

Article

Quartz Fine Particle Processing: Hydrophobic Aggregation by Shear Flocculation

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Abstract: This study investigates the hydrophobic aggregation of fine quartz particles through shear flocculation induced by dodecylamine in aqueous solutions. The effect of stirring speed, collector concentration, flocculation time, and pH were investigated. The results showed that the impact of stirring speed on particle aggregation in the absence of a collector is very limited. Quantitative analyses demonstrated that the variation of collector concentration intensified the flocculation process more than the stirring rate. Numerical optimization showed that the large volume occupied by the flocs was 12.3 mL, achieved with a stirring speed of 2135 rpm and dodecylamine concentration of $1.39 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$. The highest quartz particle aggregation was observed at pH 10.5, corroborating the importance of the non-dissociated amine molecules for particle hydrophobization. High zeta potential values did not result in reducing aggregation, indicating that hydrophobicity was the governing factor in the shear flocculation process.

Keywords: shear flocculation; fine quartz particles; hydrophobic aggregation; dodecylamine



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1. Introduction

One of the long-standing challenges of the mineral processing industry is related to the poor floatability of target minerals associated with fine and ultrafine size fractions, which leads to losing them in the tailings. One reason for this is the nature of such particles (e.g., surface heterogeneity, massive surface area, rapid surface oxidation, and low inertia/mass), and another is technological shortcomings (e.g., conventional cells, large bubble sizes, and inefficient turbulence). Detailed discussion regarding their poor recoverability is given elsewhere [1,2]. Losing such fine precious minerals to the tailings also creates low stability of tailings dams, longer thickening time, low efficiency of filtration processes and high acid mine drainage (AMD) in the case of sulfides [3].

Although a wide range of research has been conducted to explore reusing the valuable minerals disposed in tailing dams, no cost-effective and well-accepted industrial technique has been introduced yet. Over the last decades, an array of alternatives has been proposed, and shear flocculation is one of the most extensively studied techniques due to its practicality and suitability. Unlike the usual agglomeration processes, where flocculants or inorganic coagulants are applied, shear flocculation promotes the selective aggregation of the hydrophobized mineral particles by surfactants (also known as collectors) in a stirred system [4].

Flocculation–flotation (FF) is a technique to aggregate the fine particles using a polymer flocculant and hydrophobic interactions to obtain large-size clusters, also known as flocs, to tackle those issues. Hydrophobic aggregates are defined as compact structures with hydrophobic surfaces, behaving in the conventional flotation process as individual particles [5,6]. According to Warren [7], the shear flocculation process is governed by the surface charge of the suspended particles, the degree of hydrophobicity, and the hydrodynamic conditions. Lu and Song [8] claimed that the aggregation process occurs when a high dosage of a collector is added to a system, turning the particles hydrophobic, even in high zeta potential values. In such cases, a strong attractive interaction between particles arises from surface hydrophobization. This becomes the governing factor in the particle–particle interaction instead of the double-layer electrostatic (EDL) repulsion or the van der Waals (vdW) attraction forces. Similar research studies were carried out by Raju et al. [9] and Akdemir et al. [10], demonstrating that the zeta potential does not affect the hydrophobic aggregation and that the particle’s hydrophobicity plays the most important role in shear flocculation. Although aggregation results from hydrophobic attraction forces, mechanical energy must be supplied to the system, allowing the electrically charged particles to overcome the repulsive barriers, therefore forming the hydrophobic aggregates [7].

To selectively separate fine particles by shear flocculation, one should consider the key influential factors. These parameters are the particle surface characteristics, stirring rate and duration, conditioning properties, particle size and mineralogy of the ore, pH, pulp rheology, and surface-active substance features (e.g., dosage, molecular weight, and chemical structure) [11–14]. For instance, it is now known that fine particles require longer and higher stirring time and rates compared to coarse ones [4]. Excessive solid content may cause entrapment of gangue minerals [15]. With respect to the role of influential factors, Yin et al. [16] demonstrated that the shear hydrophobic flocculation of ultrafine hematite was strongly affected by the stirring speed and time, pH, and sodium oleate concentration. It was found that the flotation recovery of hematite flocs was significantly high compared with non-flocculated ultrafine hematite. Also, the hydrophobic flocculation of the ultrafine hematite-sodium oleate system was mainly dominated by electric double-layer repulsive interaction potential and hydrophobic interaction potential. Recently, Wang et al. [17] addressed the formation, breakage, and re-growth of quartz flocs generated by non-ionic high molecular weight polyacrylamide (PAM). They reported that PAM showed a strong flocculation ability to quartz particles ($d_{90} = 11.1 \mu\text{m}$). The peak values of floc size were affected by both the stirring rate and PAM concentration. Furthermore, the degree of floc breakage was highly dependent on the increased stirring rate and the shear time, while floc re-growth occurred to different extents according to the breakage durations and PAM dosages. Very recently, Li et al. [18] investigated the separation of ultra-fine hematite ($d_{85} = 20 \mu\text{m}$) and quartz ($d_{95} = 15 \mu\text{m}$) particles using asynchronous flocculation flotation (i.e., starch + DDA, PEO + DDE, and starch + PEO + DDA). Polyethylene oxide (PEO) and starch were employed as quartz and hematite flocculants, respectively, while Dodecylamine acetate was used as a collector for quartz in the reverse flotation experiments. Greater separation recovery using starch (79%) compared to dextrin (72%) was obtained, which was mainly related to both depressive and flocculation effects of starch.

Song and Lu [19] investigated the influence of the shear rate on fine quartz particles’ hydrophobic aggregation in the presence of dodecylamine (DDA). The authors observed that the maximum degree of aggregation (DoA) occurred at 1000 rpm, with a decline in the DoA for stirring speeds above this value. This result indicated a possible breakage of the aggregates due to the strong shear forces resulting from the agitation. Following this, Patil et al. [20] simulated the experimental data given by Arnold and Warren [21] and Warren [22] on scheelite particles ($<9 \mu\text{m}$). They found that the flocculation rate reduced with an increase in shear rate, and the breakage rate was approximately proportional to the 0.70 power of the floc volume. Thus, providing an optimum shear rate appears to be essential for selective floc-flotation separation. Selective aggregation of fine quartz by polyaluminum chloride as a low-cost inorganic coagulant was examined by

Wang et al. [17]. They found that the addition of polyaluminum chloride at concentrations less than 150 mg/L decreased the entrainment of quartz. Also, their results indicated that the separation efficiency of flotation increased from 74% to 77% when polyaluminum chloride was added prior to the xanthate collector and 80% with xanthate added prior to polyaluminum chloride. Ni et al. [23] studied the role of high-speed shear flocculation on the flotation rate of ultrafine microcrystalline graphite and reported that the shear speed affected the size and quality of graphite aggregates and, accordingly, that the concentrate grade and recovery and also flotation kinetics remarkably improves at high-speed shear flocculation.

Although some studies focus on the shear flocculation of different minerals, there is a considerable lack of information regarding the role of influential parameters. Specifically, there is currently no systematic investigation on hydrophobic aggregation of quartz particles considering all effective factors. Therefore, this study aims to investigate the impact of stirring speed, collector concentration, conditioning time, and pH in the aggregation of quartz fine particles ($80\% < 24.9 \mu\text{m}$) by shear flocculation. Studies on fine quartz particle processing are important to reduce the environmental impact of mining and introduce new techniques that increase fine particle recovery and, consequently, reduce the volume of tailings generated during ore processing.

2. Materials and Methods

2.1. Material, Its Preparation and Characterization

The pure quartz samples (purity $> 99\%$) were collected in the municipality of Mariana, MG, Brazil. The material was comminuted in a jaw crusher followed by a roll crusher. Subsequently, the crushed samples were milled in a porcelain mill to attain a 90% in weight below $38 \mu\text{m}$ (400# US Tyler). After the comminution process, the samples were leached by a concentrated hydrochloric acid (analytical grade, 37% *w/w*) to remove impurities. After leaching, they were washed with distilled water to remove H^+ ions from the mineral surface. This process was repeated until the washing water pH was the same as the distilled water (i.e., $\text{pH} = 7$). This cleaning process was adapted based on the previously reported studies in the literature [24].

The particle size distribution of the quartz sample after comminution was determined using a laser diffraction particle size analyzer, specifically model 1064 manufactured by CILAS, Orléans, France. The samples were treated under sonication for 1 min. The density of the samples was measured using a gas pycnometer, specifically model ULTRAPYC 1200e manufactured by Quantachrome, Boynton Beach, USA, employing helium gas. The sample holder had a volume of 19.38 cm^3 , with an automatic equilibrium time, a target pressure of 17 psi, and a purge time of 4 min.

2.2. Zeta Potential Measurements

Zeta potential measurements were carried out in order to verify how the superficial charge of the quartz particles affected the shear flocculation, in the absence and presence of DDA ($10^{-3} \text{ mol}\cdot\text{L}^{-1}$). These experiments were conducted using a Malvern Nanosizer (Z ZEN 2600). Suspensions of particles ($\sim 10 \mu\text{m}$) were prepared by dispersing the quartz particles in distilled water at a concentration of 0.01% (*w/w*). Sodium chlorate NaCl (10^{-3} M) was used to control the ionic strength of the medium in all zeta potential determinations. Zeta potential values were determined at different pH levels in both the absence and presence of collector solution with a concentration of $10^{-3} \text{ mol}\cdot\text{L}^{-1}$. For each condition, two sets of measurements were taken, with 10 scans performed for each set. The final result was determined as the mean value of the scans.

2.3. Shear Flocculation Experiments

Hydrophobic aggregation tests were carried out in a cylindrical stirring tank (75 mm inner diameter and 140 mm height). Stirring was undertaken using a stainless steel AISI 304 Rushton-type propeller (shaft) with 50 mm diameter and six paddles capable of producing

a predominantly radial flux, ideal for systems requiring intensive turbulence and shear rates. A schematic graph of such a Rushton turbine agitator can be found elsewhere [25]. The propeller was attached to an axis (9×220 mm, diameter and height, respectively) and connected to an electric motor with adjustable rotation from 120 to 5000 rpm. Four dodecylamine (DDA, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{NH}_2$) dosages ($0, 10^{-2}, 10^{-3}, 10^{-4}$ and 10^{-5} mol·L $^{-1}$) and six stirring speeds (500, 1000, 1500, 2000, 2500, and 3000 rpm) were tested based on the response surface experimental design.

Dodecylamine from Sigma Aldrich was used as a surfactant for the hydrophobization of quartz mineral. The DDA solutions were neutralized using concentrated hydrochloric acid (HCl, 37%) in order to reach the final concentration of 0.1% (*w/v*). The quartz samples (3 g per test) were added to 100 mL of DDA solution while being agitated under magnetic stirring for 1 min. After homogenization, the suspension was transferred into the stirring tank to be conditioned at a given rotation speed and time.

The Influence of the DDA dosage in the shear flocculation process was evaluated using an Imhoff cone with 1000 mL volume (480 mm height and higher diameter of 120 mm). The flocculated volume was measured after three minutes of free settling. The DoA was measured using a Photometric Dispersion Analyser (PDA2000) from Rank Brothers Ltd., Newbury, UK, operating in a continuous mode with data collection every two seconds up to 3.3 min. Detailed information regarding this technique is given elsewhere [26]. Different conditioning times (in minutes) were tested, ranging from 1 to 15 min. Figure 1 presents a schematic diagram illustrating the governing mechanisms of shear flocculation.

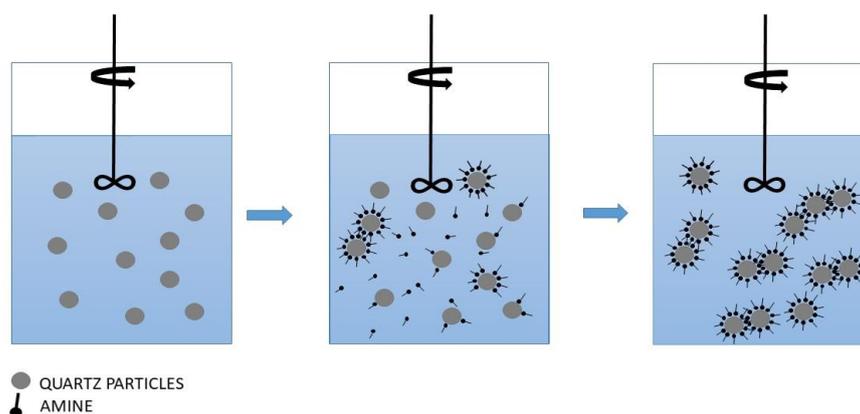


Figure 1. Schematic representation of shear flocculation.

Statistical analysis of the results was performed using the software Design-Expert 13 (Demo v.7.0.0 State-Ease, Inc., Minneapolis, MN, USA). Initially, a cubic mathematical model was developed and fitted to the experimental data, achieving a value of R^2 of 0.94. Subsequently, analysis of variance (ANOVA) and 3D surface graphs were employed to characterize the behavior of effective operating parameters and the quality of the fitted model.

3. Results and Discussions

3.1. Particle Size Analysis

Figure 2 shows the particle size distribution of representative quartz samples. As seen, 100% of the particles were below 56 μm and 80% (d_{80}) under 24.9 μm . The ultrafine fraction (particles finer than 10 μm) was equal to 34%. The quartz sample's density was 2.63 g/cm 3 , which is in close agreement with pure quartz samples given in the literature (i.e., 2.65 g/cm 3) [27]. The specific surface area was 0.891 m 2 /g.

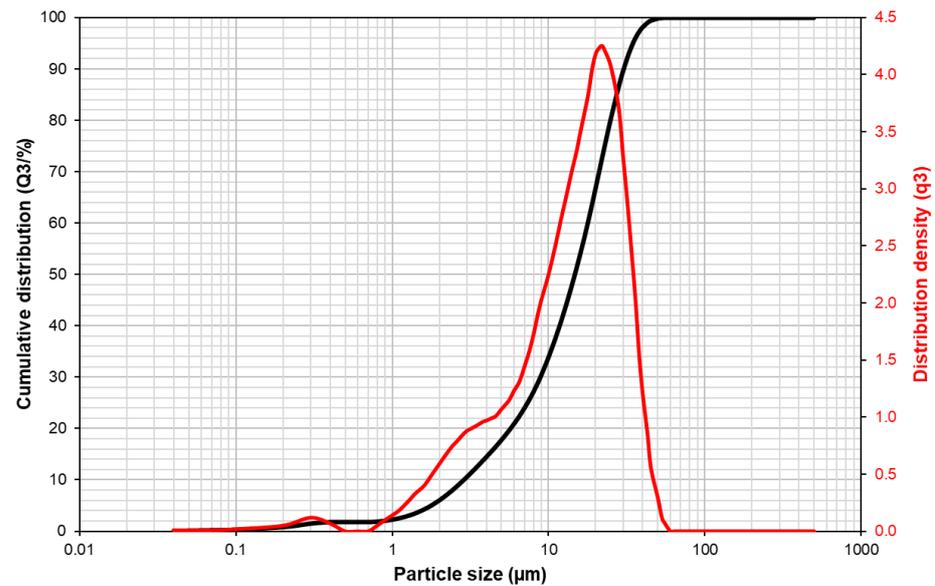


Figure 2. Particle size distribution of quartz sample.

3.2. Zeta Potential Analysis

Figure 3 shows the quartz particles' zeta potential curves as a function of the solution pH, determined both in the presence and absence of the DDA at $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$. Quartz has a surface charge character that is governed by the relative concentrations of H^+ and OH^- within the solution [28]. Upon equilibrium between quartz and aqueous solution, distinctive hydroxylated sites, specifically $\equiv SiOH_2^+$, $\equiv SiOH$ and $\equiv SiO^-$ manifest depending upon pH variation. At very high H^+ concentration, the hydroxyl-covered surface can adsorb an additional proton, resulting in a substituted surface hydronium ion [9] (Equation (1))



Under low H^+ concentrations, the negative site $\equiv SiO^-$ prevails, releasing a proton into the solution [9] (Equation (2))



In the absence of amine, the isoelectric point (i.e., p) of quartz was found at around pH 2, consistent with previous studies [29,30]. At pH values higher than, i.e., p of quartz, the density of $\equiv SiO^-$ groups is higher than that $\equiv SiOH_2^+$ groups, resulting in negatively charged quartz surfaces. Conversely, pH values lower than (i.e., p) yield a higher density of $\equiv SiOH_2^+$ groups, which results in positively charged quartz surfaces [30].

In the presence of DDA, the zeta potential of quartz particles in the pH range of 1.5–10.5 varies between 7–25 mV but drops to an average value of -35 mV at pH of 12. The change in the quartz zeta potential in the presence of a cationic collector, such as the DDA, is related to the interactions of the particles with the amine species present in the solution [31]. The positive zeta potential observed in the curves was expected to be due to a further adsorption of RNH_3^+ and amine precipitation on the quartz surface [32].

The maximum zeta potential was found at pH around 10.5. This high zeta potential value may be attributed to the balanced ratio of the species in the ionic (RNH_3^+) and molecular (RNH_2) forms, which is 1:1 [33]. According to one study [34], the coexistence of the collector in the ionic and molecular forms reduces the repulsion between the polar groups (RNH_3^+), allowing for a high adsorption density of DDA on the surface of the quartz.

The slightly alkaline pH range is most favorable for the hydrophobization of quartz, as indicated by Pinheiro et al. [35]. In very alkaline media, despite the greater availability of negative sites on quartz surface, the $(RNH_3^+)/ (RNH_2)$ ratio decreases. The adsorption of amine molecules onto silicate surfaces at pH range of 4.0–11 has been confirmed by many studies [31,36–38].

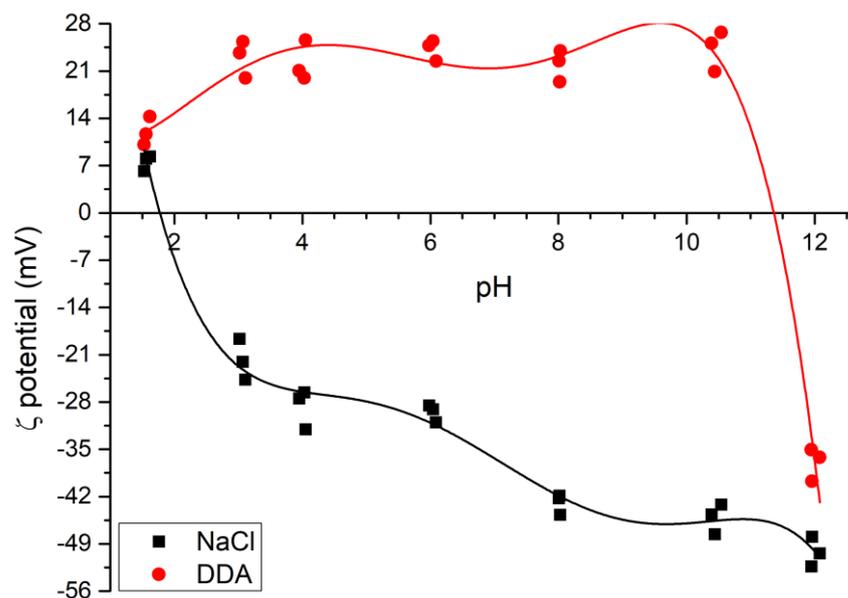


Figure 3. Zeta potential measurements for the quartz particles in the absence ($\text{NaCl} - 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) and presence of DDA (at $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) as a function of the solution pH.

3.3. Shear Flocculation Experiments

Figure 4 shows the results of the volume occupied by hydrophobic aggregates, measured in the Imhoff cone after 3 min free sedimentation. The logarithm of the DDA concentration was used for the analyses. The effect of stirring speed on particle aggregation in the absence of a collector is very limited. Generally, an increase in the stirring speed resulted in an increase in the volume occupied by the flocs, reaching a maximum of around 2000 rpm. However, further increasing the stirring speed beyond that point reduced the volume occupied by flocs due to possible floc breakage caused by high shear forces. Additionally, according to the results, the volume occupied by the flocs increased by enhancing the DDA concentration up to $1 \times 10^{-1} \text{ mol}\cdot\text{L}^{-1}$, but then decreased with a further increment. The hydrophobicity of particles is considered the most important variable in shear flocculation because the attraction among the particles is mainly determined by hydrophobic interactions [39]. The adsorbed surfactant can act as a bridge between particles, resulting in the replacement of a portion of the interface between hydrocarbon chains and the aqueous solution by a contact area between the hydrocarbon chains. This phenomenon reduces the system's surface energy through the energy associated with the contact area per particle, consequently driving the formation of aggregates [40].

Analysis of variance (ANOVA) was employed to assess the contribution of the two parameters (i.e., DDA dosage and stirring speed) on the volume occupied by the flocs (Table 1). The Model F-value of 68.46 indicates the model's significance, with only a 0.01% chance that such a value could result from noise. As the p -values for both A (stirring speed) and B (DDA dosage) factors are less than 0.05, the influence of these parameters can be considered statistically significant, while their interaction is insignificant. In terms of quantitative F-values, the variation in DDA concentration (F-value = 20.43) exerts a substantially greater effect on the process compared to stirring speed (F-value = 3.15). Numerical optimization was performed to maximize the volume occupied by the flocs within the tested parameter ranges. The higher volume occupied by the flocs obtained was

12.3 mL for a stirring speed of 2135 rpm and a DDA concentration of $1.39 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ (desirability of 0.977).

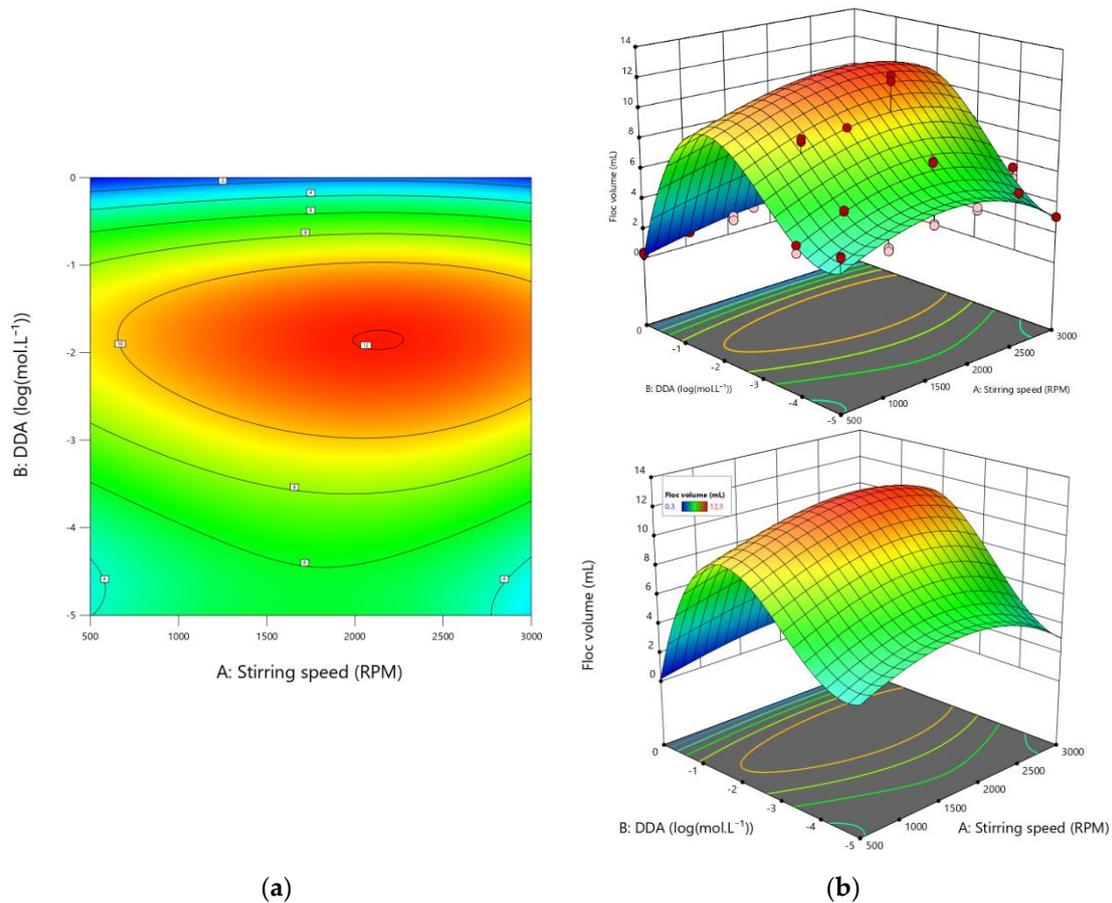


Figure 4. Influence of the stirring speed and DDA dosage on the floc volume in the Imhoff cone at pH 10.5: (a) contour plot; and (b) response surface.

Table 1. ANOVA results for the stirring speed and DDA dosage influence on the floc volume at pH 10.5.

Source	Sum of Squares	df *	Mean Square	F-Value	p-Value
Model	419.54	9	46.62	68.46	<0.0001
Stirring speed (rpm)	2.14	1	2.14	3.15	0.0842
DDA dosage ($\text{mol}\cdot\text{L}^{-1}$)	13.91	1	13.91	20.43	<0.0001
AB	1.28	1	1.28	1.88	0.1782
A ²	20.27	1	20.27	29.77	<0.0001
B ²	197.54	1	197.54	290.10	<0.0001
A ² B	1.52	1	1.52	2.23	0.1438
AB ²	1.92	1	1.92	2.81	0.1018
A ³	0.2880	1	0.2880	0.4229	0.5195
B ³	26.91	1	26.91	39.51	<0.0001

* df stands for degree of freedom.

Figure 5 presents the influence of the stirring speed and the sedimentation time on the DoA for the hydrophobized quartz particles in the presence of dodecylamine ($1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) at pH 10.5. A quartic model was employed to simulate the experimental data, yielding an R^2 value of 0.98. According to the findings, the DoA increased with increasing stirring speed. The experiments conducted at 500 rpm resulted in a DoA similar

to that observed without stirring, corroborating the hypothesis of a minimal kinetic energy requirement to promote aggregation. Meanwhile, aligning with previous research [41,42], it has been observed that a critical stirring speed must be utilized for efficient hydrophobic aggregation to take place. Aggregates formed at a stirring speed over the critical value cannot sustain the high shear stress of the turbulence flux, which results in their breakage.

The ANOVA tests demonstrated the significance of both parameters, and all their interactions, were significant, except for the A^2B^2 interaction. Numerical optimization revealed that within the tested range of stirring speed and the sedimentation time, the maximum DoA was 6.1, achieved at stirring speed of 2909 rpm and sedimentation time of 51 s (with a desirability of 1).

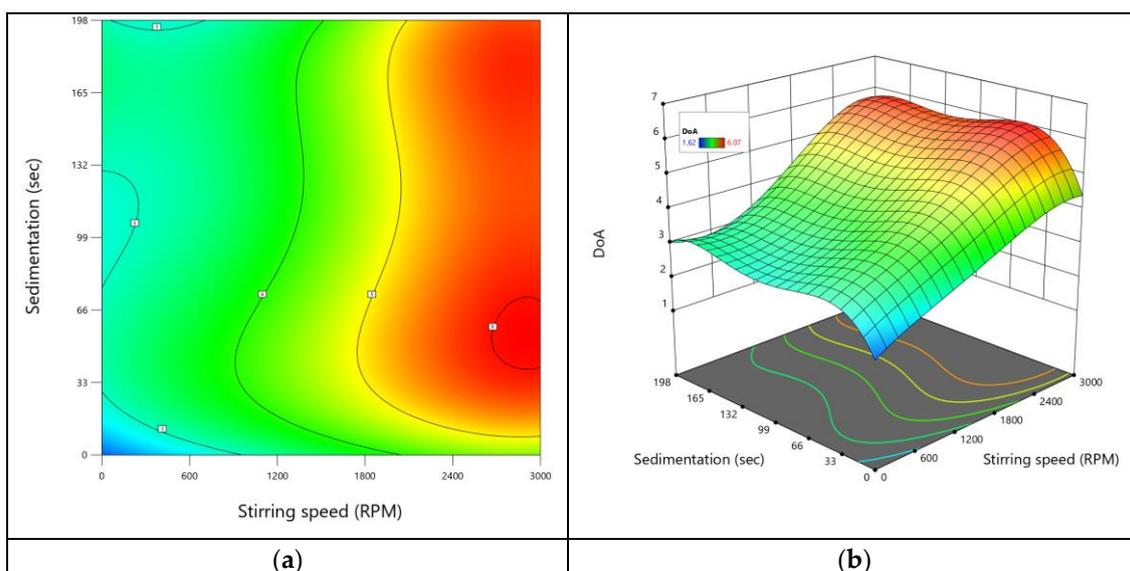


Figure 5. Influence of the stirring speed and sedimentation time on the DoA for the quartz particles with DDA at $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ and pH 10.5: (a) Contour plot; (b) Response surface.

Figure 6 presents the sedimented quartz floc volume as a function of conditioning time, with a DDA dosage of $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, pH 10.5, and a stirring speed of 2000 rpm. The green lines delineate the 95% confidence interval, representing a range of values containing the true population mean with 95% confidence. The volume of formed aggregates increases progressively within the first 10 min, presenting a flat behaviour. The same tendency was observed by Yan et al. [42] for hydrophobic apatite aggregates in the presence of sodium oleate. Similarly, Yin et al. [16] observed a minimum 10 min conditioning time for hematite hydrophobic aggregation. In addition, these aforementioned authors identified a maximum time of 20 min, beyond which aggregate breakage occurred, leading to a reduction in the aggregates' diameter.

In Figure 7, it is evident that the highest aggregation of quartz particles occurred at pH 10.5, suggesting the importance of the non-dissociated amine molecules in quartz hydrophobization [34]. Despite repulsion due to the electrical double layer, as predicted by the classic theory of colloid stability, particle aggregation still occurred. The given results suggest that a high zeta potential value (+24.2 mV) did not influence quartz aggregation in the presence of DDA. Similar results were found in the literature [43]. According to Lu and Song [8], the aggregation behaviour of a suspension without the addition of a surfactant can be effectively explained by the DLVO theory. The electrostatic repulsion between particles is very much weaker compared with the van der Waals attractive forces, insufficient to prevent agglomeration when the zeta potential is near zero (at isoelectric point). However, the addition of an appropriate surfactant in the suspension, inducing hydrophobicity on the particles' surfaces, results in aggregation even at high absolute zeta potential values. This fact suggests that hydrophobicity is the factor that plays the main

role in shear flocculation. Further in-depth information regarding the mechanisms can be found elsewhere [44–46].

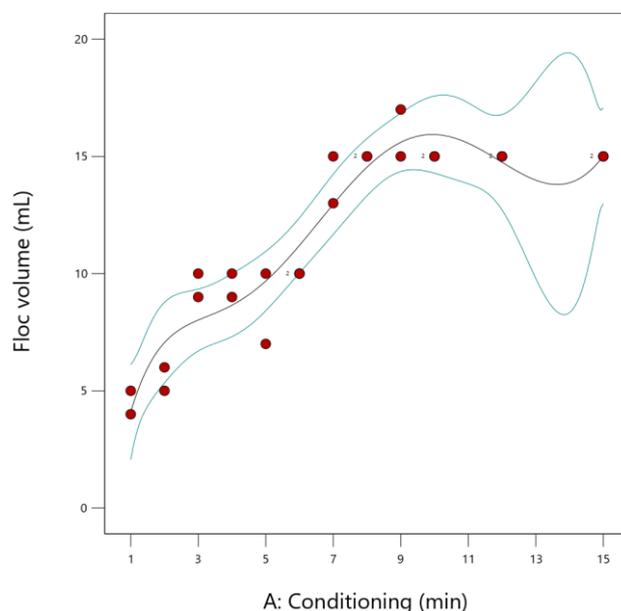


Figure 6. The volume of sedimented quartz flocs as a function of conditioning time [min] using DDA at $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, pH 10.5, and 2000 rpm stirring speed.

The volume occupied by hydrophobic quartz aggregates was similar both in the presence or absence of stirring at both pH 4.5 and pH 12. The limited aggregation at pH 4.5 may be attributed to the prevalence of ionic species (RNH_3^+), resulting in an insufficient hydrophobicity of the particles. Meanwhile, at pH 12, no aggregation was observed, due to the absence of adsorption density as a result of the lack of ionic ions (RNH_3^+) in a highly alkaline medium.

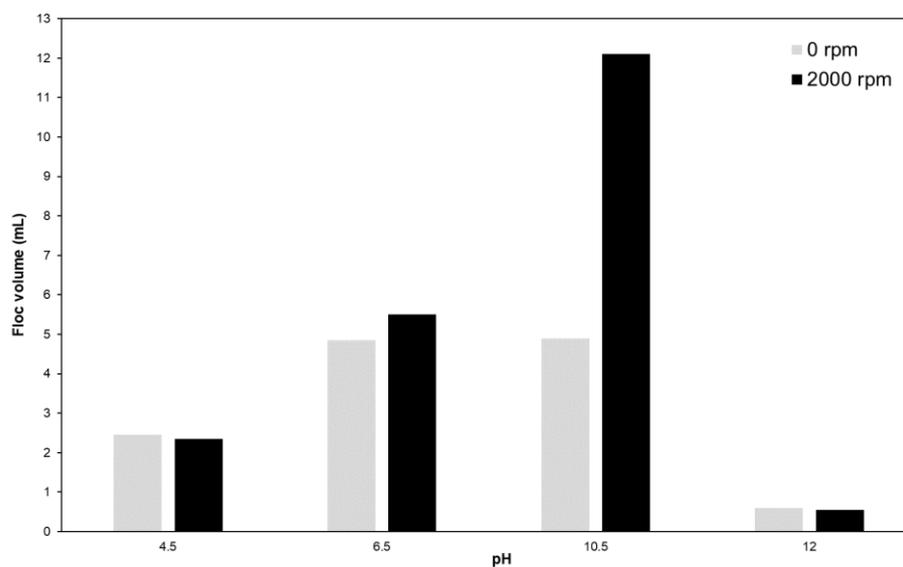


Figure 7. Sedimented quartz flocs volume as a function of the solution pH, in the presence of DDA (at $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$), both with and without stirring at 2000 rpm.

4. Conclusions

In the present work, fundamental studies of quartz shear flocculation were carried out on pure quartz samples in the absence of surfactants. No particle aggregation was observed for those tests, even when the system was conditioned under high stirring speeds. This fact suggests that particle hydrophobicity plays an important role in the formation and growth of hydrophobic aggregates.

With regard to the stirring speed, the DoA increased with the increase in the stirring speed. The DoA found in tests carried out at 500 rpm was very close to the results without stirring, evidencing the need for minimal kinetic energy for the aggregation to take place that could be understood as activation energy. Tests at 3000 rpm produced high aggregation ratios. However, the size of the aggregates formed was reduced, probably due to the breakage of the flocs caused by the strong shear strength caused by the stirring speed. The highest DoA was found at 2000 rpm and conditioning of 9 min. It was observed that flocs sedimented volume in the Imhoff cone became constant for settling times higher than 10 min. Further experimental results were required to precisely estimate the average aggregate sizes given in this work using PDA2000.

The highest quartz particle aggregation was observed at pH 10.5, corroborating the importance of the non-dissociated amine molecules for quartz hydrophobization. Conversely, no correlation between the particles' zeta potential and the system aggregation was observed, given the fact that at high zeta potential values, no reduction in aggregation occurred, in disagreement with the DLVO theory. At the same time, it is evident that hydrophobicity was the main driver in the shear flocculation process. Finally, the surfactant dosage had a key role in the quartz particles' hydrophobicity and, therefore, in the formation and growth of the hydrophobic aggregates. At concentrations of 10^{-5} mol·L⁻¹, the sedimented volume was similar to the values obtained without surfactant. Further test works using tap/process water and bulk quartz samples are essential in future works in order to apply the obtained results to industrial scale processing of fine quartz particles.

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