerals before and after conditioning with the SNLS collector at pH 10, to detect the SNLS functional group responsible for the adsorption process.

Carbonate was demonstrated by strong absorption bands between 3050 and 2850 cm^{-1}, 2650 and 2500 cm^{-1}, 1790 and 1820 cm^{-1}, 1400 and 1500 cm^{-1}, and 877, 730, and 710 cm^{-1}. The presence of these bands in the sample verified the existence of dolomite, which exhibits distinctive FT-IR absorptions at 3021, 2869, 2547, 1435, and 730 cm^{-1}. FT-IR bands were detected at 3021, 2869, 2547, and 1435 cm^{-1} with a combination of frequencies, and the band of 730 cm^{-1} was assigned to the in-plane bending (v4) mode of CO_3 in the dolomite structure [19]. The presence of absorption bands at both 2547 and 730 cm^{-1} in a sample is especially useful for indicating the presence of dolomite (Figure 14).

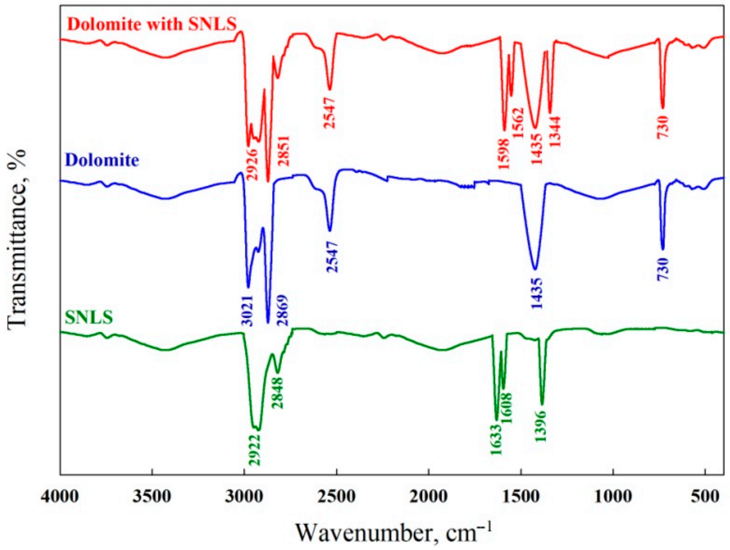

Figure 14. FT-IR spectra of dolomite and SNLS, as well as their interaction.

As shown in Figure 15, apatite has various bands in its spectrum. PO_4^{3-} is responsible for the highest peak, at 1046 cm^{-1}. P–O mode is assigned to the peaks at 792 and 606 cm^{-1}, and the v2 phosphate mode produces a 469 cm^{-1} band. There were further bands at 875, 1425, and 1646 cm^{-1} related to CO_3^{2-} ions. The stretching vibrations of adsorbed water molecules were responsible for the IR peaks at 2915 and 3436 cm^{-1} [20–25].

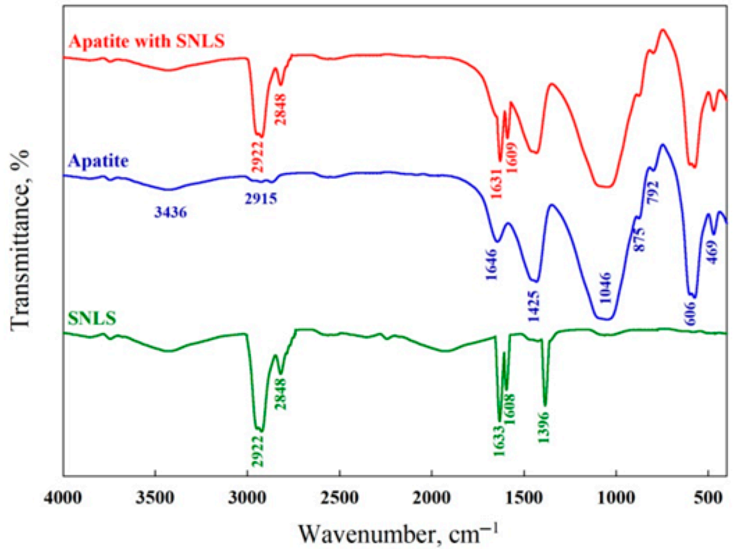

Figure 15. FT-IR spectra of apatite and SNLS, as well as their interaction.

The FT-IR spectrum of the SNLS (Figures 14 and 15) includes two peaks at 2922 and 2848 cm^{-1} from the stretching vibrations of the CH_2 and CH_3 groups, respectively. The peaks at 1608 and 1396 cm^{-1} were related to the carbonyl group stretching vibration of the carboxyl (–COO) group. Another property peak of SNLS appeared at 1633 cm^{-1}, which was ascribed to the amide carbonyl stretching vibration in –CON [26]. It was attributed to the amide carbonyl stretching in –CON after the SNLS treatment, which indicated the adsorption of SNLS onto dolomite surfaces.

Zeta-potential measurements discovered that the SNLS treatment was unfavorable for apatite adsorption, but had a selective adsorption for the dolomite surface.

New bands appeared in the FT-IR spectrum of the treated dolomite at 2926 and 2851 cm^{-1} for the CH_2 and CH_3 groups of SNLS (Figure 14). This results indicated that

SNLS was significantly adsorbed on the surface of the dolomite. The SNLS peaks at 2922, 2848, and 1396 cm^{-1} changed to 2926, 2851, and 1544 cm^{-1} after interaction with dolomite [27]. The characteristic bands attributed to the –COO and –CON groups of the SNLS were significantly shifted after their interaction with dolomite, from the original values of 1608 and 1633 cm^{-1}, to 1562 and 1598 cm^{-1}, respectively. This reveals the strong SNLS adsorption on the surface of dolomite.

The treated apatite spectrum had two new bands at 2922 and 2848 cm^{-1}, attributed to the $–CH_2$ and $–CH_3$ groups of SNLS, and two bands at 1631 and 1609 cm^{-1}, attributed to the –CON and –COO groups of SNLS, which had shifted from 1633 to 1631 cm^{-1} and from 1608 to 1609 cm^{-1}, respectively (Figure 15). There were slight band shifts of the –CON and –COO groups in the treated apatite compared to dolomite [28]. SNLS is chemisorbed onto the apatite surface, according to these findings. This result indicates that SNLS has a weaker chemical adsorption on apatite surfaces than on dolomite surfaces. The chemical adsorption of the three active O atoms of SNLS on dolomite was stronger than that on apatite. These O atoms could form a Ca–NLS complex because of the higher Ca reactivity on dolomite than on apatite (Figure 16).

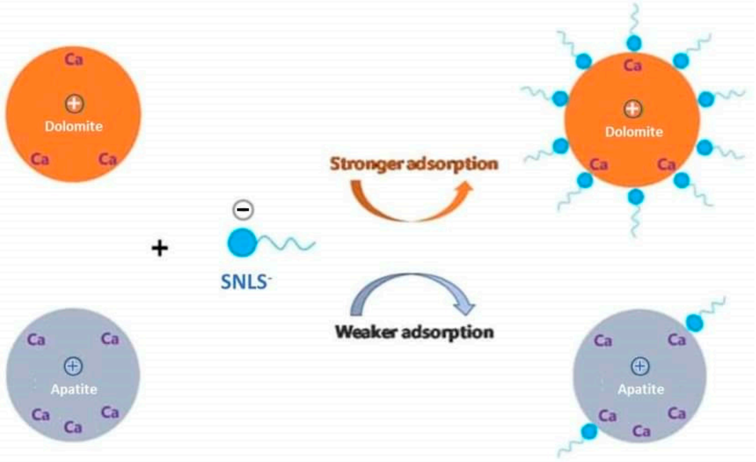

Figure 16. Schematic diagram of chemical adsorption of SNLS on apatite and dolomite surfaces.

4. Conclusions

Sodium N-lauroylsarcosinate (SNLS) has a strong selectivity for dolomite minerals over apatite minerals. The zeta-potential and PZC of the dolomite surface were significantly changed in the presence of SNLS, showing a strong interaction with the dolomite surface. Through the active O atoms of the amide and carboxyl groups, FT-IR investigations revealed that SNLS can be chemically adsorbed on both dolomite and apatite minerals, to generate Ca–NLS chelates. Based on chemical adsorption, dolomite has a higher Ca-reactivity than apatite. In the presence of 0.05 mmol/L SNLS at pH 10, the maximum floatability difference (83%) of dolomite and apatite minerals was achieved. At pH 10, the dolomite was successfully separated from its mixture of apatite, in various ratios. From a binary mixture containing 16.5 and 19.8% P_2O_5, two concentrations of 22.3 and 28.7% P_2O_5 were obtained. A concentration comprising 31.8% P_2O_5 and 0.70% MgO was obtained from the flotation of a binary mixture containing 24.7% P_2O_5 and 4.7% MgO, with a P2O5 recovery of roughly 79%. Another concentration was produced from natural phosphate ore, which contained 25.8% P_2O_5 and 5.16% MgO at pH 10 with 0.2 mmol/L SNLS, and was produced at 30.9% P_2O_5 and 0.79% MgO. Thus, SNLS can be employed as a dolomite collector on an industrial scale, due to its high selectivity and low cost.

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