

## Recent Progress in the Application of Nanoparticles in Minerals Flotation

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ISSN: 2582-3353



### Publication details

Received: 26<sup>th</sup> October 2020  
Revised: 23<sup>rd</sup> December 2020  
Accepted: 23<sup>rd</sup> December 2020  
Published: 09<sup>th</sup> January 2021

**Abstract:** In this paper, a review of published articles related to nanoparticles applications in mineral flotation has been presented. Nanoparticles have found numerous applications in mineral flotation such as collector, depressant, froth stabilizer as well as modifier. It is evident that nanoparticles can successfully enhance or fully replace novel synthetic chemical surfactants currently in use as additives in flotation of valuable minerals. Nanoparticles that are sufficiently hydrophilic or hydrophobic and colloidally stable in high ionic strength with varying pH solutions are capable of promoting flotation performance. Factors influencing nanoparticles deposition on mineral particles, such as nanoparticle dosage, type, size and conditioning time have significant influence on flotation performance. Mechanisms and key parameters like nanoparticles hydrophobicity, selectivity and nanoparticle-bubble interactions along with the challenges in nanoparticles induced flotation have also been highlighted and discussed. Overall, this review has shown great advances in nanoparticle applications in minerals flotation processes.

**Keywords:** Nanoparticles; Flotation; Hydrophobic; Collector; Froth stability

## 1. Introduction

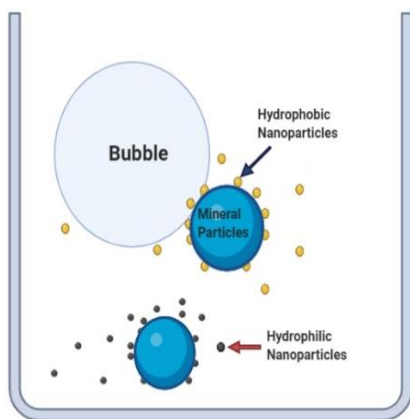
Froth flotation is a very important method for separation of mineral particles based on the differences in their ability to attach air bubbles in a slurry.<sup>[1]</sup> Flotation efficiency is determined by the collision efficiency, attachment efficiency and stability of the bubble-particle aggregate efficiency.<sup>[2]</sup> Therefore, the science of froth flotation can be defined as a sequence of events: 1) Surface modification of minerals by collectors; 2) Collision between the bubbles and the hydrophobic valuable minerals; 3) Adherence of the required mineral to the bubble and; 4) Transport to the surface of the bubble-particle aggregates to join the froth layer.<sup>[3]</sup>

Moreover, three closely associated components are usually investigated in any flotation system to improve the separation efficiency with respect to the recovery and the grade of the final concentrate: chemical (reagents and pH), mechanical (e.g. cell design), and operational (e.g. temperature, pulp density). Among all the factors listed above, more attention has been paid to chemical reagents.<sup>[4-6]</sup> To facilitate the flotation of desired minerals and to reduce the recovery of the undesirable minerals, the use of chemical reagents is important. The most common additives used for flotation include collectors, depressants, frothers and modifiers. Collectors are needed to increase the hydrophobicity at the surface of the valuable mineral and allow a selective separation.<sup>[7]</sup> The collectors most widely used in froth flotation include alkyl dithiocarbonates (xanthates), dioxanthogens, xanthogen formates, thionocarbamates,

alkyl dithiocarbamates, and dithiophosphates.<sup>[8]</sup> Frothers are non-ionic chemical additives, which are added to the flotation cell to form and enhance the froth phase by reducing the interfacial tension at the water-air interface, allowing the bubbles to agglomerate and become stable in the flotation buffer. Poly-propylene glycol derivatives, such as Unifroth series and methyl isobutyl carbinol are the most common frothers used in sulfide mineral processing.<sup>[9]</sup> Also, depressants allow separating the gangue from wanted minerals by depositing onto the most hydrophilic materials. Typically used depressants are polysaccharides such as sodium carboxymethyl cellulose or starch.<sup>[10]</sup>

The continued use of these reagents in general and xanthates in particular has caused growing environmental issues, as carbon disulfide is easily released from decomposition of xanthate and the discharge of excess xanthate is a potential threat to the environment, both humans and aquatic life.<sup>[11-14]</sup> Consequently, engineers and scholars have embarked on a quest for sustainable replacement of these synthetic chemical additives.<sup>[15,16]</sup>

Therefore, new technologies are required to enhance froth flotation in mineral processing. With recent advancements in materials science and nanotechnology, nanoparticles (NPs) have been used to induce superhydrophobicity and highly hydrophilicity<sup>[17]</sup> as demonstrated in Fig. 1. NPs have significant potential as new candidates for generating new types of flotation reagents<sup>[18]</sup> with unique performance for wettability design and control.<sup>[19,20]</sup>



**Fig. 1.** Illustrates the influence of NP hydrophobicity on the ability to facilitate air bubble attachment.

For example, unlike chemical collectors, partial covering of glass surface with cationic polystyrene NPs up to 10% reduced the surface tension to a favorable level of hydrophobicity for flotation, and it was found that the hydrophobic NPs adsorbing onto solid surface gave a high contact angle.<sup>[21]</sup> Also, the presence of NPs can enhance the surface activity and surface adsorption of the surfactants through electrostatic forces or formation of nanostructures.<sup>[22]</sup>

This article reviews novel applications of several organic and inorganic NPs as froth flotation additives. The use of NPs as collectors, depressants and froth stabilizers as well as modifiers have been extensively discussed to address challenges and future outlook of NP reagents in minerals flotation.

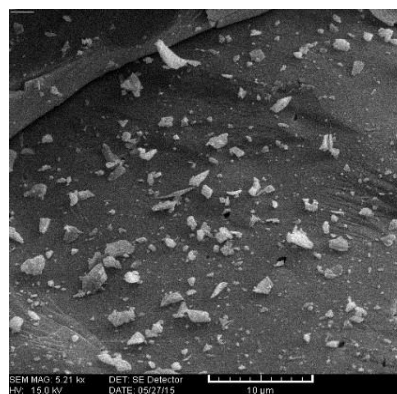
## 2. Nanoparticles in Froth Flotation

### 2.1. Nanoparticles as Collectors

Xanthates are the most commonly used collectors for recovering Cu, Ni, and Zn from sulphide ores. However, xanthates are fossil-based and toxic to the environment. Also, though xanthates are typically successful collectors, when they are associated with complex sulphide ores, they sometimes have poor selectivity between various sulfide minerals.<sup>[23]</sup> In recent years, several types of collectors including NPs have been used and evaluated as flotation collectors. To qualify as NP flotation collector, NPs should be hydrophobic enough and colloidally stable in high ionic strength solutions suitable for commercial flotation.<sup>[24]</sup> Yang et al.,<sup>[21]</sup> reported for the first time describing this new technology where hydrophobic NPs adsorbed onto much larger, hydrophilic mineral particle surfaces which facilitated the attachment to air bubbles in flotation. 46 nm cationic polystyrene NPs adsorbed onto glass beads (43  $\mu\text{m}$ ), acting as a mineral model, enabled almost complete removal of the beads. Interestingly, as little as 5% coverage of the bead surfaces with NPs promoted high flotation efficiencies.

The hydrophobic polystyrene NPs as collectors for pentlandite flotation were evaluated in another research by Yang et al.,<sup>[25]</sup>

Polystyrene NPs with imidazole groups were found to precisely bind nickel ions and facilitated the flotation of pentlandite. The NPs were considerably more able to facilitate the attachment of air

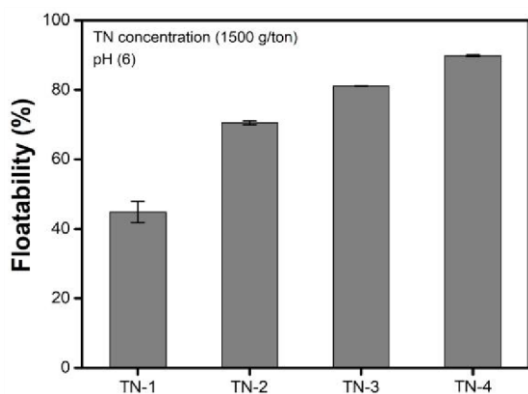


**Fig. 2.** SEM image of talc NPs in different size (white color) on the quartz mineral surface (quartz size; -250, +38, dark color in the background)<sup>[35]</sup>

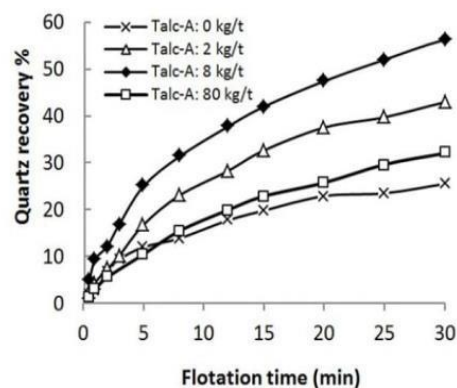
bubbles and more significantly, the attachment was greater for softer NPs. The contact region diameters were determined to be higher in soft particles than in harder Polystyrene NPs.<sup>[24]</sup> These observations led to the hypothesis that weakly adhering NPs can be dislodged from the glass bead surfaces during flotation, leaving footprints.<sup>[26]</sup> It was therefore shown that high NP/glass bead adhesion can minimize NP removal by bead/bead collisions during mixing and flotation.<sup>[27]</sup> Also, these polystyrene NPs were measured as a function of NPs diameter,<sup>[28]</sup> and in all cases, smaller NPs were more effective flotation collectors, even when compared at constant NPs concentration. In cases where NP deposition kinetics was the rate-determining, it was understood that the smaller particles deposited more quickly resulting in effective flotation. As the mean distance between neighbouring NP surfaces decreases with particle diameter, larger and harder polystyrene NPs flotation collectors were shown to be ineffective.<sup>[11]</sup>

It was further reported that the ability of these polystyrene NPs to facilitate the froth flotation of glass beads correlated well to the hydrophobicity of the NPs. The minimum NP water contact angle that gave high flotation recovery was in the range of  $51^\circ < \theta_{\text{npmin}} \leq 85^\circ$ .<sup>[21]</sup> Finally, based on the accumulated evidence, effective polystyrene NP flotation collectors are likely to be  $\sim 50$  nm in diameter, with a soft hydrophobic polymer shell and with surface functional group densities in the order of magnitude of  $0.1 \text{ nm}^{-2}$ .<sup>[29]</sup>

Hydrophobic polystyrene NPs as a collector for coal flotation was as well investigated.<sup>[30]</sup> The polystyrene NPs were used to achieve clean concentrate from floating high ash coal fines. The NPs improved the combustible recovery substantially while retaining the concentrate ash content at a low level. Although clean concentrates were collected, the coagulation of the NPs provided a high dose of NPs. This indicates that it is necessary for practical applications to increase NP colloidal stability and enhance NP deposition selectivity. Tetrahydrofurfuryl-functional polystyrene NP collector in low-rank coal flotation was studied in a similar paper by An et al.,<sup>[31]</sup> Comparatively, tetrahydrofurfuryl-functional polystyrene NPs gave a higher recovery than polystyrene NPs and diesel oil, with the smaller sized tetrahydrofurfuryl-functional polystyrene NPs being more effective flotation collectors.



**Fig. 3.** Malachite floatability as a function of the median diameter of talc NPs (TN (1-4) ranging from 178 to 1462 nm in size). The floatation tests were performed with 1500 g/t talc NPs concentration at pH 6.



**Fig. 4.** Flotation recovery of quartz size -250+38  $\mu\text{m}$  at various dosage of talc NPs versus flotation time at pH 1.5. (Reproduced from<sup>[35]</sup>)

In another study, spherical and anionic polystyrene NPs with thiazole groups were used as collector to selectively enhance microfine chalcopyrite recovery in flotation. The findings of flotation testing revealed the proper collector for the flotation of chalcopyrite was polystyrene NPs. Especially, in neutral and acidic media, the recovery of chalcopyrite exceeded 95%.<sup>[32]</sup> Hajati et al.,<sup>[33]</sup> introduced natural hydrophobic talc NPs (Fig. 2) as a collector in quartz flotation. The talc NPs size and flotation time influenced the dosage requirement of the collector. The quartz particle size reduction improved the flotation recovery and talc size reduction from 567 nm to 235 nm also decreased the amount of required talc from 45 to 1.7 kg/t within 30 min of the flotation time, and achieved a recovery of more than 90%. This observation is also well supported by a recent study that reports that the floatability of malachite increased as the size of talc NPs, used as a collector decreased.<sup>[34]</sup> The smaller talc NPs deposited more on the surface of malachite, which altered the extent of the hydrophobicity that induces interactions with bubbles.<sup>[34]</sup> The dosage of NPs also affects flotation recovery as there was an effective actual recovery (30%) in quartz showed in Figure 4 when 8 kg/t talc NPs were used in comparison with no talc NPs application. The recovery also increased from 41% to 56% after 30 min by increasing the talc NPs dosages from 2 to 8 kg/t at a -250 +38  $\mu\text{m}$  quartz size.<sup>[35]</sup> As a hematite flotation collector, Ranjbar et al.,<sup>[36]</sup> synthesized  $\text{SiO}_2\text{-TiO}_2$  hydrophobic nano-composite, which showed improved recovery and selectivity of hematite.

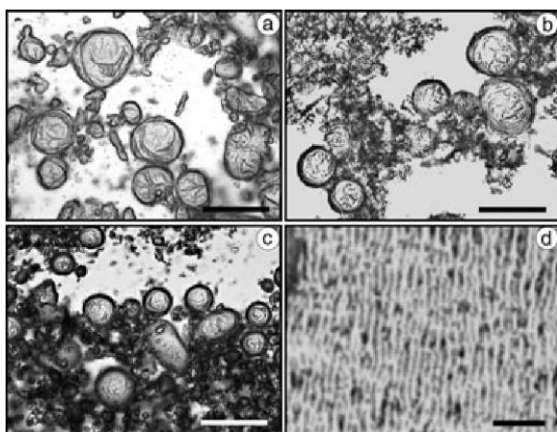
In a recent study,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{TiO}_2$  NPs have been reported to enhance the flotation performance through response surface methodology (RSM) optimization technique.<sup>[37]</sup> The findings obtained from RSM showed that pH of 12 and the NP dosage of 6 kg/t, through  $\alpha\text{-Fe}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3\text{-NP}$ , gave the maximum percentage for Cu recovery and grade. The application of  $\alpha\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$  in particular improved Cu recovery substantially by 8-10% and grade by 3-6%.

Improved coal flotation recovery was also observed when  $\text{SiO}_2$  NPs were used in a flotation process as a collector.<sup>[38]</sup> The flotation recovery of coal with  $\text{SiO}_2$  NPs was significantly higher than with the absence of  $\text{SiO}_2$  NPs. Also, strong selectivity as a flotation collector shown by lignin NPs towards Cu (Chalcopyrite), with total recoveries in Cu-Ni ore during rougher flotation tests exceeded 80%. Lignin NPs

minimized xanthate usage by 50% when floating in Zn-Pb-Cu ore. Moreover, the lignin NPs outperformed xanthates alone, with total recoveries of 91%, 85%, and 98%, respectively, for Cu, Pb, and Zn.<sup>[16]</sup>

It is reported<sup>[39,40]</sup> that amphiphilic nanocrystalline celluloses promoted the recovery serving as a collector for hematite and quartz flotation. The nanocelluloses were shown to work at the same degree at least as an ether amine collector for quartz. In another study, carboxyl-functionalized carbon black NPs acted as collectors in a hydrodynamically simplified Hallimond tube.<sup>[41]</sup> The black carbon NPs influenced malachite flotation greatly, with an increase in malachite floatability even at low concentrations of carbon black NPs. However, at a high carbon black NP concentration (over 2 kg/t), malachite floatability decreased sharply. It was reported that bulk carbon black NPs aggregation decreased the kinetic rate of interaction between the bubbles and malachite.

The capabilities of Fe/Ca/CaO NPs coating and microbubble-integrated froth flotation process for recovery of precious metals was documented.<sup>[42]</sup> The precious metals recovery rate in the flotation process was around 83-89% with Fe/Ca/CaO NP addition. Moreover, the impacts on flotation recovery were studied for various concentrations of Polystyrene/Dodecyl Trimethylammonium bromide latex NP and the immersion time of mineral surfaces. 20-30 min time of immersion was adequate to complete the surface coverage and to ensure the maximum recovery of the flotation process.<sup>[43]</sup> In another work, hexyl amine cellulose nanocrystals were studied regarding its effect on flotation operations under a turbulent system as a sustainable and environmentally safe reagent for quartz flotation. Increased cellulose nanocrystals concentrations (i.e. concentrations of  $0.667 \text{ mg}_{\text{HAC}}/\text{m}^2_{\text{QRZ}}$ ) produced sufficiently hydrophobic quartz.<sup>[44]</sup> In a similar research, a safe green renewable reagent, butyl-amine nanocrystals were synthesized from hardwood kraft pulp, for selective flotation of chalcopyrite and sphalerite. In the analysis, butyl-amine nanocrystals were found to be selective for chalcopyrite, i.e. a collector for this mineral rather than sphalerite when chalcopyrite was mixed with sphalerite. This study provided a positive performance of new nanocrystals-based collector than that of industrial flotation reagents.<sup>[23,45]</sup>



**Fig. 5.** Optical microscopy images of aqueous foams stabilized by silica NPs that contain 32% SiOH on their surfaces. Conditions and time after formation by homogenization: a) no salt, 3 wt/v% particles, 40 h, b) 8.5 mM NaCl, 0.86 wt/v% particles, 5 min, and c) 1M NaCl, 0.37 wt/v% particles, 5 min. Also shown in d) is the image of a planar monolayer of silica NPs (with 50% SiOH) at the air–water surface after compression to a surface pressure of 70 mNm<sup>-1</sup>. The corrugations are parallel to the trough barriers. All scale bars: 50 μm (Reproduced from ref. [59])



**Fig. 6.** Samples of 0.03 wt % alpha olefin sulfonate foam with (right) and without (left) nano ash (<0.05 wt %) after addition of 1 mL of Shell Ondina 919 to the generated foam (Reproduced from Eftekhari et al., 2015).

Overall, the development of NP flotation collectors<sup>[24]</sup> has been designed and applied in higher throughput screening techniques. Automatic screening for the critical concentration of coagulation and contact angle have proven successful in obtaining flotation domain maps in identifying the most promising froth flotation NP collectors. The road to commercially applicable NP flotation collectors leads to an improvement in colloidal NP stability alongside impartation of hydrophobic effects.<sup>[25]</sup>

### 2.2. Depressing Activities of Nanoparticles

Highly hydrophilic NPs have yielded good results as depressants in flotation processes. In order to increase the recovery of phosphorous-bearing minerals, new in-house produced hybrid polyacrylamide-grafted NPs were used to selectively depress silicates from plant tailings by the flotation process.<sup>[46]</sup> Sodium oleate and methyl isobutyl carbinol (MIBC) were used as a collector and frother, respectively. The findings revealed that in the first 4 min and without the need of a pH modifier, P<sub>2</sub>O<sub>5</sub> content in the plant tailings was enriched from 21.6% to 28.6% at a recovery value of 80.5%.

In another study, dicarboxylic acid nanocelluloses were used to efficiently depress hematite. Though the nanocelluloses were found to effectively depress hematite, their depressing activities on quartz were not very effective. According to the authors, the nanocelluloses were also confirmed to have functioned at least the same level as a hematite commercial starch depressant.<sup>[39]</sup>

### 2.3. Nanoparticles as Froth Stabilizers

In a froth flotation process, hydrophobic particles and frothers are essential to maintain a stable froth. In defining the quality of the structure of the froth, NPs have played crucial roles in several studies<sup>[47-50]</sup> including enhanced oil recoveries.<sup>[51-54]</sup> It is found that

the flotation performance (i.e. recovery and grade) strongly depends on the froth stability, bubble distribution, bubble mobility, and froth properties.<sup>[55,56]</sup> If the froth is too stable, then the detachment of affixed material from the froth is difficult, otherwise, the floated material is lost due to the bubble coalescence in the froth. Because of NPs distinct properties and their high surface to volume ratio, they are able to promote froth stability and enhance flotation performance.<sup>[57]</sup>

Interestingly, low concentrations of NPs appeared to improve the foaminess of frothers in flotation columns.<sup>[47,58]</sup> Hydrophobic silica NPs, for example, were dispersed to form very stability foams in water via adsorbing particulate aggregates at the surfaces of micrometer-bubbles.<sup>[59]</sup> The optical microscope image displays bubbles in pure water that are stabilized only by hydrophobic SiO<sub>2</sub> NPs (Fig. 5). Fig. 6 also shows stabilized foam with the addition of (<0.05 wt%) nano ash (100-200 nm) in an alpha olefin sulfonate surfactant.<sup>[58]</sup>

In a study by Hu et al.,<sup>[60]</sup> the static foam stability of two surfactants, cetyltrimethylammonium bromide and sodium anionic dodecyl sulfate, was enhanced with silica NPs (20, 100 and 500 nm). For both cetyltrimethylammonium bromide and sodium dodecyl sulfate, the order of increasing the stability of the foams was: 20 > 100 > 500 nm and 500 > 100 > 20 nm, respectively. Sodium dodecyl sulfate NPs stabilized foams retained their dynamics stability. These observations support theoretical use of NPs in practical flotation.

Four separate nanomaterials, namely SiO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>, were examined on a pure barite sample to determine the usefulness of these NPs as a froth stabilizer in mineral flotation process. The findings of the froth column experiments revealed that the coalescence of the froth bubbles or surface bursting can be greatly minimized with the use of the NPs, despite the rise in froth height. By using the NPs, the negative effect of increasing the froth height on froth recovery became negligible. The nano-sized Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> greatly improved the recovery of the flotation by 7-11% at the deep froth.<sup>[61]</sup> Thus, it is important to select the right type of NPs to be used during flotation. Xiao,<sup>[62]</sup> also reaffirmed that selecting the correct type of NPs can help increase dynamic froth stability and flotation performance for a specific ore. Froth stability and improved



flotation performance was observed in the flotation of complex sulfide ores using  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  NPs. With the addition of  $\text{Al}_2\text{O}_3$ , froth stability increased by about 20%. It also increased Pb grade and recovery by 40% and 4%, respectively. However, in this study,  $\text{SiO}_2$  did not help in increasing the froth stability.

According to a study by Cilek and Uysal,<sup>[63]</sup>  $\text{Al}_2\text{O}_3$  NPs were the best, followed by  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  concerning froth stability and the flotation performance. Furthermore, the flotation recovery improved from 83% to 91%, and the concentrate grade also improved by the usage of  $\text{Al}_2\text{O}_3$  NPs from 44% to 60%. The findings of the experiment also revealed that by using the  $\text{Al}_2\text{O}_3$  NPs, the dynamic froth stability and maximum froth depth can be improved 1.2 to 2 folds.

In another research by Legawiec et al.,<sup>[64]</sup>  $\text{SiO}_2$  NPs (prepared with cationic surfactant – Cetrimonium bromide) application as foam modifiers successfully increased foamability. The NPs introduced into the foam system modified most of the parameters, especially the stability which is necessary for the flotation mechanism. The results demonstrate that there is the possibility to minimize the use of synthetic surfactants, which provides a more environmentally sustainable opportunity when NPs are implemented.  $\text{SiO}_2$  and  $\text{TiO}_2$  NPs in foam stability of non-ionic surfactant Tween-20 was also investigated.<sup>[65]</sup> Foam stability and Half-life of foam were assessed and compared with and without  $\text{SiO}_2$  and  $\text{TiO}_2$  NPs usage. Also examined was the combined effect of the NPs and ethanol on foam stability. For 3 g L<sup>-1</sup> surfactant concentration: foam Half-life of 120 min for  $\text{SiO}_2$  NPs and 78.2 min for  $\text{TiO}_2$  NPs were obtained.<sup>[65]</sup>

#### 2.4. Nanoparticles as Modifiers

Modifiers typically referred to as regulators, are often used to control interactions between pulp collectors and individual minerals. Inorganic colloidal NPs were used as a replacement of caustic soda for the separation of bitumen from ore in flotation process. Kuznetsov et al.,<sup>[66]</sup> stated that biwettable ores in aqueous phase could be stabilized by hydrophilic NPs adsorbing to fine surfaces. Fine solids then shift away from the interfaces between oil and water which reduced the volume of slime coating on liberated bitumen droplets. The reduction in slime coating, which is a significant phenomenon in froth flotation,<sup>[67]</sup> therefore improved bitumen recovery by more than 5% during flotation of low-grade ore. In naphthenic and paraffinic froth processes, addition of NPs had no negative impact on froth quality, as well as on the separation of oil, water, and solids.

Further, in the presence of  $\text{Al}(\text{OH})_3$ -polyacrylamide NPs fine coal particles (+38–75  $\mu\text{m}$ ) with 25.12 wt% of ash were floated, which demonstrated the NPs played a positive role in both coal recoveries and ash rejection. The increase in the dosage of NPs, however, resulted in a decrease in the coal recovery. This problem may be due to the hydrophobic interactions of adsorption of polymer on a coal surface which results in hydrophilic groups being oriented towards the solution and thus, the flotation efficiency decreased.<sup>[68]</sup>

### 3. Nanoparticles-bubble attachment

A bubble-particle attachment mechanism is the control step for effective flotation.<sup>[69-71]</sup> Electrostatic attraction facilitates the natural

deposition of NPs on glass surfaces raising the effective contact angle to promote the adhesion of beads to air bubbles.<sup>[28,72]</sup> Stable NP-bubble attachments occur at particle-bubble distances in the range of tens of micrometers (between 25 and 50  $\mu\text{m}$ ). This shows that NPs can be attached to bubbles in an uncompressive phenomena, while pure particles only, particularly, quartz can be attached to air bubbles under substantial compression.<sup>[40,73,74]</sup> Interestingly, the distances for the successful attachment of hexyl amine cellulose nanocrystal-coated quartz particles exceeded the range of interactions documented to date in literature<sup>[75,76]</sup> and it implies the existence of structural or hydrodynamic phenomena acting between NPs and bubble surfaces.<sup>[71]</sup> There was a major increase in the floatability of the quartz, where recoveries were obtained up to 90%, in the presence of so-called non-compressive particle-bubble attachments.<sup>[44]</sup> Additionally, the bubble-particle attachment time has shown to reduce as NP dosage is increased in coal flotation.<sup>[38]</sup>

### 4. Conclusions

Numerous applications of NPs have been reported and this review has shown that up to now, much progress has been seen in the application of NPs as efficient additives (collector, depressant, modifier and froth stabilizer), with smaller NPs sizes performing better in froth flotation systems.

The use of NPs in minerals flotation process can lead to a substantial reduction of chemical reagent consumption. More so, suitable NPs can be identified to function both as a collector and froth stabilizer. Besides, the NPs are reusable,<sup>[77,78]</sup> and therefore would minimize operation cost.

However, more work should be done before its real industrial applications, such as the techniques for generating more and stabilized NPs in flotation at a low cost and scalable production. Furthermore, the mechanisms in the NP-bubble attachment, selecting the right and more selective NPs for a specific ore as well as efficient recovery of the NPs for reuse needs to be well examined.

### Conflicts of Interest

The author declares no conflict of interest.

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