Sodium Dodecyl Sulfate Modified Nano Alumina as a New Co-Collector in Increasing Copper Recovery from Oxide Sources in the Flotation Process

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ABSTRACT: *Flotation is a justifiable way to isolate valuable particles from primary ore. Collectors make mineral-rich particles connect to the froth phase and separate them in the flotation column. In this work, sodium dodecyl sulfate-modified nano Alumina as a new co-collector has been applied in the flotation process to boost the recovery of copper from oxide sources. For this purpose, the first nano alumina has been prepared by chemical precipitation method. co-collectors are some nanoparticles that have the potential to improve flotation performance in the recovery of valuable elements. The present study aims to produce spherical gamma-alumina nanoparticles and evaluate them as co-collectors to increase the flotation recovery of a natural sulfide-oxide copper mineral along with the molecular collector of Potassium Amyl Xanthate (PAX). morphology and structure of nano alumina were investigated by Field Emission Scanning Electron Microscopy (FESEM) and X-Ray Diffraction (XRD). The flotation recovery for acidic and alkaline nanoparticles was 86.65% and 93.15%, respectively. In comparison, in the absence of nanoparticles, the flotation number degraded to 53.35%. Moreover, the effect of nanoparticle dosage was investigated in this study.*

KEYWORDS: *Flotation; Co-collector; Nano alumina; Copper oxide resources; Recovery.*

INTRODUCTION

Froth flotation is one of the most important separation methods utilized for minerals in the size of 10-100 μm [1]. This process depends on the occurrence of complex phenomena between hydrophobic mineral particles and air bubbles such as their collision and adhesion [2]. When hydrophobic mineral particles adhere to the bubbles, they are transported to the surface of the pulp, which has a layer of froth. By collecting this froth, a high-quality mineral product is obtained. Using fine and coarse mineral particles is the biggest challenge of the flotation process. Fine particles due to low collision efficiency and coarse particles because of detachment efficiency reduce flotation efficiency [3, 4]. Collectors are often used to improve the attachment of particles and bubbles in flotation. Conventional collectors consist of extended molecular lengths of about 1 nm. But, in this case, recent collectors are not sufficient [5, 6]. This problem can be resolved with the aid of nanoparticle modification. Nanoparticle employment will increase the connectivity of particles to the bubbles in the froth phase and reduce the possibility of their separation. Recent studies have shown that nanoparticles can have an influence on gas holdup and can reduce chemical consumption (e.g. frother and collector). In some texts, the word "secondary collector" is used instead of nanoparticles. More hydrophobic minerals will selectively attach to bubbles using these secondary surfactants. As a result, they raise the flotation column and will separate [3, 4, 7]. In the presence of nanoparticles on the surface of minerals, they will render hydrophobic, and thus undesirable gangue particles will separate from valuable minerals [3, 4, 8, 9].

Nanoparticles are among the interesting and promising options in this regard. Nanoparticles have been widely studied by researchers because of their extraordinary properties such as the possibility of synthesis in a wide range of dimensions, the existence of several production methods, high surface area, easy separation, easy return to the cycle, ability to physical adsorption, and low environmental problems compared to other chemicals [10-12]. It is of note that the high specific surface area of nanoparticles causes better coverage of mineral particles and reduces their consumption in flotation operations [13-15]. Several factors affect the nanocollectors such as nanoparticle type, PH, and surface modifiers (surfactants), which are briefly discussed in the following.

Regarding the application of nanoparticles as a collector in flotation, *Yang et al.* used the adsorption of polystyrene-based polymer nanoparticles on glass beads. They showed that the recovery of glass beads in the presence of polymer nanoparticles increased from 30 to 90%. Besides, with increasing the coverage of glass particles by nanoparticles, the rate of recovery increased as well. They also reduced the contact angle of the nanoparticles with water and reduced the contact angle of the bubble and water by adding a frother with the nanoparticles. Furthermore, they showed that the force required to separate the particle from the bubble increased significantly in the presence of polystyrene nanoparticles. They stated that parameters such as nanoparticle shape, nanoparticle diameter, surface energy, and nanoparticle concentration play an essential role in the design of nanoparticles as a collector [3, 7, 16].

In another study, the hydrophobic polystyrene nanoparticles based on imidazole groups were used for the flotation of an ultramafic ore (Pentlandite). The results showed that although nanoparticles have a higher coagulation rate, they could be as successful as potassium amyl xanthate [17]. Moreover, surfactants have a significant effect on the performance of nanoparticles. Surfactants can have a significant effect on recovery by affecting the nature of nanoparticle surfaces, foamability, and foam stability. If the presence of a surfactant has a synergistic effect on nanoparticles, it can improve the flotation process. According to *Yang et al.*, the presence of SC surfactant along with alumina nanoparticles had a synergistic effect of surfactant on nanoparticles and improved foamability and process efficiency. Besides, surfactant factors such as surfactant type, anionic or cationic factors, and pH can have a vital influence on flotation recovery [18-21].

As mentioned earlier, pH has a vital effect on nanoparticle activity in the flotation column. According to the results of *Hajati et al.*, changes in the pH of the environment have a significant effect on the performance of nanoparticles as a secondary collector. The results showed that the maximum recovery rates calculated at pH 1.5, 6, and 10.5 were 24%, 17%, and 13%, respectively. Acidity (pH) is a key parameter in collector attraction. In the presence of a nanocollector, we can increase the recovery with the aid of physical and chemical attraction in different pH ranges. For example, in the presence of talc
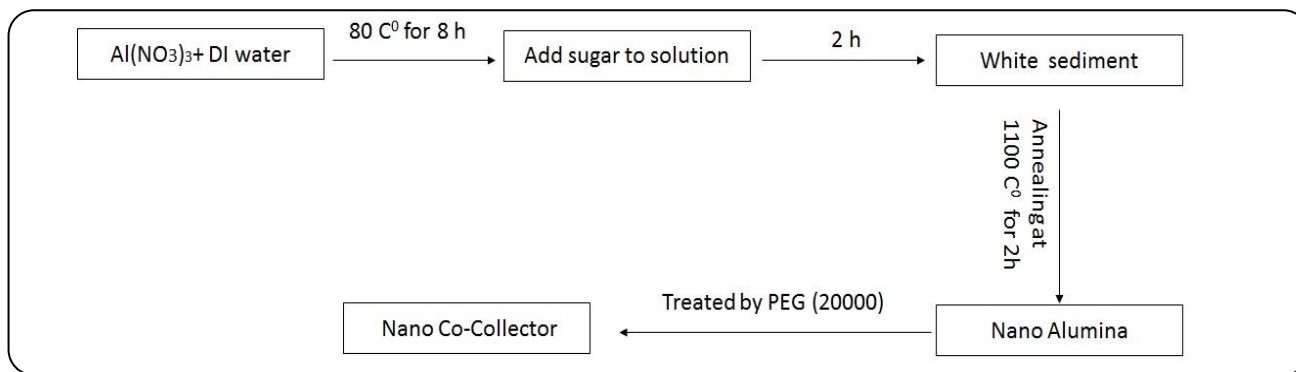
Fig. 1: Diagram of the nanoparticles synthesis process of alumina nanoparticles

and quartz, the pH must be adjusted so that the surface charge of these minerals is reversed and physical adsorption takes place. In the case of diamine as a collector and pH > 4.7, the attraction between collector and quartz minerals occurs via hydrogen bonding. In this paper, the effect of the presence of alumina nanoparticles as a co-collector on the recovery of copper from its mineral is investigated. Also, acidic and alkaline surface modifiers are used to increase efficiency and the effect of collector dosage is investigated [22].

To increase the recovery of sulfide-oxide copper ore, alumina nanoparticles were synthesized by the vaccination method, followed by using SDS surfactant to improve their performance along with Potassium Amyl Xanthate (PAX) collector. Moreover, the effect of pH and nanocollector dosage was investigated.

EXPERIMENTAL SECTION
Materials

Sodium silicate (Na_2SiO_3), sodium sulfide (Na_2S), Potassium Amyl Xanthate (PAX), alumina nanoparticles, polyethylene glycol (PEG), and sodium dodecyl sulfate (SDS) were used as a dispersant, sulfiding agent, molecular collector, nano-collector, and frother, respectively. Calcium hydroxide powder was also used to adjust the pH.

Methods

The ore prepared based on atomic absorption analysis (Varian AA800, AA240) contains 2.64% copper, of which 1.64% is oxide copper and 1.00% is sulfide copper.

Mineralogical studies were performed to identify the ore-forming minerals. In all of the sections in reflective light, chalcopyrite is the main mineral. Chalcopyrite is often

intact and is not converted to secondary minerals. In some cases, especially in the margins of some malachite crystals, it was converted to the chalcocite and covellite minerals.

Another primary sulfide mineral is Bornite. This mineral, which was observed with low frequency and as a co-growth with Chalcopyrite appears to have formed simultaneously with Chalcopyrite. Copper oxide minerals (malachite) are also present in the samples. Other minerals present in the ore include quartz, chlorite, rutile, sericite, pyrite, carbonated minerals, iron oxides, and gangue.

Synthesis of gamma-alumina nanoparticles

In this section, alumina nanoparticles were utilized. Although these nanoparticles are highly hydrophobic naturally, due to working in an aquatic environment, their nature should be altered to hydrophilic. Therefore, the surface of nanoparticles is modified by various hydrophilic agents such as organosilane compounds, amines, fatty acids, polyethylene glycol, and other nanoparticles. Among these modifiers, polyethylene glycol with a molecular mass of 20,000 could have a better response.

Synthesis of $Al_2O_3/PEG20000$ via chemical method

About 3-4 gr of polyethylene glycol with a molecular mass of 20,000 was dissolved in water and alcohol solution with the aid of a heater stirrer at 40°C Also, 0.1-0.3 g of synthesized alumina nanoparticles were hydrophilized with stearic acid in water and alcohol solution and was mixed for 1-2 h separately. After a while, these two solutions were mixed and 10 mL of LA3 (e.g. a 3 M autocalcined Lauric acid) with a surfactant solution of polyethylene glycol 200 as an auxiliary reagent was added to the. After heat refluxing the solution for 6-7 h, it was

Table 1: The size distribution of feed

Size Range (µm)	Weight (%)	Cumulative Oversize (%)	Cumulative Undersize (%)
+125	2.6	2.6	97.4
+106 -125	15.8	18.4	81.6
+90 -106	8.4	26.8	73.2
+75 -90	10	36.8	63.2
+53 -75	11.6	48.4	51.6
+38 -53	13.6	62	38
-38	38	100	0
total	100		

Table 2: Conditions of reagents in flotation tests

Reagents	Dosage in rougher (g/t)	Dosage in scavenger (g/t)	Cond. time in rougher (min)	Cond. time in scavenger (min)
Sodium silicate	500	-	4	-
Sodium sulfide	1000	-	7	-
PAX	90	45	4	2
Nanoparticles	Refer to Table 4	Refer to Table 4	4	2
MIBC	110	55	1	1

hydrothermalized at 75 ˚C in the oven for 4 days. In the next step, the solvent was evaporated completely and dried in an oven at 95 ˚C. The result is a light brown water-soluble product. Fig. 1 shows diagram of the nanoparticles synthesis process of alumina nanoparticles.

Production of F3 stock solution

F3: About 5 mL of alumina nanocomposite synthesized with polyethylene glycol 20000 was dissolved in 10 mL of 5 wt.% SDS surfactant. Stirring was continued until achieving a uniform transparent solution. The pH of the stock solution was set to 5.

F3 acid: With the aid of HCL solution (30%), pH was set to 2-3. HCL was added to a certain amount of F3 solution and F3 acid was prepared.

F3 alkali: The addition of KOH solution (30%) to the rest of F3 solution and stirring, F3 alkali with a pH range of 11-12 was achieved.

Flotation method

The ore was crushed with jaw and roller crushers and then milled with a rod mill. The size distribution of the powdered ore indicates that 80% of the particles are smaller than 112 µm (d_{80} = 112 µm). The prepared powder was used as feed in flotation tests. Table 1 shows the size distribution of the flotation feed.

Rougher and scavenger flotation tests were performed in a Denver laboratory cell with a volume of 2 liters, a solid content of 15%, and a rotor speed of 1000 rpm. The reagents used were sodium silicate, sodium sulfide, PAX collector, nanoparticle, and MIBC frother, in the order of their appearance. The pH of the pulp was adjusted to 10.2 using calcium hydroxide powder for rougher and scavenger (the weight of feed entering rougher was 300 g in each test). Also, the amount of copper in all flotation tests was determined by atomic absorption analysis. The dosage and conditioning time for reagents in flotation tests are given in Table 2.

The reagents conditioning time in rougher was 4, 7, 4, 4, and 1 min for sodium silicate, sodium sulfide, PAX, nanoparticles, and frother, respectively. Also, the concentrate was collected for 13 min. Conditioning time in the scavenger was 2, 2, 1, and 13 min for PAX, nanoparticles, frother, and the froth collecting time, respectively. It needs to be pointed out that the conditioning times of these parameters were selected based on a series of primary experiments and previous works published in this field [28, 29].

Recovery for each experiment was calculated using Equation (1):

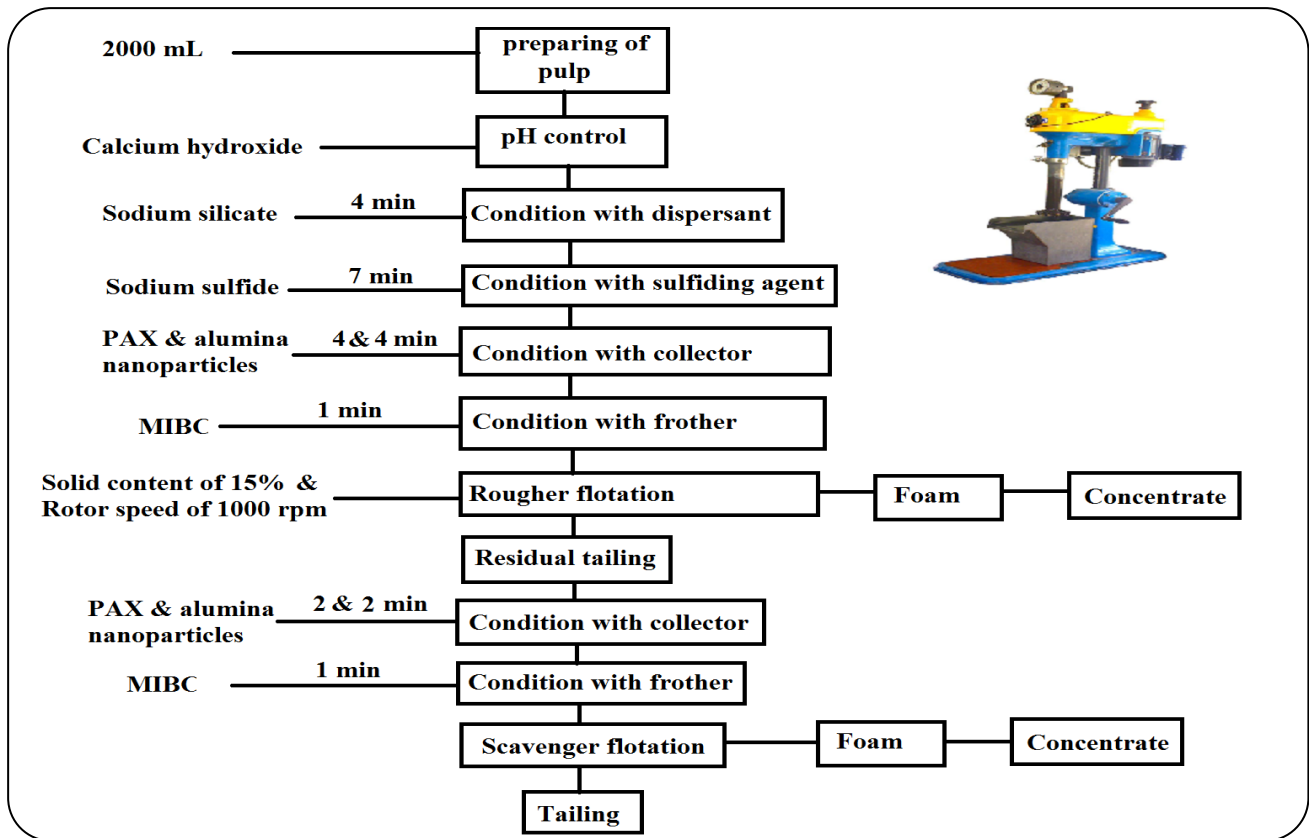$$R_t = \frac{(Ff - Tt)}{Ff} \times 100 \tag{1}$$

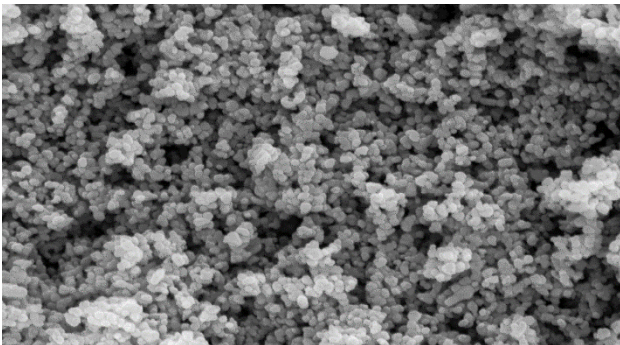*Fig. 2: Processing of the experiment and flotation reactor*

Fig. 3: FESEM image of alumina nanoparticles with spherical morphology

where R_t is the total recovery, F is the weight of feed (g), T is the weight of tailing (g), f is feed grade (%), and t is the final tailing grade (%). Processing of the experiment and flotation reactor was schematically shown in Fig. 2.

RESULTS AND DISCUSSION

Results of nano-alumina synthesis

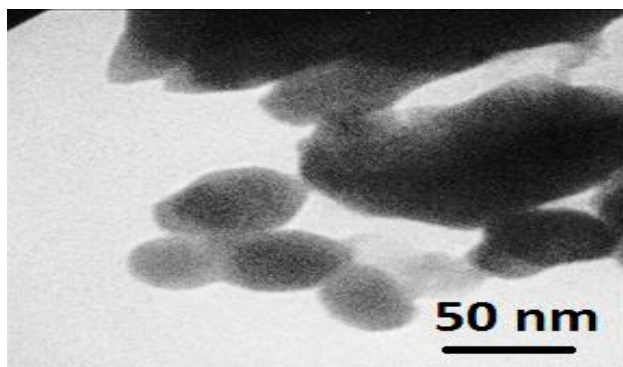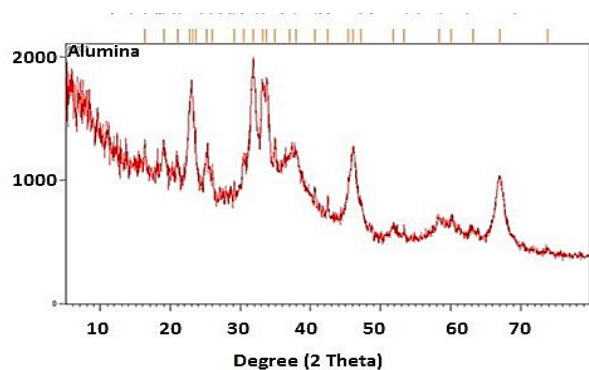*Characterization of alumina nanoparticles by electron microscopy*

Fig. 3 shows the FESEM image of nano-gamma alumina with spherical morphology. As can be seen from Fig. 4, the nanoparticles are between 60 and 50 nm in diameter. Spherical aluminum nanoparticles are synthesized here at a pH of 7 (neutral). In neutral pHs, there is no preferred growth of crystalline plates for gamma-alumina and all plates grow at the same rate. Therefore, in these conditions, the final morphology of gamma-alumina will be spherical. Neutral pH is used in most of the work done to synthesize spherical alumina nanoparticles. Therefore, the results obtained in this study are in agreement with the results of other studies. FESEM images also show that nanoparticles are highly cohesive. The reason for calcinating the samples at high temperatures are the formation of the gamma-alumina structure and the removal of impurities.

Fig. 4 also shows a TEM image of a spherical nano-gamma alumina, which is in agreement with the FESEM results. As can be seen from the image, the morphology of the spherical nanoparticles and their diameter is between 60-50 nm.

Table 3: Results of flotation test without nanoparticles

Test No.	Products	Yield (%)	Cu Grade (%)	R_t (%)
1	Rougher concentrate	3.47	25.59	53.35
	Scavenger concentrate	2.57	15.68	
	Tailing	93.96	1.32	

Fig. 4: TEM image of alumina nanoparticles with spherical morphology

Fig. 5: XRD spectrum of spherical alumina nano-gamma using hydrothermal method

Characterization of alumina nanoparticles with X-Ray Diffraction (XRD)

The XRD structural analysis is performed to examine the structure formed and to ensure the absence of secondary crystalline phases. As shown in Fig. 5, the nanoparticles formed are the crystalline phase of gamma-alumina. Based on the calculation of the size of the crystals synthesized using the Debye-Scherrer formula, the size of the nanocrystals is about 53 nm. The Debye-Scherrer formula is as follows.

$$D_P = (0.94\lambda)/(\beta\cos\theta)$$

Where λ is the wavelength, which is 1,54060 Å, β is the peak width at half-height, and θ is half the value of the peak that appears at an angle of 2θ.

Results of flotation tests

As a comparison-based test, the flotation of ore was performed without nanoparticles (Table 3). As can be seen in Table 3, the total recovery and final tailing grades were 53.35 and 1.32%, respectively.

As mentioned earlier, alumina nanoparticles were utilized to promote the flotation process. The presence of these secondary collectors (e.g. alumina nanoparticles) and their adsorption on the surface of copper ore particles facilitate the flotation process. The most important effect of the presence of nanoparticles in the flotation process is improving the collision of mineral particles to froth phase bubbles and preventing their separation. In the presence of nanoparticles, valuable ores will be separated from unwanted ones by changing their surface hydrophobicity. Besides, it was proven that the employment of suitable surfactants can play a vital role in nanocollector function. Applying an appropriate surfactant such as SDS could have a better influence on recovery. SDS with strong foam ability has the potential to hydrophobized ore particles and lower their detachment possibility. It has been reported that the use of SDS improves the surface nature of the particles and better bonding of mineral particles to the collector [23, 24]. These results are attributed to the improved foamability and foam stability. According to *Yang et al.*, all these events occur if the surfactant (e.g. SDS) and nanoparticles (e.g. alumina nanoparticles) have a synergic effect on each other [18].

Here, we have used two acidic (e.g. HCL) and alkaline (e.g. KOH)-based modifiers to investigate the influence of PH on flotation recovery and surfactant-nanoparticle response [22, 25, 26]. F3 KOH and F3 acid alumina nanoparticles were used in flotation tests 2 and 3 (Table 4). The total recovery for these nanoparticles was 89.65% and 93.15%, respectively, and the final tailing grade was 0.41% and 0.29%, respectively. By comparing the flotation test recoveries with and without nanoparticles, an increase in recovery was observed in the presence of nanoparticles. This gives us several results. In the presence of nanoparticles as a collector, flotation efficiency will increase and thus enhance the specific surface area of nanoparticles. In other words, after the deposition of nanoparticles on the minerals, because of the specific surface area of the nanoparticles, a high-quality connection is established between the bubble and the minerals. Accordingly, the possibility of detachment will be lowered, leading to the higher flotation recovery

Table 4: Results of flotation tests with nanoparticles

Test No.	Nanoparticle	Dosage of nanoparticle	Products	Yield (%)	Cu Grade (%)	R_t (%)
2	F3 KOH	3 mL	Rougher conc.	24.23	8.57	89.65
		1.5 mL	Scavenger conc.	9.1	1.66	
		-	Tailing	66.67	0.41	
3	F3 Acid	3 mL	Rougher conc.	26.53	8.53	93.15
		1.5 mL	Scavenger conc.	11.07	1.21	
		-	Tailing	62.4	0.29	
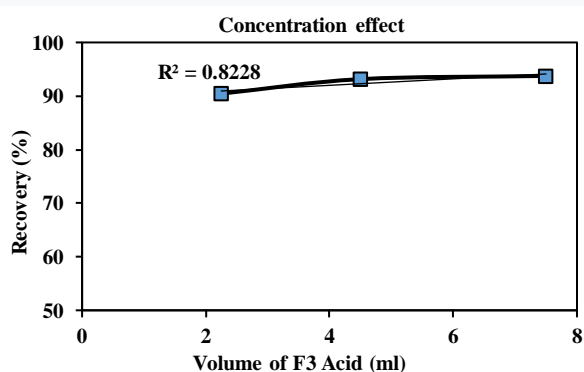
Fig. 6: The effect of F3 acid nanoparticle concentration on flotation recovery
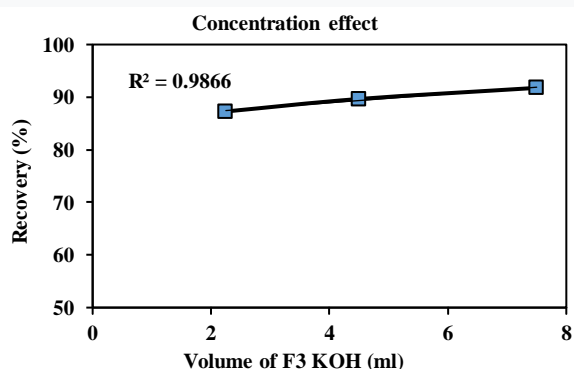
Fig. 7: The effect of F3 KOH nanoparticle concentration on flotation recovery

of copper ore in the presence of nanoparticles compared to flotation recovery without alumina nanoparticles [3, 4, 7, 22, 25]. Moreover, the presence of SDS had a synergistic effect on nanoparticles, improved the foam phase, and thus increased flotation efficiency. Furthermore, it seems that in the presence of SDS, adsorption of oppositely charged surfaces via electrostatic interaction has become easier and, as a result, the surfaces become more hydrophobic [18, 27, 28].

Recovery in the presence of F3 KOH nanoparticles increased from 53.35% to 89.65%. Also, for F3 acid, it increased from 53.35 to 93.15%. These tests have shown that using nanoparticles as a co-collector has a good and promising result in increasing the recovery rate and can be considered a potential for this work. Higher recovery in F3 acid nanoparticles compared to F3 KOH can be the result of better bonding of nanoparticles and mineral particles to the froth phase. In this process, acidity modification of alumina NPS with HCL caused more attachment between SDS and NPS, leading to the production of more surface and a stronger connection with the froth phase. According to *Hajati et al.*, higher recovery in acidic mode than in alkaline mode can be related to surface charge. In the presence of HCL, the charged surface of alumina nanoparticles and SDS particles is more opposed and has caused a stronger bond between them. However, in the other cases (acidity modification of alumina NPS with KOH), this difference (surface charge of alumina NPS and SDS) is less and has led to a weaker connection. As a result, with a stronger connection in acidic mode, the probability of separation of minerals from the froth phase (due to the increase in specific surface area) will increase the flotation efficiency in acidic mode [2, 22, 25].

The effect of the concentration of F3 Acid and F3 KOH nanoparticles on flotation recovery

The effect of F3 acid nanoparticle concentration on flotation recovery was investigated in 2.25, 4.5-, and 7.5-mL volumes (for rougher and scavenger with a ratio of 2:1). Fig. 6 shows that by increasing the concentration of nanoparticles, the recovery of flotation increases as well. This increase in recovery continues until the 4.5 mm of nanoparticle and then becomes almost constant. This could be due to particle aggregation, changing pulp viscosity, entrainment, or longer bubble resistance time. Recovery

in these tests was 90.45%, 93.15%, and 93.79%, respectively.

Also, investigating the effect of F3 KOH nanoparticle concentration with the same volumes (Fig. 7) reveals that the recovery of flotation with the help of this nanoparticle increases with increasing concentration, but it does not reach a constant level. Recovery in these experiments was 87.28%, 89.65%, and 91.76%, respectively. These results also confirm the nanoparticles' ability to improve copper sulfide-oxide mineral floating. It seems that increasing alkaline-modified NPS has had a good effect on particle and bubble connectivity and increased recovery. Besides, the adjustment of pH in the presence of KOH has led to changes in the surface charge of nanoparticles. So, the surface charge of alumina nanoparticles is the opposite to the surface charge of SDS particles and has caused these two to be attracted to each other. Furthermore, due to the presence of some charge on the surface of the set of particles (alumina NPS and KOH) and their buoyancy load, it causes repulsion between them and prevents adhesions and aggregation, which is a factor in reducing recovery. That is why the recovery in this case has increased [22, 29].

CONCLUSIONS

In this study, gamma-alumina nanoparticles were produced by the chemical method and were applied in the flotation process for enhancement of oxide copper recovery. To improve the attachment of particles and bubbles in flotation and hydrophobicity of copper ore particles' surface, alumina nanoparticles were utilized as co-collectors along with PAX. The results show the synergic effect of SDS reagent with alumina nanoparticles in both acidic and alkaline pH. Flotation recovery with PAX as a basic collector was about 53.35%, while the recovery of oxide-sulfide copper ore in the presence of SDS-modified nanoparticles in the alkaline and acidic states was 89.65% and 93.15%, respectively. With the aid of nanoparticles as co-collectors, the specific surface area of minerals will increase. Therefore, the quality of the connection of mineral particles with the bubbles of the froth phase will be improved and the possibility of separation of minerals from the bubbles will be reduced. The higher the recovery in the acidic state, the higher the opposite surface charge and the interaction between nanoparticles and modifiers (surface and reagent particles). Therefore, they will attract each other because of the higher opposite surface charge. Also, the effect of nanoparticle dosage in acidic and alkaline modes was investigated. In alkaline mode, the addition of modified nanoparticles (2.25 to 7.5 mL) led to recovery promotion from 87.25 to 91.76%. In the acidic state, increasing the concentration initially increased the recovery but then remained constant. Particle aggregation, changing pulp viscosity, entrainment, or longer bubble resistance time could be the reason for this result.

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