Enhancement of Phosphate Flotation by Ultrasonic Pretreatment

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ABSTRACT: *Removal of carbonate impurities in sedimentary phosphate is one of the most important issues in the industry. Poor selective flotation of those ores is due to the similarity of Physico-chemical surface properties, solubility, and electrokinetic characteristics of sparingly soluble phosphate and carbonate minerals. In this study the effect of ultrasonic irradiation as a pretreatment method on reverse flotation of low-grade sedimentary phosphate sample from Lar Mountain deposit was investigated. Ultrasonic was utilized before flotation at different ultrasound intensity. This study was performed by two flotation approaches; i) using experimental design (Plackett-Burman method with 11 variables), and ii) try and error method. Initial mineralogical studies showed that the feed sample contains 10.34%P_2O_5, 48.01%CaO, and 9.22%SiO_2. The collected data from experimental design were analyzed by DX7.0 software to assess the influence of each parameter on flotation performance. The results indicated that ultrasound intensity, collector dosage, and dispersant dosage were the effective parameters. The results of the try and error method showed that the conditioning time was the most effective parameter in which by reducing ultrasonic preparation time the recovery was increased relative to 33.29%. Finally, the kinetic flotation tests and SEM studies were performed. The results proved surface cleaning of phosphate minerals which treated by ultrasound irradiation that led to better adsorption of chemicals which increased the recovery and grade of P_2O_5 for 87.88% and 14.45%, respectively. However, the application of the ultrasonic treatment reduced the flotation chemicals' consumption which is a prominent issue for phosphate treatment.*

KEYWORDS: *Ultrasonic; Reverse flotation; Sedimentary phosphate; Pretreatment.*

INTRODUCTION

About 95% of the world's production of phosphate rock is used for the fertilizer industry. With an increasing world population, the need for more food production, and producing chemical fertilizers, phosphate rock demands increased. Therefore, it is essential to extract and process of low-grade reserves, as well. A large portion of these reserves is sedimentary phosphates [1]. Most of sedimentary phosphates are cryptocrystalline and associated gangue are dolomite, quartz, hematite, aluminosilicates, and clay minerals. Upgrade of phosphate ores by flotation has been an important part of the concentration process since the 1920s. If associated gangue of sedimentary phosphate is a silicate, the flotation is one of the best chose to process, but with carbonate gangue, because of similarity

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in physicochemical properties, flotation is too difficult and requires some strategies [2]. In the last two decades, because of the decreasing of high-grade phosphate rock and need to produce materials with an appropriate grade to generate phosphoric acid, many attempts were done to increase flotation recovery [1]. A lot of studies were carried out on selective separation of carbonate and phosphate minerals and new methods and reagents were presented [3-6]. Methods like double reverse flotation, flotation with using micro and nanobubbles, using a mixture of ionic and non-ionic reagents, use of new chemical substances and using acoustic effect on flotation, were suggested [2, 5, 7-10].

In the last two decades, using ultrasonic as a pretreatment method was investigated by researchers in laboratory and pilot scales. The ultrasound energy is a form of mechanical energy in which its frequency is higher than the limitation of human hearing (higher than 20 kHz). In the early 1970's in the former Soviet Union, the first studies on the application of ultrasonic in mineral processing were carried out with a focus on the effect of ultrasonic on the flotation and extractive metallurgy. Birkin and Silva Martinez investigated the effect of ultrasonic on the electrochemical phenomena. They employed microelectrodes, to resolve single transient cavitation events. Distance and temperature dependencies proved to agree with both the acoustic pressure field generated by the ultrasonic horn and cavitation bubble collapse violence with decreasing vapor pressure within the bubble, respectively [11]. Ozkan employed ultrasonic for the beneficiation of Magnesite slimes, as a result, the ultrasonic had a positive effect on recovery values [12]. Also, he investigated the effect of ultrasound on colemanite concentrate from waste and showed that ultrasonic had a positive impact on ultimate recovery by increasing preparation time and reducing pulp density [13, 14]. *Kursun* and *Ulusoy* used ultrasonic in column flotation of zinc sulfides and improved the grade and recovery of flotation. It was because of increasing diffusion of ultrasound, enhancing adsorption of the collector, and the hydrodynamic cavitation that generated small bubbles attaching to the hydrophobic particles, therewith enhancing contact angle and attachment [15]. *Videla et al.,* applied ultrasound for increasing flotation recovery of copper from waste, and revealed that the recovery could be increased up to 3.5% [16]. *Haghi* used ultrasonic to improve the quality of low-grade silica and achieved the desired results [17, 18]. The impact of the ultrasonic on flotation performance is more than the other pretreatments. It stems from the cleaning surface particles generated by cavitation bubbles, produce stable bubbles with a smaller size, better distribution of reagents, and increase the activity of chemical substances in pulp [19-21]. Ultrasound irradiation caused to simply adsorb of reagent on particle surfaces, and accordingly increase the flotation recovery [20, 22]. Effects of the pulp nature on desulphurization and de-ashing during high-sulfur coal flotation were investigated by *Kang* and coworkers. They monitored solution oxygen, pH value, temperature, and surface tension before and after ultrasonic conditioning to assess changes in pulp nature. They found that ultrasonic treatment causes to reduce the oxygen content and the interfacial tension and increment the pH value and the temperature of the pulp. Furthermore, the perfect index of flotation and the perfect index of desulphurization of fine coal increased by 25.19% and 18.03%, respectively, after the pulp was ultrasonically conditioned. They indicated that ultrasonic treatment can change the pulp nature, and improved the degree of desulphurization during high-sulfur coal flotation [23]. Influence of ultrasonic pretreatment of pulp on the flotation of sulfide ores was studied by *C. Aldrich* and *D. Feng*. They demonstrated that after ultrasonic incitement, the floatability of the sulfides improved dramatically, and the silicates were depressed to some extent. Also, they indicated that compared to conventional conditioning; ultrasonic irradiation could enhance the flotation rate, value grades and recoveries and decreased the dosages of flotation reagents appreciably [24]. *Ghadyani et al.* investigated the effect of ultrasonic irradiation as a pretreatment method on high-ash coal flotation and kinetics. It was found that the most significant factor in ultrasound-assisted flotation for combustible recovery was interactions between ultrasound power and collector dosage. Using a low amount of collector in the presence of sonication the combustible recovery increased significantly [25]. Effect of ultrasonic pre-treatment and aeration on flotation separation of chalcopyrite from pyrite was studied by *Taheri* and *Lotfalian*. They indicated that using ultrasound cause to separate chalcopyrite from pyrite effectively [26].

In the current study, ultrasonic pretreatment inquired for flotation of sedimentary phosphate ore using batch laboratory flotation cell. This research was targeted to assess the influence of ultrasonic on efficiency and selectivity of phosphate flotation and chemical usage with ultrasonic preconditioning. Furthermore, flotation kinetic and SEM analysis were performed to investigate the differences produced by the use of ultrasonic irradiation and compare the collected results of flotation before and after ultrasonic treatment.

EXPERIMENTAL SECTION

Head sample properties

Phosphate ore sample used in this study was prepared from Lar Mountain deposit located in the southwest of Iran, approximately 50Km of north Gachsaran and 17 Km of the southeast of Dehdasht. A D8-Advance Bruker axs 2θ-θ device was applied to X-Ray Diffraction (XRD) analyzes. These studies indicated that the dominant minerals in the sample were calcite, fluorapatite, quartz and clay minerals. According to the X-Ray Fluorescence (XRF) studies, feed sample contained 10.34% P_2O_5, 48.01%CaO, 9.22%SiO_2 and 0.44%MgO. Due to high values of calcite and silicate minerals, it could be stated that the Lar Mountain phosphate deposit is sedimentary reserves, with carbonate-silicate gangue. In addition, due to the small amounts of P_2O_5 in the sample, the deposit can be classified as low grade reserves [7]. Microscopic studies revealed that groups of fossil foraminifera, pellets, oolite, calcite and group of apatite minerals includes fluorapatite, carbonated hydroxyapatite and collophane are the most important ingredients of the sample. Liberation studies indicated that the apatite particles are not associated with contaminant minerals in the size range of -150+100 microns and its liberation degree for this size was up to 81%.

Chemicals

The chemical substances used in this research work included sulfuric acid 96.5%, sodium hydroxide 98%, as pH modifier, aluminum sulfate pure crystal, sodium, potassium tartrate 99%, orthophosphoric acid 85%, citric acid pure crystal, as phosphate depressant, all these reagents were supplied by Merk industry, Darmstadt, Germany. Industrial sodium silicate 43%, industrial oleic acid 99% as carbonate collector, pamak 4 (fatty acid from tall oil) supplied by Hercules industry, and fuel oil as promoter.

Equipment

A laboratory Denver rod mill was used to grind the samples. The conventional Denver D12 (2-liter) flotation cell, was used for the flotation experiments. The ultrasonic probe device (Qsonica Q700, QSonica, LLC., Newtown, CT, USA, 20 kHz) equipped with a probe was employed for direct ultrasound irradiation within the conditioning phase of reverse flotation experiments.

Process route

According to the results of previous studies on this sample [7], reverse flotation with two mixed depressants was selected. Reverse flotation tests were conducted with and without ultrasonic in the conditioning phase. For this purpose, samples were ground and deslimed using laboratory hydrocyclone so that particles finer than 38 microns were discarded (about 21% with a grade of 7.5% of P_2O_5). For each test, a 400g sample with d_{80}=100 microns was used. In each experiment, an adequate quantity of reagents was added. The phosphate sample was conditioned in tap water (30% solid percent) at 1300rpm of rotor speed while the ultrasonic probe was placed in the pulp with the different ultrasound intensity. During the conditioning time, the pulp pH was monitored and adjusted to the appropriate level with H_2SO_4 and NaOH solution. After ultrasound preparation time was finished, tap water was added to decrease solid percent to 13%, and then the froth was collected. The concentrates and the tailings were filtered, dried, weighed and analyzed for P_2O_5 and CaO content. The experimental setup, and schematic flowsheet for phosphate purification, combining ultrasonic probe with a reverse flotation are presented in Figs. 1a and 1b.

According to the previous study [7, 27] and the results of the preliminary tests which were carried out on this sample, regarding many parameters, Plackett-Burman design in Design-Expert 7.0 (DX7.0) software (trial version) with 11 factors in two levels, was used to determine the effects of pH (A), collector type (B), collector dosage ([g/t], C), depressant type (D), depressant dosage ([g/t], E), dispersant dosage ([g/t], F), oil dosage ([g/t], G), conditioning time for depressant ([min], H), ultrasonic intensity ([W/cm^2], J),conditioning

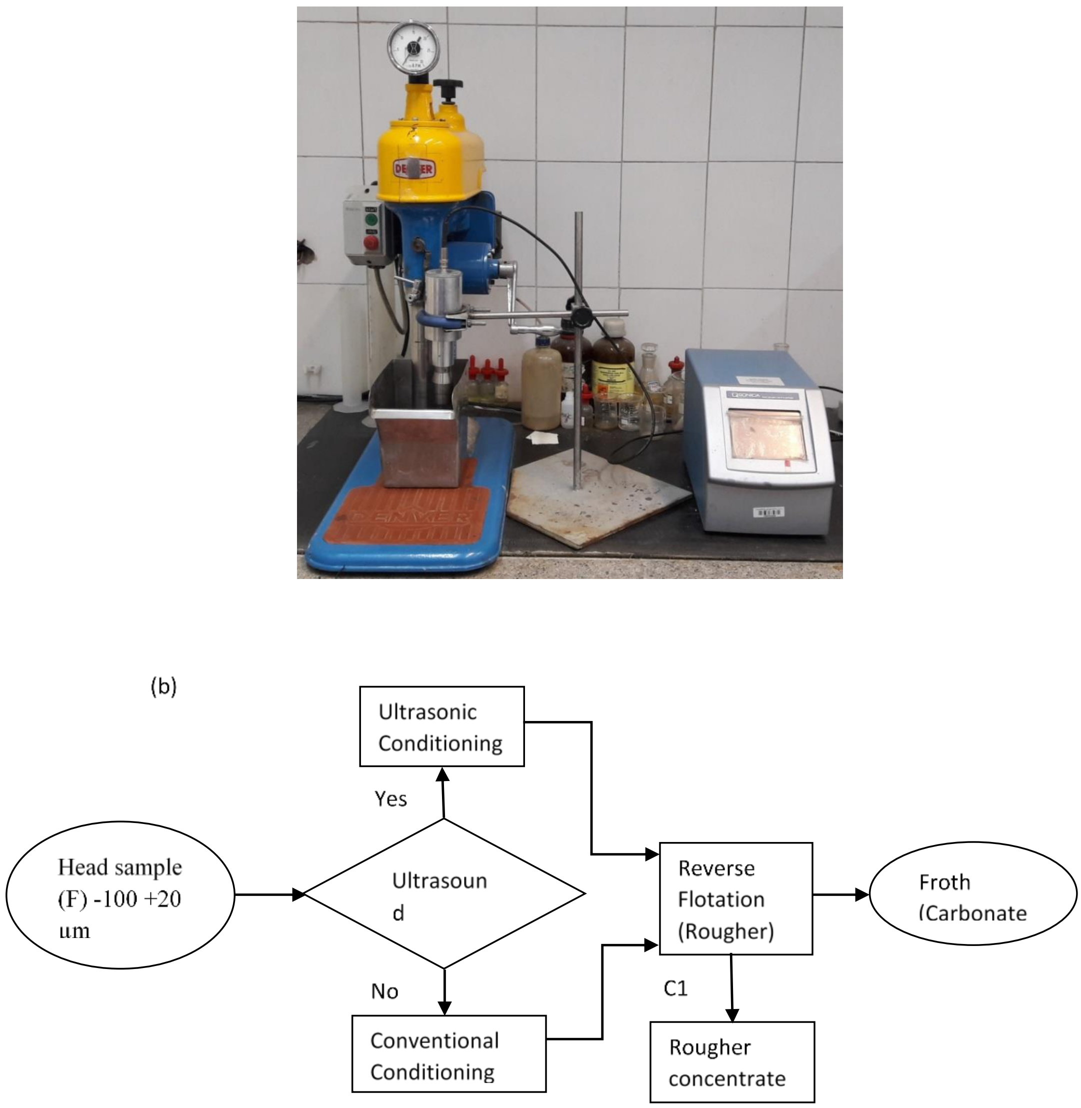

Fig. 1: (a) Designed setup and (b) Schematic flowsheet, for reverse flotation of phosphate combined wit the ultrasound irradiation device.

time for collector ([min], K) and froth collecting time ([min], L), on the phosphate flotation performance. Therefore, 16 tests with 4 center points were conducted. The grade ([%], R_1), the recovery ([%], R_2) and the yield ([%], R_3) were responses variables in the analysis of the results. Table 1 shows high and low levels of various parameters. The matrix of design variables and experiments runs are shown in Table 2.

In order to optimize the obtained effective factors from previous section (collector dosage ([g/t], C), dispersant dosage ([g/t], F) and ultrasound intensity ([W/cm^2], J)), the response surface central composite was applied. Thereby, 18 tests were conducted and the grade ([%], R_1), the recovery ([%], R_2), and the yield ([%], R_3) were considered as response variables. The experimental plane, variables, and responses of flotation tests are presented in Table 3.

To clearly show the effect of ultrasonic pretreatment on phosphate flotation, a series of tests were conducted under the same conditions by the try and error method.

Table1: Levels of parameters studied in the experiments.

Factor	Name	Unite	Low level	High level
A	pH	Arbitrary	5.50	8.50
B	Collector type	Arbitrary	Oleic acid	Pamak 4
C	Collector dosage	g/t	1000	2000
D	Depressant type	Arbitrary	Aluminum sulfate+ (Na, K) tartrate	Phosphoric acid+ Acetic acid
E	Depressant dosage	g/t	1000	2500
F	Dispersant dosage	g/t	0	1000
G	Oil dosage	g/t	500	1000
H	Conditioning time for depressant	Minute	6	8
J	Ultrasonic intensity	W/cm^2	0	40
K	Conditioning time for collector	Minute	2	4
L	Froth collecting time	Minute	3	5

Table 2: Pattern of flotation experiments.

Standard order	A	B	C	D	E	F	G	H	J	K	L	R_1	R_2	R_3
1	2	2	1	2	2	2	1	1	1	2	1	9.76	80.38	74.04
2	1	2	2	1	2	2	2	1	1	1	2	10.76	88.03	75.02
3	2	1	2	2	1	2	2	2	1	1	1	11.38	73.73	57.40
4	1	2	1	2	2	1	2	2	2	1	1	11.10	93.91	91.29
5	1	1	2	1	2	2	1	2	2	2	1	14.26	76.02	57.52
6	1	1	1	2	1	2	2	1	2	2	2	13.03	74.33	61.55
7	2	1	1	1	2	1	2	2	1	2	2	10.10	84.14	72.60
8	2	2	1	1	1	2	1	2	2	1	2	11.80	80.87	75.78
9	2	2	2	1	1	1	2	1	2	2	1	12.16	73.04	64.81
10	1	2	2	2	1	1	1	2	1	2	2	9.50	90.11	83.94
11	2	1	2	2	2	1	1	1	2	1	2	13.18	68.76	56.29
12	1	1	1	1	1	1	1	1	1	1	1	9.55	93.26	84.76
13	c.p	1	c.p	1	c.p	c.p	c.p	c.p	c.p	c.p	c.p	16.31	65.36	43.25
14	c.p	2	c.p	1	c.p	c.p	c.p	c.p	c.p	c.p	c.p	12.49	80.68	69.70
15	c.p	1	c.p	2	c.p	c.p	c.p	c.p	c.p	c.p	c.p	13.91	73.30	56.86
16	c.p	2	c.p	2	c.p	c.p	c.p	c.p	c.p	c.p	c.p	11.65	86.16	79.80

c.p: central point

Table 3: Experimental plan, variables and responses of flotation tests.

Standard order	C	F	J	R_1	R_2	R_3
1	1400	400	15	13.83	77.03	60.10
2	2400	400	15	15.06	69.44	49.75
3	1400	1400	15	13.18	79.98	65.48
4	2400	1400	15	15.08	66.64	47.68
5	1400	400	55	13.23	78.25	63.82
6	2400	400	55	14.19	71.99	54.74
7	1400	1400	55	13.76	74.96	58.78
8	2400	1400	55	14.60	70.36	52.00
9	1059.10	900	35	13.39	74.53	60.06
10	2740.90	900	35	16.78	60.34	38.80
11	1900	59.10	35	12.74	79.72	67.52
12	1900	1740.90	35	17.19	63.90	40.11
13	1900	900	1.36	16.64	70.55	45.75
14	1900	900	68.64	15.81	60.57	41.34
15	1900	900	35	13.16	78.08	64.02
16	1900	900	35	15.40	71.38	50.01
17	1900	900	35	13.65	77.48	61.25
18	1900	900	35	13.99	79.03	60.95

In this series, chemical consumption was lower than those in previous tests, and dispersant dosage, ultrasound intensity, and ultrasonic preparation time were investigated, individually. Table 4 shows the different ultrasound intensity and dispersant dosage used for these experiments. The different ultrasonic conditioning times were 3, 4, 6, and 11 minutes. According to the previous study [24, 25], chemical usage was decreased in the presence of sonication. Therefore, in the following test collector and depressant dosage considered as 1000g/t and 1500g/t, respectively.

RESULTS AND DISCUSSION

The replicable results of the first series of flotation tests conducted by experimental design were analyzed by the DX7 software which determined the appropriate model and effective parameters. Table 2 shows the results. Figs. 2a, 2b, and 2c present the Pareto chart of t-value of effects for grade, recovery, and yield. According to this chart, factors that above of Bonferroni limit line are the effective and factors which are between Bonferroni and t-value limit lines, have less influence on responses, and factors under t-value limit lines are insignificant. The analysis of variance (ANOVA) of three responses was carried out to determine the most important factors. The statistical terms of ANOVA table such as Sum of Square (SS), Mean of Square (MS), and variance ratio (F-value) of each factor on each response were calculated by DX7.0 software. Tables 5-7 present the analysis of variance (ANOVA) for grade, recovery, and yield. Figs. 3-5 show the curves of effective parameters on the grade, recovery, and yield of concentrate.

As can be seen in the Tables 5-7, regarding the selected confidence interval for this research work (95%), the p-values less than 0.0500 demonstrate the model terms (for the grade, yield, and recovery) are significant. According to Figs. 2a and 3, and Table 5, it could be stated that ultrasound intensity had a remarkable influence on the grade, and also collector type and dosage and dispersant

Table 4: Different ultrasound intensity and dispersant dosage used for reverse flotation.

Test number	Ultrasound Intensity(W/cm^2)	Dispersant Dosage (g/t)
1	0	0
2		1000
3	20	0
4		1000
5	30	0
6		1000

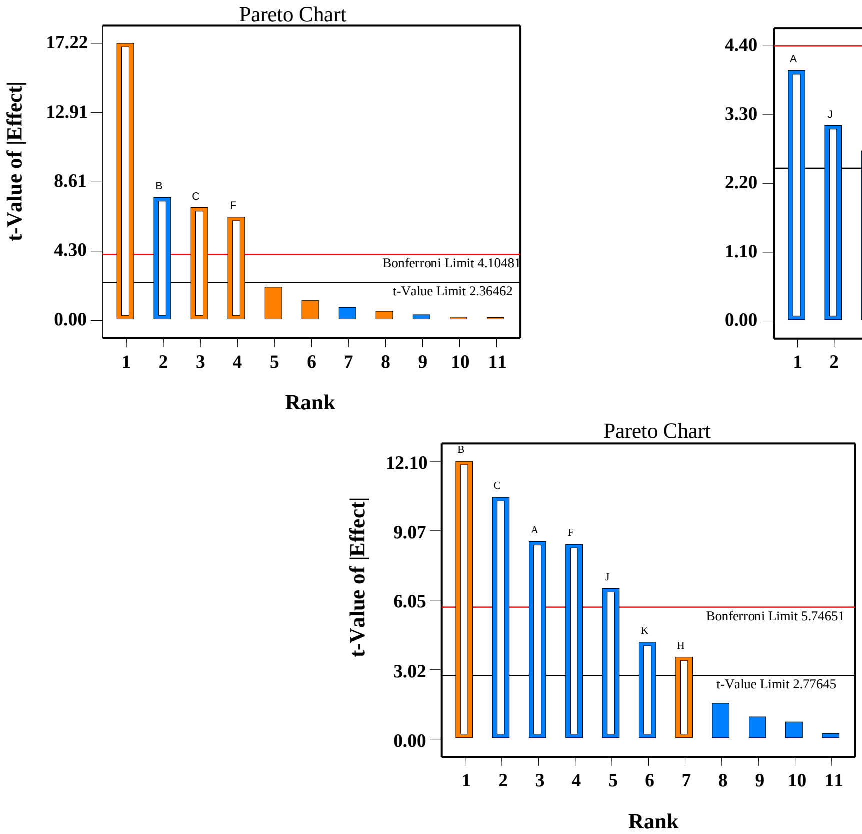

Fig. 2: Pareto chart of effects for the grade (a), recovery (b), and yield (c).

dosage was the effective parameters on the grade. This means that ultrasound intensity increased the concentrate grade from 10.71% to 13.23%, using oleic acid the grade increased from 10.85% to 11.92%. Concentrate grade enhanced from 11.43% to 12.40% when the collector dosage increased. Growth in dispersant dosage caused the increase in grade up to 12.37%. Figs. 2b and 4, and Table 6 reveal that pH had the greatest influence on the recovery and decreasing pH value led to the increase of recovery from 73.81% to 82.94%. Collector type and low value of ultrasound intensity and collector dosage were the other effective parameters on the recovery. As it was clear, increasing the ultrasound intensity decreased recovery relatively to 7%. Figs. 2c and 5, and Table 7 demonstrate that ultrasound irradiation was one of the effective parameters on the yield of concentrate. Collector type and dosage, pH, conditioning time for depressant, and conditioning time for collectors were other effective parameters. Using oleic acid the yield decreased from 77.48% to 65.02%. Collector dosage, dispersant dosage

Table 5: Analysis of variance for the grade of phosphate concentrate.

Source	Sum of Square	DOF*	Mean Square	F-Value	P-Value Prob. >F
Model	32.57	4	8.14	138.17	<0.0001
B	3.43	1	3.43	58.29	0.0001
C	2.90	1	2.90	49.23	0.0002
F	2.43	1	2.43	41.24	0.0004
J	17.47	1	17.47	296.50	<0.0001
Curvature	20.77	4	5.19	88.13	<0.0001
Residual	0.41	7	0.059		
Cor Total	53.76	15			

**Degree of Freedom*

Table 6: Analysis of variance for the recovery of phosphate concentrate.

Source	Sum of Square	DOF	Mean Square	F-Value	P-Value Prob. >F
Model	849.66	5	169.93	10.94	0.0056
A	249.71	1	249.71	16.07	0.0070
B	108.60	1	108.60	6.99	0.0383
C	115.32	1	115.32	7.42	0.0344
J	152.08	1	152.08	9.79	0.0204
Curvature	170.62	4	42.66	2.57	0.1297
Residual	93.21	6	15.54		
Cor Total	1113.49	15			

Table 7: Analysis of variance for the yield of phosphate concentrate.

Source	Sum of Square	DOF	Mean Square	F-Value	P-Value Prob. >F
Model	2014.04	7	287.72	90.39	0.0003
A	235.50	1	235.50	73.98	0.0010
B	465.75	1	465.75	146.31	0.0003
C	352.52	1	352.52	110.74	0.0005
F	228.64	1	228.64	71.83	0.0011
H	40.55	1	40.55	12.74	0.0234
J	136.82	1	136.82	42.98	0.0028
K	56.68	1	56.68	17.81	0.0135
Curvature	490.73	4	122.68	38.54	0.0019
Residual	12.73	4	3.18		
Cor Total	2517.50	15			

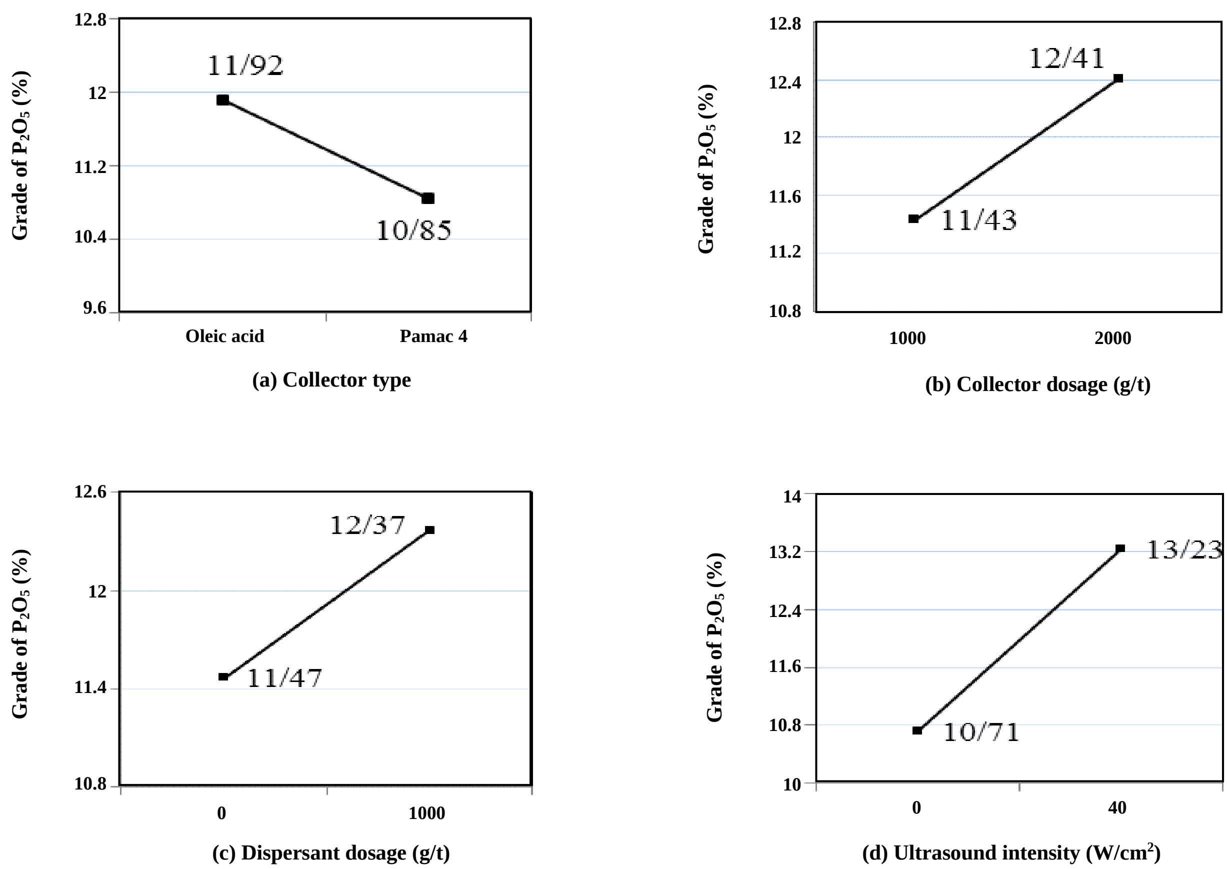

***Fig. 3:** Effect of collector type (a) and dosage (b), dispersant dosage (c), and ultrasound intensity (d) on the concentrate grade.*

and conditioning time for collector had a negative effect on the yield and with increasing them the yield was decreased. Considering Fig. 5a, decreasing ultrasound intensity, increased the concentrate yield, from 61.64% to 68.4%. These results were contrary to the results of the previous studies [11-13, 15, 23, 24], in which ultrasonic pretreatment enhanced the recovery compared with conventional conditioning. Furthermore, the depressant type was insignificant, that it was contrary to previous research on this sample [7], and had no effect on response variables. This would be for the following reasons:

(1) In the Plackett-Burman method, it is impossible to study the interaction of parameters, and it is probable that one or more parameters have synergism effect, and may decrease or neutralize the influence of ultrasonic.

(2) The impact of ultrasonic treatment was very complex and unexpected. Therefore, its effect could not be seen just by performing a series of experiments that follow a particular pattern.

(3) It could be possible that the ultrasound intensity and the number of chemical substances were higher than the appropriate quantity of reagents which cause to increase complicated of pulp chemistry.

(4) The results of the response surface central composite design present in Table 3 and the analysis of variance for recovery shows in Table 8. Fig. 6 presents the effect of collector dosage and ultrasound intensity on the recovery.

(5) According to Tables 3 and 8, the model was significant and collector dosage was merely an effective parameter on phosphate recovery, in which with increasing collector dosage the recovery decreased from 76.53% to 68.38% (Fig. 6a). Fig. 6b and Table 8 indicated that decreasing ultrasound intensity cause to increment the recovery from 71.41% to 73.51%. The recovery increased with a diminishing dispersant dosage. As it was cleared, ultrasound pretreatment, decreased chemicals usage, meanwhile, flotation performance was improved with decreasing chemical consumption.

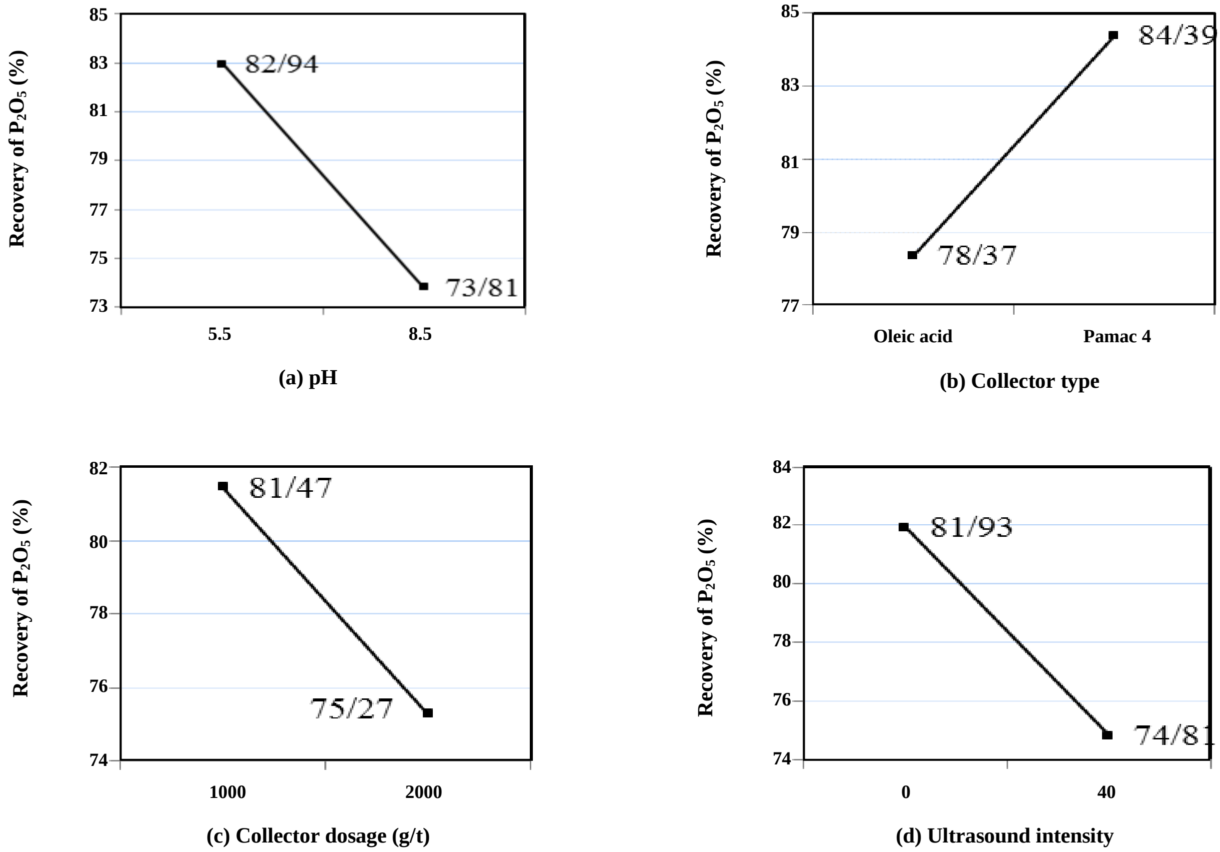

Fig. 4: Effect of pH (a), collector type (b), collector dosage (c), and ultrasound intensity (d) on the concentrate recovery.

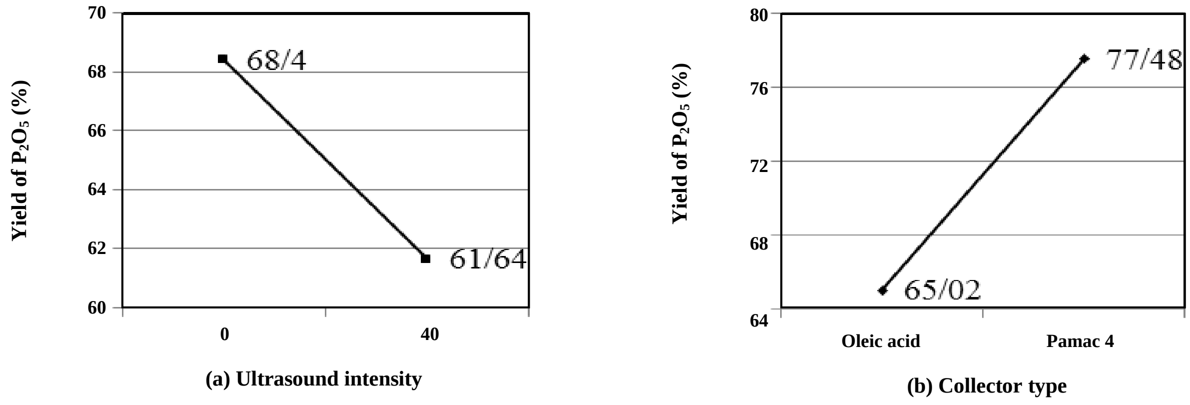

Fig. 5: Effect of ultrasound intensity (a), and collector type (b) on the concentrate yield.

(6) The results of different ultrasound intensity and dispersant dosage that conducted by try and error method, are shown in Figs. 7 and 8.

(7) Fig. 7 shows that the best grade was obtained when dispersant was used (15.94%, test 6) in the presence of ultrasonic irradiation (30 W/cm^2), and without using dispersant the grade of P_2O_5 dropped dramatically from 15.94% to 11.09% (tests 6 and 3). Moreover, with reducing ultrasound intensity (from 30 to 20 W/cm^2, tests 6 and 4), the grade was reduced from 15.94% to 12.85%, but recovery increased dramatically from 65.93% to 84.67%. It should be considered that the P_2O_5 recovery

Table 8: Analysis of variance for the recovery of phosphate concentrate.

Source	Sum of Square	DOF	Mean Square	F-Value	P-Value Prob.>F
Model	313.89	3	104.63	3.91	0.0320
C	226.80	1	226.80	8.48	0.0114
F	72.08	1	72.08	2.70	0.1228
J	15	1	15	0.56	0.4662
Residual	374.24	14	26.73		
Lack of Fit	338.17	11	30.74	2.56	0.2382
Pure Error	36.07	3	12.02		
Cor Total	688.13	17			

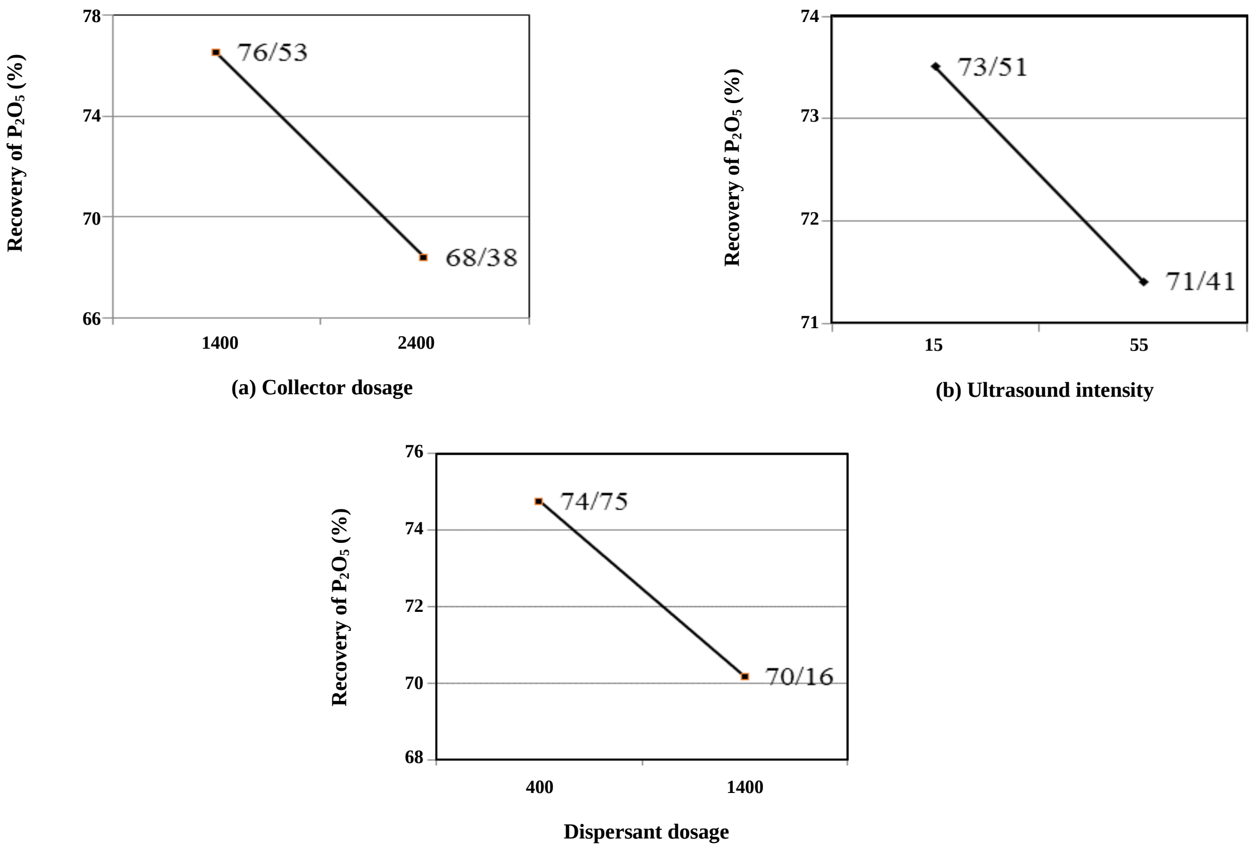

Fig. 6: Effect of collector dosage (a), ultrasound intensity (b), and dispersant dosage (c) on the concentrate recovery.

in conventional flotation without ultrasonic was 10% lower than those in the presence of ultrasonic in similar chemical conditions. Fig. 8 indicates that the best yield occurred when the ultrasound intensity was 20 W/cm^2 and without dispersant dosage. The yield of phosphate flotation was increased from 44.86% to 81.74 with increasing ultrasound intensity from zero to 20 W/cm^2, and with 1000g/t dispersant dosage.

(8) Preparation time is one of the effective parameters in the flotation process. The ultrasound conditioning time permits decreasing depressant dosage with unchanged selectivity [28]. The influence of ultrasonic preparation

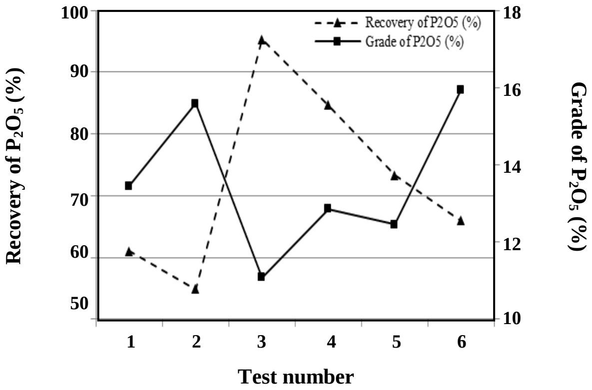

Fig. 7: The effect of ultrasound intensity and dispersant dosage on the grade and recovery of phosphate concentrate.

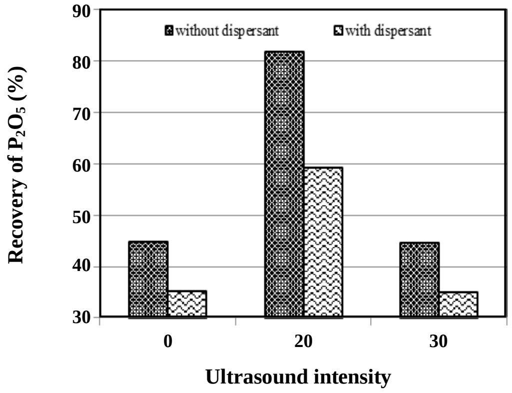

Fig. 8: The effect of ultrasound intensity and dispersant dosage on the yield of phosphate concentrate.

time on the reverse flotation of phosphate presents in Table 9. Fig. 9 presents the related grade-recovery curve.

(9) As it was anticipated, diminish the preparation time caused the increment of the recovery. With reducing the ultrasound conditioning time from 11 to 6 minutes, the grade was gently decreased, but the yield and recovery significantly increased. Long conditioning with ultrasonic treatment might be cause to damage chemical adsorption on the particle surfaces and resulted in decreasing recovery. Fig. 9 shows that with decreasing conditioning time the recovery increased dramatically, but the grade decreased slightly, as well. As it was mentioned, chemical consumption in these tests was approximately ½ compared with previous section (1000g/t and 1500g/t collector and depressant dosage in these test compared with 2000g/t and 2500g/t in the first series of tests), and with comparing tests 3 and 5, it could be concluded that grade, yield, and recovery of ultrasonic conditioning flotation were better than those in conventional conditioning flotation in similar conditions.

(10) In general, sedimentary phosphate flotation performance was better when treated by ultrasonic than untreated. This could be due to the surface cleaning generated by cavitation bubbles which cause better adsorption and uniformly distribution of chemicals, and resulted in increment of the grade and recovery and diminish the chemical usage. These results were proved by SEM studies. It should be mentioned that rougher stage aimed to increase the recovery with acceptable grade; therefore, the best conditions for rougher step were selected as 6 minutes of conditioning time, using an ultrasonic probe with an intensity of 30W/cm^2, pH=9-9.5, oleic acid as carbonate collector, the mixture of aluminum sulfate and sodium, potassium tartrate as a depressant with a ratio of 1:2, 1000g/t sodium silicate as a dispersant, without promoter and frother, and impeller speed=1300 rpm. Under these conditions the average grade and recovery of P_2O_5 were 14.45% and 87.88%, respectively.

Study the Effect of Ultrasonic Irradiation

To investigate the effect of ultrasonic irradiation on the cleaning of particle surfaces, kinetic flotation experiments, and the study of particle surface by Scanning Electron Microscope (SEM) were conducted.

Effect of ultrasonic irradiation on flotation Kinetics

To study the influence of ultrasonic pretreatment on the recovery-time graph, two kinetics flotation tests were performed with and without using ultrasonic. These tests were carried out under the best-collected conditions from the previous section. The effect of sonication before flotation on the accumulative phosphate recovery after 30, 60, 120, 180 and 270 seconds of flotation time, is shown in Fig. 10. It should be noticed that in reverse flotation of phosphate, the carbonate minerals delivered to the froth section as tailing and the phosphate minerals remained in the flotation cell as a concentrate. In these tests, at different intervals, samples were collected from the froth section, and then they were filtered, dried and their P_2O_5 content was measured. This graph shows the number of phosphate particles

Table 9: The effect of conditioning time on flotation tests in the presence of ultrasonic.

Test number	conditioning time (min)	Grade of P_2O_5 (%)	Recovery (%)	Yield (%)
1	3	14.11	80.28	66.10
2	4	14.61	82.37	65.96
3	6	14.45	87.88	66.19
4	11	15.94	65.93	34.97
5 (US=0)	6	12.55	81.60	59.10

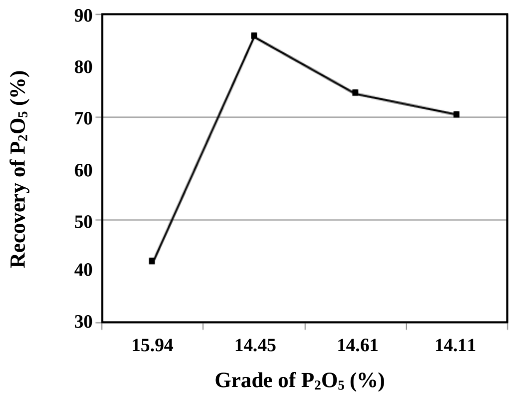

Fig. 9: The grade-recovery curve in variable conditioning time in the presence of ultrasonic.

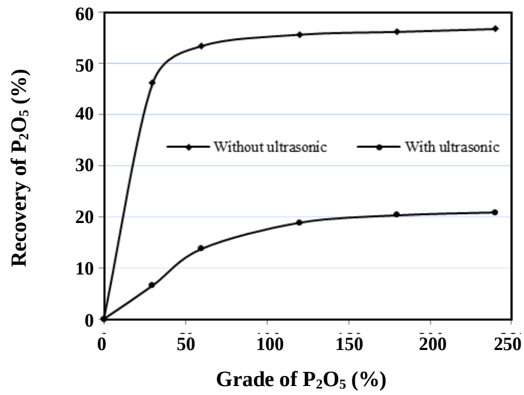

Fig. 10: The results of P_2O_5 recovery versus flotation time in different flotation approach, with and without ultrasonic.

which reported to tailing (froth section). Therefore, whatever the amount of phosphate reported to the froth is less; it would be better and desirable. The slope of the time-recovery graph shows the kinetic flotation, and as can be seen, when using ultrasonic pretreatment prior to flotation, the slope of the graph was lower compared to the untreated conventional method. It means that less amount of P_2O_5 was reported to tailing with sonication. This may be due to this fact that the surfaces of particles were cleaner when ultrasonic treated than untreated, which leads to better absorption of chemicals on mineral particles, and chemicals' performance was accordingly improved.

SEM studies

To better understand the effect of ultrasonic irradiation on the cleaning particle surfaces, the SEM device CamScan-MV2300 model was employed. Samples of flotation feed concentrate, and tailings with and without using ultrasonic pretreatment, were used in these studies.. The related results are presented in Fig. 11. Figs. 11b and 11d show apatite particles in concentrate and tailing acted by ultrasonic irradiation, and Fig. 11f presents a carbonate particle in tailing treated by ultrasonic. Fig. 11a shows an apatite particle in flotation feed and Figs. 11c and 11e present apatite mineral in the concentrate and tailing of conventional flotation without using ultrasonic, respectively. As can be seen, particles in Figs. 11b and 11d are very cleaner than others. According to Figs. 11b and 11f, it would accordingly be postulated that the ultrasonic performance on phosphate and carbonate minerals were non-selective. Surface cleaning of particles due to cavitation bubbles was the most important effect of ultrasonic that was performed very well for sedimentary phosphate ore. When a clean surface is exposed to chemicals, it is accordingly led to better adsorption of reagents on the particles and reduce chemical consumption, and this would increase recovery and grade [20, 21, 29].

CONCLUSIONS

The target of this research work was to study the effect of ultrasound irradiation as a pretreatment method on flotation performance of low grade sedimentary

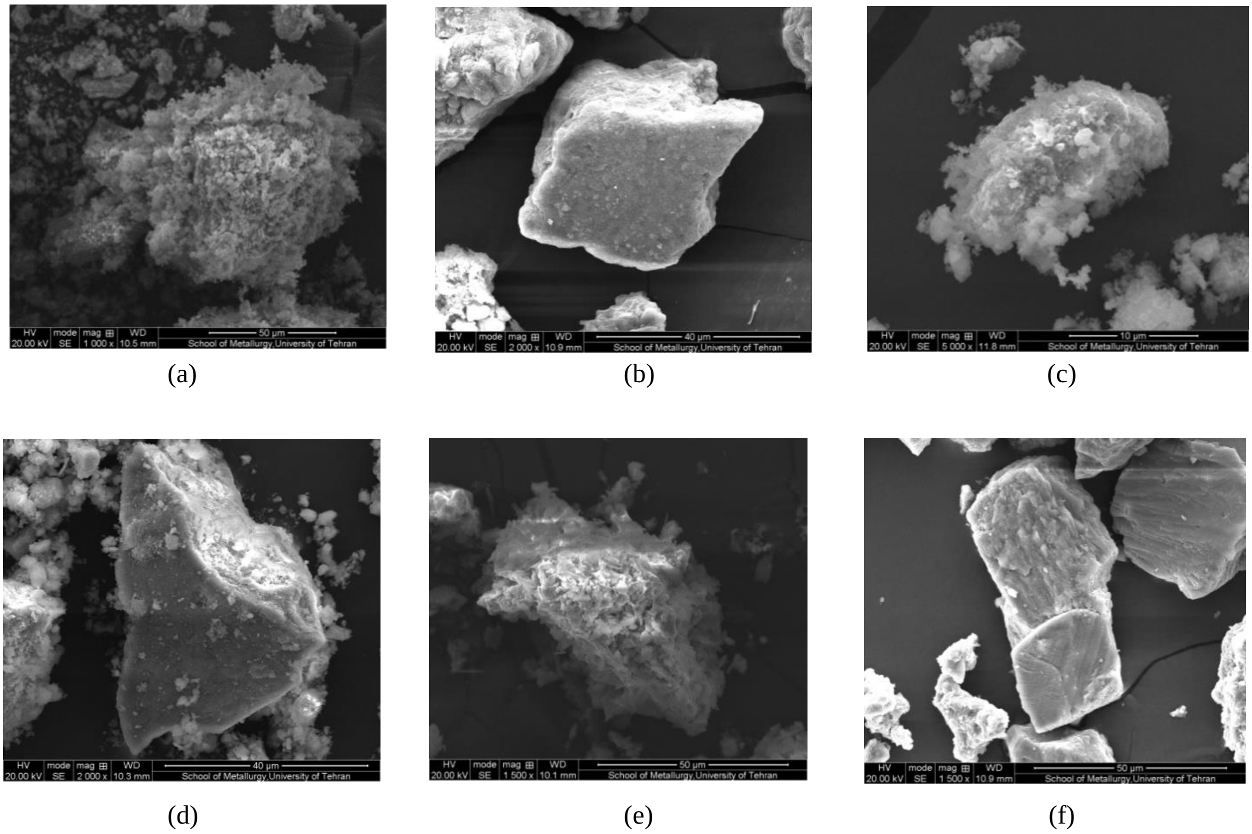

Fig. 11: SEM micrograph of particle surface morphology; a) apatite mineral in flotation feed, b) apatite mineral in concentrate treated by ultrasonic, c) apatite mineral in concentrate of conventional flotation, d) apatite mineral in tailing treated by ultrasonic, e) apatite mineral in tailing of conventional flotation, f) carbonate mineral in tailing treated by ultrasonic.

phosphate deposit. According to the results of various experiments, the following conclusions were made:

The collected data from the experimental design showed that ultrasound intensity was the most effective parameter on the P_2O_5 grade. Also, collector type and dosage and dispersant dosage were the other effective parameters. Furthermore, with increasing the ultrasound intensity, decreased recovery. It might be due to long ultrasound conditioning time that causes chemical adsorption on particles to destroy. Also, it could be because of the synergistic effect of the high level of chemical usage and ultrasonic intensity. The results obtained from the try and error method considering chemical consumption lower than the first series tests indicated that ultrasound conditioning time was the most important parameter on phosphate flotation performance, and with reducing it from 11 to 6 minutes, the recovery increased notably from 65.93%to 87.88%. Furthermore, reducing reagents usage had a positive effect on flotation performance in the presence of ultrasound irradiation which is the critical issue facing phosphate industries. Kinetic studies showed that ultrasonic conditioning prior to flotation cause to phosphate reported to tailing section was significantly lower in comparison with conventional conditioning. SEM studies illustrated the clean surface of particles (all minerals of apatite groups and carbonates) when ultrasonic irradiation was applied, therefore, chemical performance would be easier (chemical adsorption was facilitated and their distribution were monotonous) resulted in increment the grade, yield, and recovery. Also, the SEM micrograph presented that the ultrasonic had no selective behavior for both apatite and carbonate minerals.

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