EFFECTS OF OXIDE NANOMATERIALS USED IN FLOTATION PROCESS IN WASTEWATER TREATMENT

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Abstract. – Effects of oxide nanomaterials used in flotation process. Important challenges in the global water situation, mainly resulting from worldwide population growth and climate change, require novel innovative water technologies in order to ensure a supply of drinking water and reduce global water pollution. For this purpose, highly advanced nanotechnology offers new opportunities in technological developments for advanced water and wastewater technology processes. This paper presents an important method used in the wastewater treatment and in the mineral separation, named the flotation. Also, this paper presents the factors that influence the froth flotation process, such as: nanoparticle hydrophobicity, nanoparticle diameter, particle softness etc.

Key-words: nanomaterials, flotation process, froth flotation, hydrophobicity, nanoparticle diameter, bubble size

1. INTRODUCTION

The global water situation is dependent on the growth of the world population and global climate change. So, the constant growth of the world's population, which is estimated to be nearly doubled in 2050, will lead to a predicted needed growth of agriculture production of 70%, by 2050. Thus, taking into account that for agricultural irrigation are already accounted the main part of the world's freshwater withdrawals, the demand for fresh water is growing dramatically. Around 64 billion cubic meters of fresh water are consumed every year. Thus, important challenges in the global water situation, mainly resulting

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from worldwide population growth and climate change, require novel innovative water technologies in order to ensure a supply of drinking water and reduce global water pollution. For this purpose, highly advanced nanotechnology offers new opportunities in technological developments for advanced water and wastewater technology processes (Gehrke et al., 2015).

The flotation process has always been considered one of the most effective techniques for particle and fats separation (Ramirez et al., 1999). This process of flotation represents the water treatment process based on the adsorption or attachment of materials on the surface of gas bubble passing through a solution or suspension.

At the beginning of the 20 century, a new technology named froth flotation was developed and used for the concentration of sulfide minerals. After that, this method has been used also for the processing of nonsulfide ores (such as oxides, carbonates, silicates), soluble minerals (halite and sylvite) or for energy minerals (coal and bitumen). Another application of the method, developed in recent years, was for several nonmineral applications, like wastewater treatment, resource recovery from industrial wastes or deinking of paper for recycling (Ramachandra Rao, 2004).

The nanotechnology can be used in the mineral separation which is a challenge. It provides a more efficient method to separate gold, silver, copper and other valuable materials from rock and ore. This method assume the employing of hydrophobic nanoparticles to replace conventional low molecular weight, water-soluble flotation collectors.

2. THE FORTH FLOTATION PROCESS

Through the technique named froth flotation, nearly 450 million tons of minerals are processed each year. By this method, mineral ores are crushed into small particles and floated in water containing “collector” substances that can attach to the valuable particles and determine them to reach to the bubbling top of the water where they can be easily skimmed off (24).

In one paper is described this technology, the froth flotation (Fig. 1), where hydrophobic nanoparticles adsorb onto much larger, hydrophilic mineral particle surfaces to facilitate attachment to air bubbles in flotation. By the adsorption of 46 nm cationic polystyrene nanoparticles onto 43 μm diameter glass beads, a mineral model, it was realized almost the complete removal of the beads by flotation. So, the high flotation efficiencies is proved by the about 5% coverage of the bead surfaces with nanoparticles. By micromechanics it was measured the maximum force required to pull a glass bead from an air bubble interface into the aqueous phase, and the results show that the pull-off force was 1.9 μN for glass beads coated with nanoparticles, while for clean beads the force was 0.0086 µN (Yang et al., 2011).

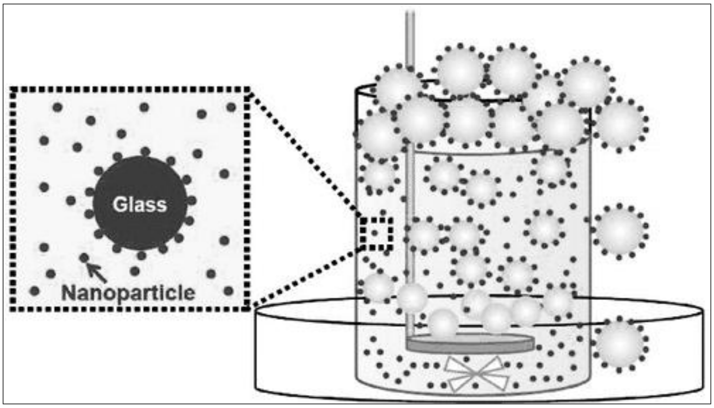

Figure 1. The mechanism of froth flotation (Yang et al., 2011)

Another study shows that the nanoparticle hydrophobicity has an influence on the froth flotation process (Fig. 2). Thus, the study presents that the hydrophobicity of the nanoparticles influence the ability of polystyrene nanoparticles to facilitate the froth flotation of glass beads. In order to probe the hydrophobicity of hydrophilic glass surfaces decorated with hydrophobic nanoparticles, were made contact angle measurements.

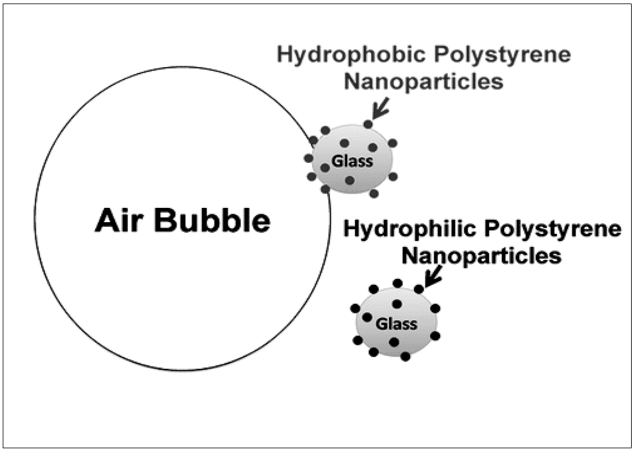

Figure 2. The influence of nanoparticle hydrophobicity on froth flotation, (Yang and Pelton, 2011)

Thus, it was measured the sessile water drop advancing angles, θa, and the attached air bubble receding angle measurements, θr. It was observed that the flotation recovery, which represents a parameter for the efficiency of the flotation process, increased with increasing values of each type of contact angle, in the case of glass surfaces saturated with adsorbed nanoparticles. As expected, the advancing water contact angle on nanoparticle-decorated, dry glass surfaces increased with surface coverage, the area fraction of glass covered with nanoparticles. However, with higher nanoparticle coverages the water did not completely wet the glass surfaces between the nanoparticles. A series of polystyrene nanoparticles was prepared to cover a range of surface energies. In order to rank the nanoparticles in terms of hydrophobicity, the water contact angle, θnp, was measured, on smooth polymer films realized by organic solutions of dissolved nanoparticles. Glass spheres were saturated with adsorbed nanoparticles and were isolated by flotation. The high flotation recovery (Fig.3) was obtained at the nanoparticle with the minimum water contact angle between $51° < \theta npmin \leq 85°$ (Yang and Pelton, 2011).

Another factor that affects the forth flotation process is represented by the nanoparticle diameter, as it is shown in another study. Thus, the researchers study the dependence between the nanoparticle diameter and the ability of polystyrene nanoparticles to promote glass bead flotation.

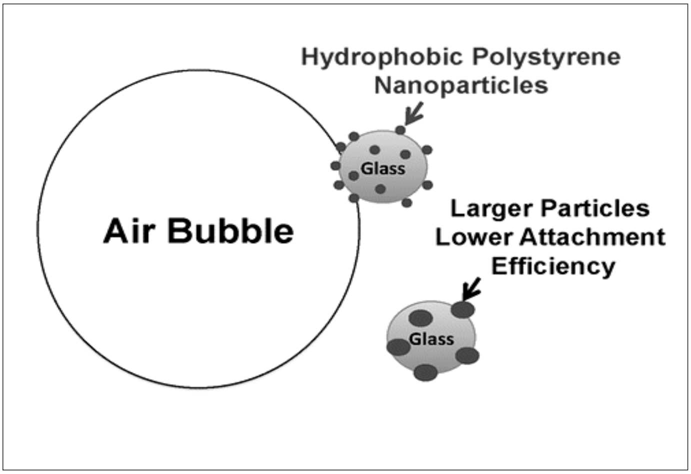

Figure 3. The influence of nanoparticle diameter on froth flotation, (Yang et al., 2012).

By all the experiments, it was observed that smaller nanoparticles were more effective flotation collectors, even when compared at constant nanoparticle number concentration. The efficiency of nanoparticles with smaller diameter is obtained due to the following actions. In first place, it was proved that smaller particles deposit more quickly giving more effective flotation in those cases where nanoparticle deposition kinetics is rate determining. In second place, the mean distance between neighboring nanoparticle surfaces decreases with particle diameter, for a given coverage of nanoparticles on the glass beads (Yang et al., 2012).

The forth flotation process is also affected by the softness of the nanoparticles, as it can be observed by another study. In this study it is shown that the ability of the nanoparticles to promote air bubble attachment and perform as flotation collectors was significantly greater for softer nanoparticles, when the nanoparticle size, surface charge density and hydrophobicity were approximately constant. This conclusion can be explained by the fact that softer nanoparticles were more firmly attached to the glass beads or mineral surface because the softer particles had a greater glass/polymer contact areas and thus stronger overall adhesion (Fig. 4) (Yang et al., 2013).

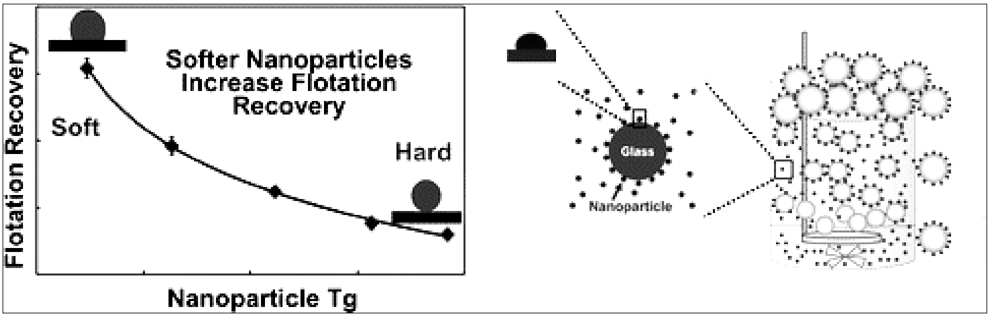

Figure 4. The influence of particle softness on the froth flotation, (Yang et al., 2013).

The froth phase ability to transport the hydrophobic mineral particles into the concentrate launder is strong related to the structure and stability of the phase. Thus, the froth stability, bubble coalescence and bubble size distribution are parameters that determine the separation efficiency and selectivity of the flotation process (Schwarz and Grano, 2005; Gupta et al., 2007; Zanin et al., 2009; Farrokhpay, 2011). Toghether with the physical and chemical factors of the froth flotation, the frothers has an important influence on the flotation rate, grade, recovery, water recovery and bubble size distribution. The frothers ability to prevent bubble coalescence leads to the most important effect of them on flotation, which is the effect on bubble size (Laskowski, 1998; Cho and Laskowski, 2002; Grau et al., 2005; Harvey et al., 2005; Nguyen et al., 2006; Wang and Yoon, 2006; Gupta et al., 2007).

So, it can be said, regarding the researches made in this field, that recovery of flotation and froth phase performance are strongly dependent of froth stability, bubble coalescence, froth mobility, entrainment and drainage of particles (George et al., 2004).

Another conclusion resulted from various studies is that the froth stability is influenced toghether by the type and concentration of the frother used in the flotation and by the characteristics of the particles present in the froth (Nguyen and Schulze, 2004; Pugh, 2005; Grau et al., 2005; Schwarz and Grano, 2005; Nguyen et al., 2006; Gupta et al., 2007; Zanin et al., 2009; Farrokhpay, 2011).

Some researchers studied the changes in bubble size in the froth zone of a flotation column and found the bubble growth rate is influenced by the degree of hydrophobicity of particles present in the froth zone. Moreover, the maximum froth stability was obtained while it was utilised moderately hydrophobic particles (Ata et al., 2003). Another study shows that fine quartz particles rendered bubbles to be more resistant to coalescence and promoted the production of the stable froth (Tao et al., 2000).

The coarse particles, show other researchers, are the only that can perform like buffers between bubbles and prevent bubble coalescence, leading to a better froth stability (Tao et al., 2000). Another study reported that, in order to obtained a more stabile froth, it is necessary to use more hydrophobic particles ((Tao et al., 2000). In another paper, studying the same influence, the authors observed that the particles of intermediate hydrophobicity (of contact angle ~65°) would increase froth stability, while more hydrophobic particles ($\theta > 90°$) would destabilise the froth and more hydrophilic particles ($\theta < 40°$) would not influence the froth properties (Tao et al., 2000).

A research was made in order to investigate the usability of nanomaterials as a froth stabiliser in mineral flotation. Thus, an experimental study was performed using a froth column and a modified flotation cell. In the experiments were used four different nanomaterials: SiO_2, TiO_2, Fe_2O_3 and Al_2O_3. The froth column tests were carried out to measure the Sauter-mean bubble size and dynamic froth stability under different operating conditions. Single mineral flotation tests were realized with or without the nanomaterials and using a pure barite sample. In the following figure it is represented the schematic experimental setup.

The results of the experiments shows that the effect of the increase in the froth height on the Sauter-mean bubble size or the bubble coalescence has no important role when are used nanomaterials in all pH values (from neutral to basic).

Also, it was observed that the addittion into the froth phase of supplementary foam containing the nanomaterials is an efficient method in the use of nanomaterials in the flotation experiments.

Another conclusion of the study was that the nanomaterials used for the experiments did not contribute to the flotation efficiency, in the case of shallow froth. Moreover, it was observed a significant increase in barite recovery (7–11%) at deep froth, using the nanomaterials, especially nano-sized Fe_2O_3 and Al_2O_3. So, it can also be said, that an important role is represented by the selection of the nanomaterials type used in the experiments.

As a result of the use of the nanomaterial, the decrease in the flotation performance at deep froths was found to be negligible (Fig. 5) (Cilek and Karaca, 2015).

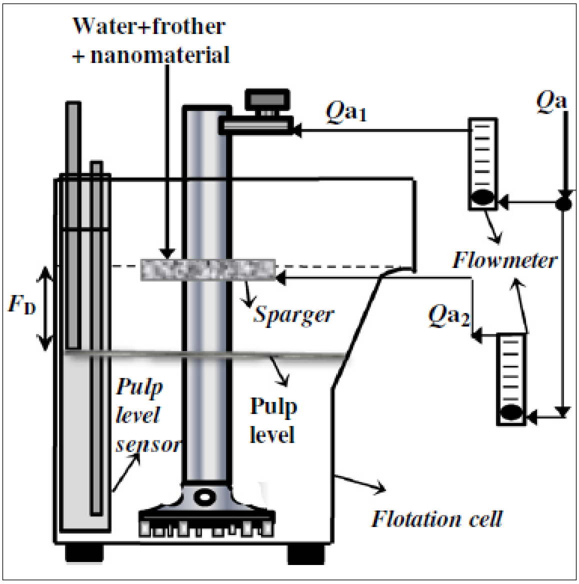

Figure 5. Schematic representation of the experimental setup
(Cilek and Karaca, 2015)

3. CONCLUSIONS

Nanotechnology offers new opportunities in technological developments for advanced water and wastewater technology processes, but also in mineral separation.

Through the technique named froth flotation, nearly 450 million tons of minerals are processed each year. By this method, mineral ores are crushed into small particles and floated in water containing “collector” substances that can attach to the valuable particles and determine them to reach to the bubbling top of the water where they can be easily skimmed off.

It is presented that the hydrophobicity of the nanoparticles influence the ability of polystyrene nanoparticles to facilitate the froth flotation of glass beads.

From literature studies, it was observed that smaller nanoparticles were more effective flotation collectors, even when compared at constant nanoparticle number concentration.

It is also shown that the ability of the nanoparticles to promote air bubble attachment and perform as flotation collectors was significantly greater for softer nanoparticles.

The froth stability, bubble coalescence and bubble size distribution are parameters that determine the separation efficiency and selectivity of the flotation process.

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