Effect of bulk nanobubbles on flocculation of kaolin in the presence of cationic polyacrylamide

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Abstract: The study explores the impact of nanobubble flotation technology on fine mineral processes, focusing on its interaction with cationic polyacrylamide (CPAM) in kaolin flocculation. Nanobubbles influence particle size and promote aggregation. Experimental procedures involve bulk nanobubble preparation, kaolin suspension, and CPAM solutions, with analysis of sedimentation rates, turbidity, and zeta potential. Results show accelerated sedimentation and reduced turbidity with nanobubbles compared to traditional methods. Zeta potential measurements and DLVO theory support nanobubbles' role in reducing electrostatic interaction, facilitating flocculation. This research advances understanding in nanobubble-mediated mineral processing, highlighting eco-friendly flocculants and practical implications for optimization.

Keywords: bulk nanobubbles, kaolin, flocculation, cationic polyacrylamide, DLVO theory

1. Introduction

Nanobubble flotation technology is widely used for fine/ultra-fine mineral beneficiation processes such as coal (Chang et al., 2020; Liu et al., 2021; Zhou et al., 2020), pyrite (Wu et al., 2023), chalcopyrite (Ahmadi et al., 2014), graphite (Bu et al., 2018; Ma & Tao, 2022; Nazari et al., 2022), molybdenite (Wang et al., 2022), etc. The introduction of nanobubble in the flotation system improves the apparent size of the fine particles, which is due to the aggregation of fine particles through bridging roles of cavitation nano-bubbles (Calgaroto et al., 2015; Nazari et al., 2019; Zhang et al., 2021; Zhou, et al., 2022a; Zhou et al., 2020). After being modified by nanobubbles, the attachment probability of these particles/aggregates to conventional flotation bubbles is improved, effectively increasing the flotation efficiency. It is notable that the applications “nanobubbles” in some related literatures includes both micro- and nano-scale bubbles (Bu et al., 2022; Etchepare et al., 2017; Zhou et al., 2022a). Meanwhile, nanobubbles applied in mineral flotation can be divided into bulk and surface nanobubbles (Alheshibri et al., 2016; Li & Zhang, 2022a, 2022b; Zhou et al., 2022b). Surface nanobubbles can often be generated in situ on hydrophobic mineral surfaces by hydrodynamic and acoustic cavitation (Bu & Alheshibri, 2021; Zhou, 2018; Zhou et al., 2009). It is reported that no aggregates were detected when only nanobubbles were present in the bulk solution (Zhou et al., 2022a). Compared to bulk nanobubbles, the enhancement mechanisms in nano-bubble flotation performance are mainly related to surface nanobubbles, which can be attributed to that the in-situ generation of surface nanobubbles can produce a higher attachment efficiency with hydrophobic mineral particle surface (Tao, 2022; Zhou, 2018; Zhou et al., 2009). It is demestated that collectors can coat surfaces of nanobubbles, which can also facilitates the fine particles’ aggregation. (Calgaroto et al., 2014; Zhou et al., 2020).

Similar to hydrophobic particles, the attachment of hydrophilic particles with bubbles can also be observed in contactless flotation (Derjaguin & Dukhin, 1961). Fan et al. (2004) proposed that the attachment of purified quartz particles to air bubbles in surfactant-free aqueous solutions is possibly
due to that the OH$^-$ ions on air bubble surfaces formed hydrogen bonds with silicon and oxygen atoms in $\equiv$Si–O–Si$\equiv$ or with the adsorbed OH group on quartz surfaces. Jiang et al. (2010) proved that electrostatic attraction plays an important role on the attachment between a hydrophilic solid and a bubble. Wu et al. (2015) anticipated that the hydrophilic alumina particles and bubbles are most likely attracted to each other at the deep primary minimum of interaction potential without the formation of three phase contact line. Huang and Yoon (2020) experimentally reported that the wetting films formed between a air bubble and a hydrophilic silica plates are stable due to both the repulsive van der Waals and electrical double-layer (EDL) forces. In addition, it is demonstrated that the presence of bulk nanobubbles can promote the formation of porous kaolinite cluster (Lei et al., 2020; Li et al., 2020; Żbik & Horn, 2003). However, it is notable that the overall increase of attachment area (Aa) induced by nanobubbles was only to a marginal extent (less than 1%) (Zhou et al., 2022).

Coagulation-flocculation is one of the physico-chemical methods employed in industries to destabilize particles that are dispersed in water (Lagaly & Ziesmer, 2003; Lee et al., 2010). The coagulation of clay dispersions can be described by the DLVO theory and explained by the reduction of electrostatic interaction energy, which is commonly achieved by the addition of salt ions (Agno Hernández, 2023; Mishchuk et al., 2020). The use of flocculants is important and efficient for clay settling, which is attributed to the formation of large flocs induced by the flocculation of clay particles (Lee et al., 2014). Synthetic organic polymers such as cationic, anionic, and nonionic polyacrylamide (PAM) have been extensively applied as flocculants in wastewater treatment of mineral processing and papermaking operations, which can form large and strong flocs of clay particles with acceptable settling performance. However, these polymers are non-biodegradable, expensive and sometime cause health hazards (Yang et al., 2016). Recently, the production of environmentally friendly polymers such as such as starch, chitosan, and cellulose have been research focus due to their biodegradability and renewability (Gao et al., 2016; Li et al., 2015; Tian & Xie, 2008; Wang et al., 2009; You et al., 2009). Furthermore, some physical or chemical modifications, such as gelatinization, etherification, esterification, and grafting have been used to develop starch-modified flocculant, which is an environment-friendly flocculant (Ding et al., 2023; Ding et al., 2022; Liu et al., 2017). Compared to conventional flocculants, starch-modified flocculant has a network macromolecule with excellent properties of starch and acrylamide and a wide molecular chain and good thermal stability, which produces a better flocculation performance for wastewater (Su et al., 2016; Yang et al., 2014).

Therefore, the synergistic effect of nanobubbles and flocculants in the flocculation process of clay minerals has not been reported yet. To fill the gap, this article studied the effect of bulk nanobubbles on the flocculation effect of kaolin under the presence of cationic polyacrylamide (CPAM). Firstly, prepare CPAM solutions with pure water and bulk nanobubble water, respectively. Then, the sedimentation rate and supernatant turbidity of kaolin with or without bulk nanobubbles were investigated under different CPAM dosages. Finally, the mechanism of the synergistic effect of bulk nanobubbles and CPAM on kaolin flocculation was discussed through microscope observation and zeta potential measurement.

2. Materials and methods

2.1. Materials

The kaolin sample was purchased from the Hongtu Mining Company (Guangdong, China). CPAM ([\(-\text{CH}_2\text{CH}-(\text{CONH}_2)\)-]_X, 1200 million g/mol) is obtained from Tianjin Zhiyuan Chemical Reagent Co., Ltd. The particle size distribution of the kaolin sample was measured using a laser diffraction particle size analyzer (Bettersizer 3000, Bettersize Instruments, Dandong, China). The particle size distribution of the kaolin sample is given in Fig. 1. The average particle size ($d_{50}$) of the kaolin sample was approximately 2.32 μm.
2.2. Preparation of bulk nanobubbles

The bulk nanobubbles were generated by GWN micro-nanobubble preparation machine (GWN-0.31, Gongyuan Environment company, Wuxi, China). The airflow rate and preparation of the micro-nanobubble preparation machine was selected as 60 mL/min and 10 min respectively. Then, the milky solution was left for 10 min to eliminate the unstable microbubbles. Details concerning the impact of preparation duration and aeration rate on the characteristics of bulk nanobubbles (NBs), along with similar procedure to obtain bulk nanobubble water can be found in the literature (Zhou et al., 2022b). The bulk nanobubble size was assessed via nanoparticle tracking analysis (Nanosight-NS300, Malvern, UK). The size distribution of bulk NBs is shown in Figure 2. Notably, the predominant peak in the bulk NB size distribution falls within the range of 50 to 500 nm.

2.3. Flocculation and settlement tests

CPAM solutions of 0.1% w/v concentration were prepared for flocculation and settlement tests using ultrapure water and bulk nanobubble water, respectively. Kaolin particles (5 g) was dispersed using 250 mL pure water (or bulk nanobubble water) with a magnetic stirrer at 1000 r/min for 4 minutes. Then, 0.5 mL of CPAM solution was added into the kaolin suspension with 2 min stirring time. After that, the kaolin suspension was poured into a 250 mL graduated cylinder. The height of the clarification zone was started recorded after flipping the cylinder 5 times. The turbidity of the supernatant of the kaolin suspension was measured using a WZS-186 turbidity meter (Shanghai Yidian Scientific Instrument Co., Ltd.).
2.4. Zeta potential measurement and polarizing microscopy observation

The supernatant of the kaolin suspension after 2 min settlement time was used for the zeta potential measurement (Zeta Plus, Brookhaven, US). A polarizing microscope (Sunny Optical-Instrument, Zhejiang, China) was utilized to observe the flocs after settlement process. A small number of samples were extracted from the graduated cylinder and placed on a glass slide until the water evaporated, and the samples were observed under the microscope.

3. Results and discussion

Fig. 3 presents the supernatant’s heights and turbidity values of kaolin suspensions with different flocculant dosages in the absence and presence of bulk nanobubbles, respectively. It is observed from Fig. 3 (a) that the supernatant height increases significantly with the increase of the flocculant dosages, which indicates that the settling rate becomes faster. Similarly, the decrease in the supernatant’s turbidity is displayed in Fig. 3 (b) with the increase in the flocculant dosage. Thus, these results indicated that more and more kaolin particles are employed to form large flocs by the bridging effect with the higher flocculant dosage (Zhou et al., 2022). This can also be verified by the images of flocs under different CAPM concentrations in Fig. 4.

With the same flocculant dosage, the dispersed CPAM solution using bulk nanobubble water can produce a higher supernatant height than that of CPAM solution prepared using ultrapure water (Fig. 3 (a)). In other words, the presence of bulk nanobubbles in CAPM solution can promote the sedimentation of kaolin particles. Furthermore, the presence of bulk nanobubbles can significantly decrease the supernatant’s turbidity compared to the absence of bulk nanobubbles (Fig. 3 (b)). The literature reported that the same kaolinite sample settled more slowly in nanobubble water compared to water, which is attributed to the formation of a much lower-density sediment and flocs having by having edge-edge contacts stabilised by gas bubbles (Lei et al., 2020). In this study, the enhancement of bulk nanobubbles can be related to the adsorption of CPAM on bulk nanobubbles. The pre-adsorption of reagent molecules on surfaces of gas bubbles are high-efficient for the bubble-particle interaction of flotation process compared to the conventionally bare gas bubbles (Tao, 2022). As observed from Fig. 4, the application of bulk nanobubbles and CPAM can produce larger flocs compared to the use of only CPAM. This further proves that the synergy roles of bulk nanobubbles and CPAM in the kaolin flocculation process.

It is obvious from Fig. 5 (a) that the application of bulk nanobubbles in CAPM solution preparation can decrease the absolute value of zeta potential of kaolin particles compared to the CPAM solution without bulk nanobubbles. The zeta potential values under the flocculant dosage of 0.5 mL and the particle size of 2.32 μm (d50) were used for the DLVO theory calculation process. The zeta potential of kaolin suspension with the absence and presence of bulk NBs were −23.44 and −15.85 mV, respectively. The calculation equations of Van der Waals potential energy (EA), electrostatic potential energy (EE) and the total potential energy (Et) are expressed by the following formula from EDLVO theory (Ni et al., 2018; Wang et al., 2021).

![Fig. 3. (a) supernatant’s heights and (b) turbidity values of kaolin suspensions with different flocculant dosages in the absence and presence of bulk nanobubbles](image-url)
Fig. 4. The floc images under different flocculant dosages

\[ E_T = E_W + E_E \]  
(1)

where \( E_T \) is the total interaction energy, \( E_W \) is the van der Waals interaction, and \( E_E \) is the electrical double-layer interaction. The specific calculation process of the three interactions will be described in detail.

Van der Waals interaction, \( E_W \), can be calculated according to equation 2:

\[ E_W = \frac{-A_{132}R_1R_2}{6H(R_1+R_2)} \]  
(2)

where \( R_1 \) and \( R_2 \) are the radii of minerals 1 and 2 (\( R_1 = R_2 = 2.32 \mu m \)), \( H \) is the interaction distance between minerals 1 and 2, \( A_{132} \) is the Hamaker constant of the minerals 1 and 2 in the medium 3

\[ A_{132} \approx (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \]  
(3)

where \( A_{11}, A_{22}, \) and \( A_{33} \) are the Hamaker constants for the interaction of mineral 1, mineral 2, and water (4.0 \( \times 10^{-20} \) J) (Lu et al., 2015) in vacuum, respectively. The Hamaker constant of kaolinite (\( A_{132} \)) in water is \( 4.68 \times 10^{-21} \) J in this study.

Electrical double layer interaction, \( E_E \), is calculated using equation 4:

\[ E_E = \frac{\pi \varepsilon_0 \varepsilon R_1R_2}{R_1+R_2} \left( \phi_1^2 + \phi_2^2 \right) \left( \frac{2\phi_1^2 + \phi_2^2}{\phi_1^2 + \phi_2^2} \ln \left[ 1 + \exp(-2\kappa H) \right] + \ln \left[ 1 - \exp(-2\kappa H) \right] \right) \]  
(4)

where \( \varepsilon_0 \) is the absolute dielectric constant in vacuum (8.854 \( \times 10^{-12} \) F/m), \( \varepsilon \) is the relative dielectric constant of the dispersion medium (for water, 78.5 F/m), \( \kappa \) is the Debye constant, \( \phi_1 \) and \( \phi_2 \) are the surface potential of mineral 1 and mineral 2 that are usually replaced by the zeta potential \( \xi \). Debye constant is considered as \( 3.33 \times 10^8 \) m\(^{-1}\) for the electric double layer interaction calculation (Ni et al., 2018).

As seen from Fig. 5 (b), the presence nanobubbles can reduce the electrostatic interaction energy significantly, which leads to the significant increase in the “energy barrier” between kaolin particles. Therefore, the presence of bulk nanobubbles in CPAM solution is helpful for the occurrence of the flocculation of kaolin particles.

Fig. 5. (a) zeta potentials and (b) DLVO theory calculation results of kaolin particles in using ultrapure water (CPAM) and bulk nanobubble water (NBs-CPAM).
4. Conclusions
The integrated use of bulk nanobubbles and cationic polyacrylamide (CPAM) proves to be a promising strategy for enhancing kaolin flocculation in mineral processing. This synergistic approach fosters effective bubble-particle interactions, resulting in improved settling rates and reduced supernatant turbidity, ultimately enhancing mineral processing efficiency. Zeta potential measurements and DLVO theory calculations substantiate the positive impact of bulk nanobubbles, diminishing absolute zeta potential and amplifying the "energy barrier" between kaolin particles. Microscopic examination affirms the generation of larger flocs with the concurrent application of bulk nanobubbles and CPAM. This study advocates for the amalgamation of bulk nanobubbles with conventional flocculants like CPAM, providing a sustainable and efficient approach for mineral processing applications.

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References


