Research Article

Operating Parameters Affecting the Formation of Kaolin Aerated Flocs in Water and Wastewater Treatment

The formation of aerated flocs (aeroflocs) and the main operating parameters involved were studied to improve the rapid solid/liquid separation by flocculation–flotation. A continuous flow system at the laboratory scale was used that coupled micro-bubbles dissolved air flotation and a flocs generator reactor (FGR). The aerated floc characterization technique was employed to characterize the aggregates obtained using a non-ionic polymer (920SH SNF-Floerger®). Flocculation–flotation studies evaluated the effect of the suspension flow rates (Qc: 0.12, 0.24, 0.36, and 0.48 m³/h), the air/solid rates (A/S: 0.01, 0.02, 0.03, and 0.04 mg/mg) and the forms of flocculation (flocculation form I: a primary flocculation after coagulation inside a stirred tank, followed by mixture with air bubbles into the FGR and flocculation form II: full flocculation in the FGR). The main results demonstrated that the mixture of particles, air micro-bubbles and polymeric macromolecules in a proper turbulent flow inside the FGR was the key to the effective generation of very light aerated flocs. These aggregates had higher uprising rates, which ranged between 70 and 150 m/h and represented 83% of the flocs population at an air/solid rate of 0.02 mg/mg and a flow rate of 0.24 m³/h. It is believed that, by maximizing operating parameters, improvements are achieved, mainly, both increasing the removal efficiencies and the design of the equipment that can be more compact requiring fewer areas than conventional units.

Keywords: Dissolved air flotation; Flocculation–flotation; Polymer-coated bubbles

Received: February 7, 2013; revised: May 31, 2013; accepted: June 5, 2013
DOI: 10.1002/clen.201300050

1 Introduction

The classical dissolved air flotation (DAF) process remains one of the most commonly used physicochemical methods for removing fine colloidal dispersions, fine and ultrafine solid particles, microorganisms, and oils from water and wastewater. In the DAF process, a stream of treated wastewater (recycle) is saturated with air at elevated pressures (>3–4 atm). Bubbles are formed by reducing the pressure of the water in the saturator vessel and are then forced to flow through needle valves or special orifices. Clouds of bubbles (30–70 μm) are produced immediately downstream of the flow constriction [1–6]. These micro-bubbles become attached or entrapped within the flocs, allowing the aggregates to rise and the fast separation of solids/liquids.

Flocculation and rapid flotation have demonstrated a significant potential as unitary or ancillary processes in many areas because the efficiency of new reagents vary and the design of the separation units requires minor areas [2, 7–10]. According to Edzwald [11], Haarhoff and Edzwald [12], Kiu [13], Rodrigues and Rubio [2], and Rubio et al. [8], the trend in current research efforts is to decrease flocculation times and to increase DAF loadings by developing compact (small footprint) and efficient treatment units.

Industrial applications of DAF in mining and metallurgy are scarce but growing. It is believed that this growth is the result of the combination of DAF (conventional or unconventional) and high-throughput flotation devices (>15 m/h). According to Edzwald [11], in the last 20–25 years, there have been major advances in the science and engineering technology of DAF. The science has contributed to the fundamental understanding of DAF, and technological developments have succeeded in reducing the pre-treatment flocculation times, enhancing the hydraulic loadings. According to this author, conventional rate DAF is considered to show hydraulic loadings of 5–15 m/h, and was used exclusively until the late 1990s. It is still used, but high rate DAF is an alternative and shows hydraulic loadings of 15–30 m/h and greater.

The main developments in DAF installations have been achieved as a result of changes in their design, incorporating new elements to enhance the hydraulic loadings. Rapid DAF is being achieved by modifying the cell design (taller tanks) and by placing lamellae inside the separation tanks [13].

Another approach to obtain high-throughput flotation units is based on a wide bubble size distribution and formation of aerated flocs. These aggregates are composed of bubbles (trapped and/or adhered) and flocculated particles that have high up-rising rates,
accelerating the separation of solids/liquids in flocculation–flotation units and enhancing process throughput [14].

A number of important studies [2, 15–22] on aggregation–flotation with aerated flocs formation have been described in the literature. Most of these studies only observed and described the presence of these aggregates. The characterization of these structures have shown important features in the environmental area, mainly due to promoting high up-rising rates, low moisture content and large bubbles entrapped in and attached to these flocs (e.g. www.lume.ufrrgs.br/handle/10183/1) [17, 18].

In this context, Oliveira et al. [18] developed the aerated floc characterization (AFC) technique, which employed image processing and provided a detailed evaluation of the aerated flocs (namely their size, shape factor, up-rising rate, fractal dimension, and density). Furthermore, the adhered, attached, and entrapped bubbles in the flocs were characterized by a quantitative analysis of the captured multiphase system images. This work also showed that the presence (formation) of large bubbles within the flocs increased the air volume and lowered the floc density.

In a previous paper [23], we have evaluated the formation phenomena of aerated flocs in kaolin dispersions with a flow system consisting of a floc generator reactor (FGR), and a DAF and AFC device. These authors showed photomicrographs of the multiphase systems that presented new evidence of the flocculation mechanisms between interacting particles and polymer-coated bubbles (which become the bubbles in flocculation nuclei), where the flocculated particles generated new structures. These polymer-coated bubbles can interact with other bubbles, particles and/or flocs. These interactions result in numerous bubbles (of different sizes, depending on coalescence) in the floc structures, thereby improving their rising rates. Overall, these findings enlarged the field of knowledge regarding the mechanisms and interactions leading to the generation of aerated flocs.

Considering that the process of flocculation may be influenced by the intensity of the applied shear force, and the hydrodynamic forces influence the polymer adsorption phenomena and the collision efficiency among particles, determining the overall rate of flocculation [24–27]. The present work considers that the phenomenon of aerated flocs formation by the new concept of polymer-coated bubbles (shown by Oliveira and Rubio), may be significantly influenced by different operating parameters in the environmental area, such as feed rate, aeration rate, and flocculation form. So, this paper is a continuation of a series of articles on the formation of aerated flocs for particulate separation. Herein, such operating parameters in flocculation–flotation of kaolin particles were studied in aerated floc formation.

2 Materials and methods

2.1 Materials and reagents

A kaolin sample was procured from Cadam S/A, Brazil, and was of high purity (approximately, 100% of kaolinite evaluated by X-ray diffraction analysis as shown by Oliveira [17]). The mean particle diameter was determined to be 0.9 μm; the specific surface area measured by BET method was 17 m²/g, and the specific mass was 2.3 g/cm³. The kaolin is a particle model widely used in the flocculation research area to simulate the pollutant suspensions in water and wastewater treatments. Reagent-grade aluminum sulfate (Al₂(SO₄)₃·14H₂O) from Cynth® was added to the suspension to promote coagulation of the kaolin particles. Flocs were formed using a high molecular weight non-ionic polyacrylamide (920SH) procured from SNF-Floerger®. This polymer was chosen in previous studies [17] using different polyacrylamides to evaluate the optimal kind and concentration of flocculant added to the kaolin suspension in the same conditions (pH, temperature, and particle concentration) used in the present work. According to the manufacturer, this polymer would correspond to a high molecular weight polyacrylamide and has been characterized in previous studies by this research group [17, 18]. According to these authors, this sample had a molecular weight of 6.02 × 10⁶ g/mol and a negative charge density over a wide pH range (2–10), where the zeta potential was approximately −10 mV in the working range of pH 5–7. In general, nonionic polymers are far from being pure substances, having residual fractions of anionic groups (within the range of 1–3%) due to ongoing hydrolysis of amide groups. This phenomenon appears to be related to the specific conditions of the polymerization reactions [28] and the presence of monomers and polymer chains of varying molecular weights. According to Vorchheimer [29], hydrolysis grades <1% can be obtained by controlling the concentration of monomers, pH, and temperature.

2.2 Methods

A rig composed of an FGR with DAF technique was developed to carry out the flocculation–flotation studies in a continuous flow apparatus at laboratory scale. To obtain a full characterization of the flocs and multiphase systems (water/air bubbles/flocs), the AFC technique (developed and described by Oliveira et al. [18]) was coupled to this system. A detailed illustration of this experimental set-up is given in Fig. 1.
A suspension of kaolin particles was prepared in 5 L of water in an ultrasonic bath for 30 min and then transferred to a tank (with water) where the particle concentration was adjusted to 1 g/L. Such concentration was applied to simulate usual operational conditions in the water and wastewater treatments. An optimal concentration of aluminum sulfate (2.5 \text{ molAl}^3 \text{g}^{-1}) was added into this suspension to promote the coagulation step. This optimal value was previously determined by Oliveira [17], who showed a residual turbidity of 153 nephelometric turbidity units (NTU) and a slight negative charge density (zeta potential of $-7.4$ mV). The fine particles of kaolin could not be flocculated only with polymers or with inorganic salts (coagulation). A combination of these reagents (sensitization mechanism) was essential to form the aggregates.

After 10 min of mixing (to aid adsorption and aggregation), the suspension (now containing coagulated particles) was pumped into the FGR. Polymer was added in the flow line where this suspension crossed. Water flows were pumped to the saturator vessel under 4 atm of saturation pressure ($P_s$). The air-saturated water crossed a needle valve, where the shear flow from the depressurization generated the air micro-bubbles, and injected at the inlet flow of the FGR. Then, after mixture of the kaolin particles, polymer and air bubbles inside this reactor, the aggregates (floc-bubbles) flowed to the flotation cell for solid/liquid separation (aggregates/water).

The tube of the AFC technique was opened for sampling of the rising flocs (approximately 300 aggregates in each experiment), which were characterized by the capture and processing of images (see details in Oliveira et al. [18]). Sub-natant liquid samples were collected, and their remaining turbidities were measured in a turbidimeter (Hach 2100N) and expressed in NTU. This parameter was also measured in the feed stream and the percentage of turbidity, which was removed was determined and named “turbidity removal”. All of the experiments and measurements were performed in duplicate.

The main operating parameters evaluated in this system were the effect of suspension flow rate and floculation forms at different air/solid rates (A/S).

2.2.1 Influence of the suspension’s flow rates ($Q_s$)

The effect of kaolin suspension flow rates ($Q_s$: 0.12, 0.24, 0.36, and 0.48 m$^3$/h) was investigated in detail using an air/solid rate (A/S) of 0.02 mg/mg (30% of recycle ratio) and various polymer concentrations (0.5, 0.8, 1 mg/g, 1.25, 2.5, 5, 7, 10, 15, 20, and 25 mg/g).

---

**Figure 2.** Kaolin aerated flocs separation by DAF. Effect of polymer concentration on turbidity removal under the experimental conditions: nonionic 920SH polymer; [kaolin] of 1 g/L; [Al$^{3+}$] of $2.5 \times 10^{-5}$ mol$_{Al^{3+}}$/g; A/S = 0.02 mg/mg; $P_s$ = 4 atm.

**Figure 3.** The distributions of kaolin flocs up-rising rates (DAF) at different kaolin suspension flow rates. Experimental conditions: [kaolin] of 1 g/L; [Al$^{3+}$] of $2.5 \times 10^{-5}$ mol$_{Al^{3+}}$/g; [920SH polymer] of 1.25 mg/g; $P_s$: 4 atm; A/S of 0.02 mg/mg; $Q_s$: of (a) 0.12 m$^3$/h; (b) 0.24 m$^3$/h; (c) 0.36 m$^3$/h; (d) 0.48 m$^3$/h.
2.2.2 Influence of the flocculation forms and A/S

Different flocculation forms were evaluated using two aggregation procedures. In the first flocculation form I, a primary flocculation was carried out after coagulation inside of the suspension tank, where the primary flocs were formed at a polymer concentration of 1.25 mg/g. These primary flocs were then pumped to the FGR and mixed with air bubbles to generate the secondary flocs. The second form (flocculation form II) comprises the full flocculation in the FGR with the same polymer concentration added in the flow line. Both experimental procedures using the flocculation forms (I and II) were conducted at different air/solid rates (A/S: 0.01 mg/mg; 0.02, 0.03, and 0.04 mg/mg or 20, 30, 40, and 50% of recycle ratio, respectively).

3 Results and discussion

3.1 Effect of $Q_s$

Studies involving different kaolin suspension flow rates and nonionic polymer concentrations (920SH) have shown the optimal conditions inside the FGR. The results (Fig. 2) showed that a polymer concentration of about 1.25 mg/g provided high turbidity removal (99%) and are in agreement with the optimal concentration data obtained in previous batch studies [17] for the same suspension. This fact confirms the good efficiency of the FGR in promoting dispersion and adsorption of the polymer and efficient particle flocculation. In addition, the 0.12 m³/h flow rate caused insufficient mixture for flocculation. This fact was clearly view during the experiments, where the production of flocs into FGR was not good, showing a floc formation only into the flotation cell. This fact did not enable a suitable formation and capture for air bubbles and, therefore, the most flocs showed settling instead of flotation. Also, the flow rates of 0.36 and 0.48 m³/h offered low residence times and rapid flocculation that led to floc breakage. This fact was also viewed and confirmed by decreased of turbidity removal. These results are in agreement with the results reported by Carissimi [30] (www.lume.ufrgs.br/handle/10183/8974) who studied the flocculation of iron hydroxide colloidal precipitates (Fe(OH)₃) in an FGR of similar dimensions to those used in this work.

Figure 4. Kaolin flocs up-rising rate and size distributions of the flocs generated in flocculation form I (primary flocculation inside the suspension tank and secondary inside of the FGR) at different air/solid rates. Experimental conditions: [kaolin] of 1 g/L; [Al³⁺] of $2.5 \times 10^{-5}$ mol Al³⁺/g; [920SH polymer] of 1.25 mg/g; $Q_s$ of 0.24 m³/h; $P_s$ of 4 atm; A/S of: (a) 0.02 mg/mg; (b) 0.03 mg/mg; (c) 0.04 mg/mg.
These findings were confirmed by flocs characterization, which showed a higher incidence of aerated flocs (90–140 m/h) when using feed suspension flow rates of 0.24 m³/h compared to 0.12, 0.36, and 0.48 m³/h (Fig. 3). These data show that knowledge of the optimal conditions in the FGR is essential to improve both the generation of aerated flocs and solid–liquid separation by flotation.

3.2 Effect of flocculation forms and A/S

The studies using flocculation form I led to the formation of very slow flocs with low up-rising rates for majority of A/S studied. In this case, the A/S rate of 0.01 mg/g was not suitable due generate a low bubble concentration to the suspension. This fact is according to the operational conditions in the DAF systems that, normally, use an A/S rate >0.02 mg/mg (30% of recycle rate) (e.g. www.inpi.gov.br) [2, 11, 31].

The distribution of flocs up-rising rates were in the range of 10–90, 10–70, and 10–50 m/h at the A/S rates of 0.02, 0.03, and 0.04 mg/mg, respectively (Fig. 4). The corresponding flocs populations (99, 96, and 92% of the flocs, respectively) consisted of aggregates with up-rising rates lower than 50 m/h. This absence of aerated flocs indicated the importance using suitable mixture condition in the FGR for flocs formation in a mixture of polymers, bubbles and particles. This results confirm the importance of a suitable mixture speed among particles, bubbles and polymers such as found by Oliveira and Rubio [23] to promote interactions between polymer-particles and the polymer-bubbles as well as particles-polymer-coated bubbles and/or flocs-polymer-coated bubbles are important. According to these authors, these interactions can form structures with large bubbles that improve the up-rising rate of the aggregates, generating aerated flocs.

In addition, floc breakup was demonstrated by an increase in the air/solid rates that caused higher break of the flocs, possibly due to a turbulence in the system. The flocs generated at the A/S of 0.02 mg/mg had a size distribution in the range of 0.5–1.9 mm (Fig. 4) with 26% of

---

Figure 5. Distributions of kaolin flocs up-rising rates and sizes generated in full flocculation (flocculation form II) inside of the FGR. Experimental conditions: [kaolin] of 1 g/L; [Al³⁺] of 2.5 × 10⁻⁵ mol/L; [920SH] of 1.25 mg/g; Qₕ: 0.24 m³/h; Pₛ: 4 atm; A/S: (a) 0.02 mg/mg; (b) 0.03 mg/mg; (c) 0.04 mg/mg.
aggregates <0.7 mm. Conversely, at the A/S of 0.03 and 0.04 mg/mg, the size distributions were between 0.4–0.9 and 0.4–0.7 mm, with 94 and 98% of aggregates <0.7 mm (Fig. 4). These data showed that increasing the air/solid rates increased the number of small flocs, likely due to the rupture of large flocs, which may have either broken due to an excessive mixture or difficulty growing at rapid flocculation. According to Hu et al. [32], this fact is especially true when the turbulence causes the aggregates to break due to attrition and shear forces generated in the liquid. These results are similar to those published by Carissimi et al. [33] who developed basic studies to determine the hydrodynamic parameters of an FGR and their correlation with particle aggregation efficiency. These authors showed that a higher feed rate caused a decrease in the settling rates of the flocs due to a rupture of these aggregates at high superficial flow velocities (high velocity gradient and shear). They emphasized that the hydraulic parameters are quite important and should always be considered in transport processes because they greatly affect the aggregation phenomena.

Studies using the flocculation form-II (full flocculation inside of the FGR) demonstrated the importance of a suitable mixture of particles, air micro-bubbles and polymer inside the reactor. Here, studies at an A/S of 0.02 mg/mg provided the appropriate generation of kaolin-aerated flocs with an up-rising rate distribution between 40 and 150 m/h (containing 65% of fast flocs that had up-rising rate values between 90 and 150 m/h). In addition, flocs sizes fluctuated between 0.3 and 1.9 mm, as shown in Fig. 5a.

The aerated flocs presented in Fig. 6 contain large air bubbles that are adhered to and/or entrapped in their structures. This fact concurs with recent results published by Oliveira et al. [18] and Oliveira [17], whose studies gave evidence to the presence of these large bubbles, which were very important for the rapid flocs to attain high up-rising rates by enhancing the air volume inside of the flocs, likely due to air bubble nucleation and/or coalescence, which are mechanisms that appear to be favored in techniques using turbulent flows, such as, FGR [15, 30, 31, 33, 34], flocculation–flotation [19, 35, 36], air-sparged hydrocyclones [30] and centrifugal flotation systems [37], among others.

Moreover, the results (Fig. 5) showed that the frequency in the population of the structures discovered by Oliveira and Rubio [23], named “flocculant bubbles”, was influenced by mixture conditions in the FGR, which was observed in studies using flocculation form II and air/solid rates of 0.03 and 0.04 mg/mg, providing less efficient conditions for interactions between these structures, causing an excessive amount of single “flocculant bubbles” (non-aggregated to the aerated flocs), as can be seen clearly in Fig. 7a and b. These structures were included in the flocs characterizations, and their features appeared in the up-rising rate (higher) and size distributions (Fig. 5b and c). According to these histograms, the generated structures (flocs and “flocculant bubbles”) showed up-rising rates in the range of 25–675 and 25–425 m/h at A/S of 0.03 and 0.04 mg/mg, respectively, and size distributions between 0.3–0.6 and 0.2–0.8 mm, respectively. In both cases, the flocs represented 43 and 58% of the population and the “flocculant bubbles” represented approximately 57 and 42% of the population of the studied aggregates, constituting 33% of the total population of flocs represented by aerated flocs containing large “flocculant bubbles” (Fig. 7c and d).

The present results demonstrated that the flocculation form is very important to promote a satisfactory mixture among particles, polymers and air bubbles, showing that the polymer adsorption
onto bubbles and particles should occur together to improve the “floculent bubbles” formation, flocs formation, and their interactions to generate the rapid aerated flocs formation.

4 Concluding remarks

Kaolin aerated flocs formation was highly favored under proper mixing conditions inside a FGR, which was due to interactions among polymeric macromolecules, particles, and air bubbles (namely, micro-bubbles and large bubbles formed after nucleation of bubbles onto the surfaces), growth and coalescence mechanisms. The result is the generation of very rapid flocs (aerated flocs) with an up-rising rate >140 m/h. The present study demonstrated the efficiency of this reactor in promoting dispersion and adsorption of the polymer and, thus, efficient particle flocculation. Low suspension flow rates cause insufficient mixture for flocculation; high values cause low residence times and rapid flocculation, leading to flocs breakage. Mixing conditions in this reactor are also influenced by the air/solid rate, with an optimal value of 0.02 mg/g in the present system. The current study contributes to the knowledge of operating parameters for aerated flocs formation, enhancing particle aggregation, and solid/liquid separation, mainly due to show a possibility to improve the process using different operational conditions in a real waste. So, it is believed that air/solid rates and flow rates have a great potential for formation of these aggregates, improving several fields, including mining and metalurgical and physico-chemical separation in different removal of pollutants.

Acknowledgements

The authors would like to thank the Cadam© and Floerger® corporations for technical information and for providing the kaolin and polymer samples. The authors would also like to thank all of our colleagues at the LTM and the Universidade Federal do Rio Grande do Sul; CNPq; Capes; Finep and all institutions supporting research in Brazil.

The authors have declared no conflict of interest.

References


E. Carissimi, J. Rubio, Reator gerador de flocos e processo para tratamento de águas e efluentes, Patente PI 0406106-3, Brazil 2005, in Portuguese.


J. Rubio, J. Da Rosa, R. Beal, Equipamento e processo para tratamento e reciclagem de água de lavagem de veículos e efluentes similares, PI 0006390-8, RPI 1691, Brazil 2003, in Portuguese.