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Experimental Investigation of Bentonite Flocculation in a Batch Oscillatory Baffled Column

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ABSTRACT

We report, for the first time, the preliminary results of flocculation of bentonite particles in a batch oscillatory baffled column. The effects of floc settling time, mixing intensity, polymer dose, and polymer injecting mode on percentage of flocculation were investigated. The optical density of bentonite suspension prior to and after polymer injection was measured as the means to quantify the percentage of flocculation. The results show clearly that the intensity of oscillation is an important factor to the flocculation rate, and the two-stage mixing mode produced a higher percentage of flocculation than the single-stage mode for low polymer dosages up to 10 ppm. The advantages of the incremental polymer injection method over the slug method are also discussed.

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Key Words. Bentonite flocculation; Flocs; Polymers; Polymer dosage; Polymer dose mode; Settling time; Oscillatory baffled column; Oscillation intensity

INTRODUCTION

The aggregation of small particles in liquids to form flocs which are large enough to settle, or to be filtered, is a common type of separation processes in water treatment and in other related industrial processes because these particles are often in the micron or submicron size range and are difficult to remove by the conventional sedimentation or filtration methods. The flocculation of particles by the addition of a water-soluble polymer is a typical example and generally considered to go through several phases (1): (i) polymer distribution within the solid–liquid suspension, (ii) polymer adsorption to the particles, (iii) particle collisions, and (iv) particle growth. The interplay of the stages, the dynamics of the individual stages, and their relationships to the type of reactor employed are very important to the flocculation process. It was reported that the rate and extent of flocculation were determined by the time allowed for adsorption of the added polymer before particle collisions occurred (1, 2).

Flocculation requires that particles collide with polymer molecules for adsorption of the polymer and that the coated and uncoated particles collide with each other for particle growth. Both these activities are controlled by shear in orthokinetic flocculation. Thus the mechanical agitation which produces high velocity gradients promotes rapid and uniform polymer adsorption and a fast rate of particle–particle collisions. However, excessive agitation can be detrimental to the flocculation process since it can cause floc breakup and limit the floc size (3). As a result, the final floc size distribution is a balance between particle growth and breakage. The structure of flocs at a steady state also depends on the process conditions (4–6).

In addition to the actual polymer dose, the mode of adding the polymer to the system is also important in determining the outcome of the flocculation process. It had been observed that there was an optimum polymer dose needed to flocculate particles (3). Excessive polymer can lead to a reduction in the extent of flocculation; either through charge reversal in the case of opposite charged polymer and particles, or through reduction in polymer attachment sites in the case of polymer bridging. Recent evidence suggests that the extent of flocculation increases when the polymer is added dropwise over the mixing period compared with when the polymer is added as a slug (2, 7).

The mixing characteristics of a reactor in the flocculation process should be able to provide an environment in which rapid dispersion of a viscous polymer is achieved to allow even absorption of the polymer to all the particles and also provide a suitable environment for floc growth. Most flocculation studies have been performed in stirred tanks using agitator blades of various designs. These vessels will inevitably have regions of high shear around the impeller tips and regions of low shear remote from the mixing blades. The flocculation reported in this paper utilizes a different sort of reaction vessel, i.e., the oscillatory baffled column, to provide the necessary absorption and suspension in the process of flocculation. It has been shown that combining fluid oscillation with periodically spaced baffles in a column produces significant radial motion, where events at the wall are similar to events at the center of the device, leading to excellent mixing within the device (8–11). The mechanism of fluid mixing in such a column is that with each oscillation cycle, fluid near the wall of the tube is drawn into a downstream vortex formed behind each baffle as flow accelerates. On flow reversal, the vortex is swept into the center; this provides an effective way to move fluid from the wall to the center of the tube, as shown in Fig. 1.

This type of column has been exploited as a single-phase reactor (12), a solid–liquid suspensor (13, 14), gas–liquid mass transfer columns (15, 16),

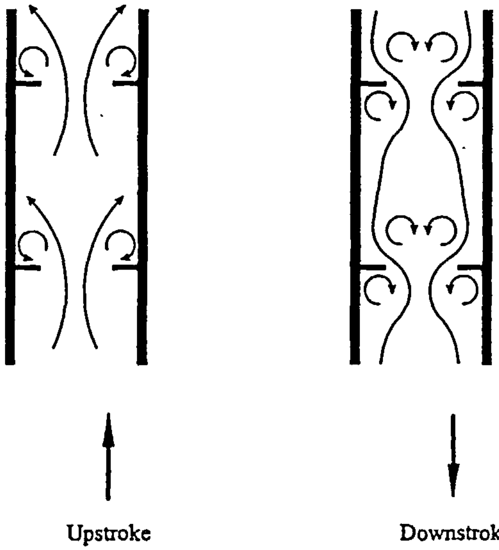

FIG. 1 Mechanism of fluid mixing in the oscillatory baffled column.

and polymerization reactors (17). Recent studies on polymer dispersion and chemical crystallization indicate that the oscillatory baffled column is capable of mixing viscous fluid, achieving a uniform state in the device and also producing a narrow crystal particle size by optimizing oscillation intensity (18).

As a prelude to the investigation of flocculation of bacteria, *Alcaligenes eutrophus*, in an oscillatory baffle vessel, this paper reports the initial studies using bentonite. This study was conducted to identify the influence of key reactor operating variables on the polymer flocculation using bentonite particles. The emphasis was placed on the effect of mixing intensity, polymer dose, and polymer addition mode on flocculation in such a column, from which further investigation of flocs size distribution and the effect of shear rate on the distribution can be carried out using particle image velocimetry.

MATERIALS AND METHODS

The Oscillatory Baffled Column

A schematic diagram of the batch oscillatory baffled column is shown in Fig. 2. The device consists of a Perspex column of internal diameter 50 mm and 500 mm long. It has a liquid capacity of 1 L. Baffles are made from 3 mm thick PTFE. The baffle spacing can be adjusted between 50 to 100 mm

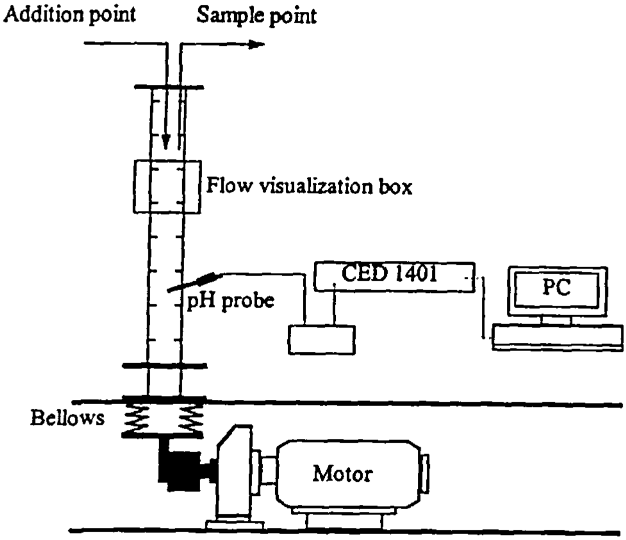

FIG. 2 Schematic of the oscillatory baffled column.

(1 to 2 times the tube diameter), where the most used baffle spacing was 75 mm which was optimized by Brunold et al. (8) for effective mixing over a broad range of oscillation amplitudes and frequencies. For each set of experiments there were six baffles supported within the column using two 2-mm stainless steel rods. One end of the column was flanged onto a 50-mm diameter stainless steel bellows assembly, which was driven by a cam together with an electrical motor through a control box. The controlled rotating speed of the motor provided oscillation frequencies from 1 to 10 Hz to the system. The oscillation amplitudes of 1 to 12 mm center-to-peak can be obtained by adjusting the length of the connecting rod linking the bellows assembly and the drive unit. The flow visualization box was used to correct for distortion effects during the imaging process. The pH level of the bentonite suspension was continuously monitored by a CW711/DWG1391 (Russell, UK) glass combination pH probe which has a temperature compensation function. The output signals were displayed at a CD640 bench top pH meter and recorded by an IBM computer through a CED1401 interface.

Polymer Solution

Magnafloc 1697

A stock of polymer solution containing 1000 ppm of the cationic DADMAC polymer Magnafloc 1697 (Allied Colloids, UK) was prepared by dissolving 0.5 g in 0.5 L of distilled water and stirred on an orbital shaker at 30°C for overnight. The Magnafloc 1697 has a low molecular weight (MW $= 1.2 \times 10^5$) and high charge density (5.5 meq/g).

Zetag 89

Initially a 1% solution of the Zetag 89 was prepared. One gram of the dry Zetag 89 (Allied Colloids, UK) was weighted into a 250-mL glass jar and followed by 5 g of acetone (BDH, UK). The jar was then swirled to completely "wet out" the polymer prior to adding 95 g of deionized water. The swirling action was maintained at intervals while adding the water to prevent the polymer clumping into insoluble lumps. The jar was sealed and then placed in an orbital incubator at 30°C for 3 hours. A stock of polymer solution containing 1000 ppm of Zetag 89 was then prepared by diluting 40 g of 1% solution into 360 g of distilled water and stirring on an orbital shaker at 30 °C for overnight. In contrast to the Magnafloc 1697, the Zetag 89 has both high molecular weight (MW $= 1.0 \times 10^7$) and charge density (3.5 meq/g), which is ideal for a comparison study. Although there would be a difference in the viscosity of the two polymer solutions, it would not be in the final mix because of the dilute effect (19). As a result, the effect of viscosity on flocculation is insignificant.

Bentonite Suspension

Three and a half grams of dry bentonite (Allied Colloids, UK) and 0.35 g of sodium chloride (BDH, UK) were weighed out and dispersed into 7.0 L of distilled water using a SL2T Silverson mixer. This supply was used within 1 to 2 hours.

Flocculation Procedure

Flocculation was achieved by adding different volumes of the prepared stock polymer solution into 1 L of bentonite suspension in the oscillatory baffled column. Two methods of polymer addition were used: slug and incremental addition. For the slug addition the required volume of the stock polymer solution was pipetted into the bentonite suspension in the column as a single pulse injection. For the incremental addition method the polymer was added in increasing incremental volumes of 1 mL, commencing with 1 mL and sequentially adding further volumes of 2, 3, 4, 5, and 6 mL to give final polymer concentrations of 1, 3, 6, 10, 15, 21, and 28 ppm. These are equivalent to 2, 6, 12, 20, 30, 42, and 56 mg polymer/g bentonite.

Assessment of Flocculation

The extent of flocculation was assessed after a mixing duration of 5 minutes in the column (either incremental or slug addition) by withdrawing a 3.5-mL sample with a wide bore pipette and transferring the suspension into a plastic cuvette. After a settling period of 40 minutes, the optical density (OD) at 560 nm was measured by a spectrophotometer (Shimadzu UV-120-02, Japan). Controls were run at the same time with the bentonite suspension in the absence of the polymer to provide the background settling. The percentage reduction in OD was calculated based on the readings from both the final OD of the test and its control, and this OD was then used to describe the percentage of flocculation throughout the experiments as

$$\% \text{ Flocculation} = \frac{OD_{control} - OD_{test}}{OD_{control}} \tag{1}$$

Mixing Period

Variations in the mixing conditions were achieved by adjusting the combination of oscillation amplitude and frequency. At a given oscillation amplitude, two modes of oscillation condition were employed during the mixing period: two-stage and single-stage mixing. The two-stage mixing was achieved by oscillating the column at a high frequency (7 Hz) for half a minute, then changing to a low frequency (4 Hz) for the remaining 4.5 minutes within the flocculation period. This two-stage mixing mimics the classic stirred jar test where a period of high stirrer speed is initially used and followed by a period of low speed. The one-stage mixing was achieved by using a single frequency for the whole flocculation period.

RESULTS AND DISCUSSION

It was observed that the size of flocs appeared to grow very quickly in the first 30 seconds after the polymer addition and then began to break up into smaller ones which remained for the rest of the flocculation period. We will report a study of this phenomenon together with associated velocity gradients in a later paper. In this paper, however, we report our experimental findings in particle flocculation in the batch oscillatory baffled column. For all the experiments carried out, it was found out that the pH values of the bentonite suspension remained relatively constant (6.5–6.6) throughout the flocculation process, therefore the effect of pH on particle flocculation is minimized.

Floc Settling Time

The floc settling time refers to the minimum time required for flocs to settle under gravity in small containers, such as cuvettes, and is a function of a number of variables, e.g., mixing intensity, polymer dose, etc. Measurements of percent flocculation are carried out at a specific settling time. It is thus necessary to ensure the settling time is adequate for all our samples. Figure 3 shows the optical density as a function of floc settling times for

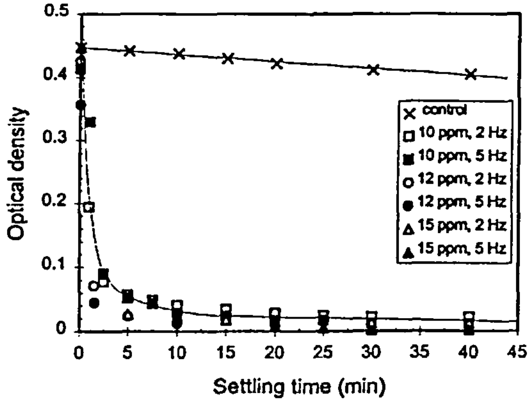

FIG. 3 Optical density vs settling time of samples at various polymer dosages and oscillation frequencies. Oscillation amplitude = 4 mm, polymer = Magnafloc 1697.

three polymer dosages at two oscillation intensities. The line with crosses indicates the control runs where no polymer was present in the bentonite suspension, and this is the profile for the background settling. It is evident that a settling period of 40 minutes is sufficient to remove all flocculated material, leaving unflocculated single particles in suspension, and is used in the following experiments.

Effect of Oscillation Intensity

Fluid oscillation intensity produces vorticity in the oscillatory baffled column and hence generates the shear rate experienced by the particles. This enhances polymer dispersion and adsorption within the bentonite suspension in the column. However, excessive fluid mechanical forces break up flocs and hence limit the floc size. A series of experiments was conducted to investigate the effect of oscillation intensity on the flocculation process. Some of the results are shown in Figs. 4 and 5 where the polymer was added in the incremental mode. With a frequency of 2 Hz (Fig. 4), increasing the amplitude increased the amount of flocculation. However, when a frequency of 5 Hz was used, the enhancement of flocculation with increasing amplitude was only seen with the smaller amplitudes, e.g., 4 and 8 mm (Fig. 5). At the most vigorous mixing condition (5 Hz and 12 mm), the percentage flocculation decreased at the lower polymer dose. This is most likely due to the shear conditions which erode the floc sizes. At higher polymer doses the flocs are presumably stronger and the percentage of flocculation remained constant.

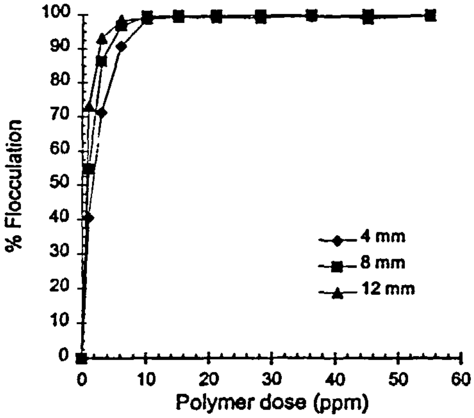

FIG. 4 The effect of oscillation intensity on flocculation of bentonite. Oscillation frequency = 2 Hz, polymer = Magnafloc 1697.

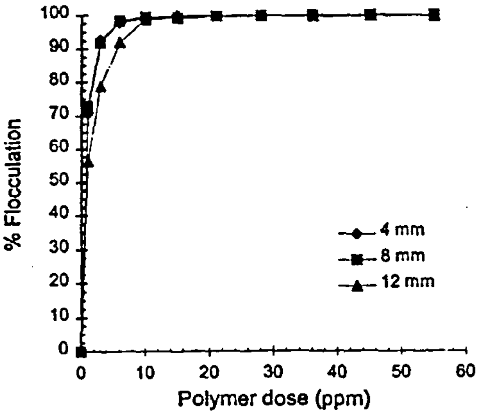

FIG. 5 The effect of oscillation intensity on flocculation of bentonite. Oscillation frequency = 5 Hz, polymer = Magnafloc 1697.

The experimental results indicate that there existed an optimal oscillation intensity at which a maximum percentage of flocculation was obtained.

Effect of Mixing Mode

Flocculation studies carried out in stirred tanks generally involve a period of high stirrer speed preceding a period of lower one. Thus, in this study, the effect of mixing mode on flocculation rate in the oscillatory baffled column was also investigated. The results are shown in Fig. 6. It can be seen that the mixing mode did affect the percentage of flocculation, but only at the lower polymer dosages up to 10 ppm where the two-stage mixing mode produced on average a higher percentage of flocculation than the single-stage mode. For the polymer dosages beyond 10 ppm, the percentage of flocculation in the two-stage mixing mode decreased and became lower than that in the single-stage mode of mixing. It can be argued, bearing in mind that the polymer was added incrementally, that once sufficient polymer has been added to provide strong flocs, further additions of polymer will have no effect (7). Figure 6 also shows that under the single-stage mixing mode, almost all the percentages of flocculation were higher at a low frequency than at a high frequency. This supports our previous suggestion that there exists an optimal mixing intensity at which maximum flocculation can be obtained.

Effect of Mode of Polymer Addition

Robinson et al. (2) found that the mode of polymer addition greatly affected the outcome of the flocculation process in a stirred tank reactor. We thus

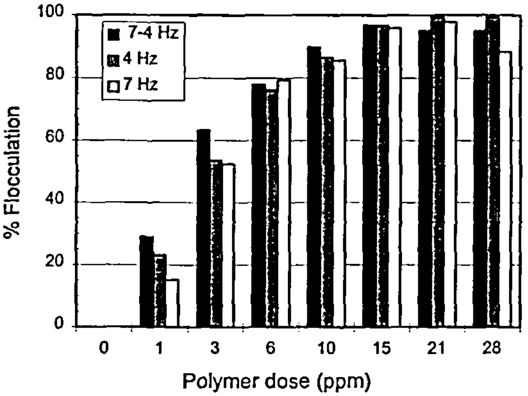

FIG. 6 The effect of mixing mode on flocculation in the oscillatory baffled column. Oscillation amplitude = 4 mm, polymer = Magnafloc 1697, polymer injection mode = increment.

investigated the effect of the methods of polymer injection, i.e., the slug or incremental in the oscillatory baffled column, and the results are shown in Figs. 7 and 8 for Magnafloc 1697 and Zetag 89 polymers, respectively. It can be seen that under the same polymer dosage and mixing intensity, the slopes of increase in the percentage of flocculation were steeper for the incremental mode than for the slug mode, indicating that the former gave on average a better flocculation rate than the later method for both Magnafloc

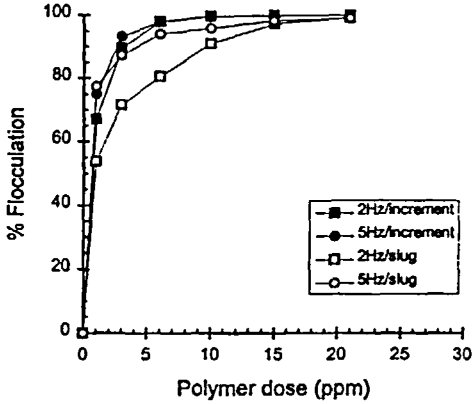

FIG. 7 Effect of polymer addition mode on flocculation in the oscillatory baffled column. Oscillation amplitude = 8 mm, polymer = Magnafloc 1697.

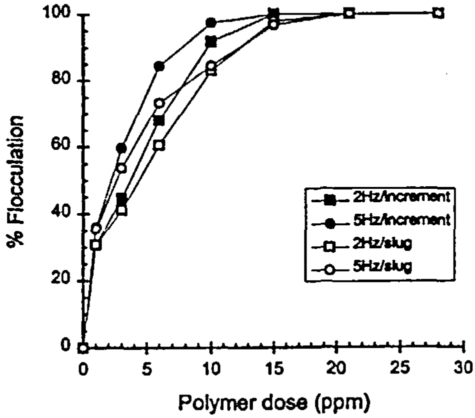

FIG. 8 Effect of polymer addition mode on flocculation in the oscillatory baffled column. Oscillation amplitude = 8 mm, polymer = Zetag 89.

1697 and Zetag 89 polymers. The same trends were also obtained for an oscillation amplitude of 4 mm (not shown in this paper). An explanation for the poor percentage flocculation associated with the slug addition of polymer is that adsorption of the polymer occurs faster than collisions between particles, hence the particles become coated with too much polymer, denying the opportunity of flocculation by charge neutralization (where particles of zero charge are needed) or by bridging (where free space is needed on some particle for attachment of the bridging polymer).

In addition, no evidence of overdosing was observed with the combination of a high polymer dose and the slug addition, where the percentage of flocculation either increased or held constant with the increase of polymer dosage. This contrasts to the work with stirred tanks, where the percentage of flocculation decreased with the increase of polymer dosage. Although no direct comparison can be made between the oscillatory baffled column and stirred tanks using bentonite, in a study using kaolin (a similar type of clay particle) Kage et al. (20) found that charge reversal of cationic polymers occurred above a dose of 2 mg polymer per gram kaolin. This is equivalent to a concentration of polymer of 2 ppm in our system. In stirred tanks the dispersion time for the polymer may be sufficiently slow to allow pockets with a high concentration of polymer to contact the particles (21). These particles could adsorb the polymer in excess, which again would manifest itself by charge reversal and poor flocculation, if the flocculation is brought about by the charge of the polymer rather than its molecular weight and bridging. Magnafloc 1697 is a low molecular

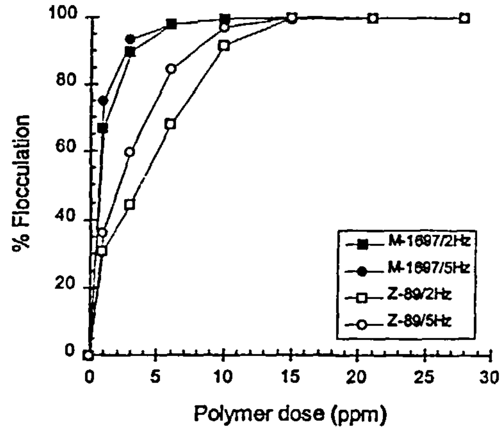

FIG. 9 Effect of polymer dosage on flocculation for both Magnafloc 1697 and Zetag 89. Oscillation amplitude = 8 mm, polymer addition mode = increment.

weight polymer with a high charge density while Zetag 89 is a high molecular weight polymer, also with a high charge density. It is thus expected that the flocculation process is by charge neutralization, but may not carry sufficient charge to cause charge reversal at the dosage employed in this study.

It can be seen from Figs. 7 and 8 that increasing the oscillation intensity (by either amplitude or frequency) increases the amount of flocculation

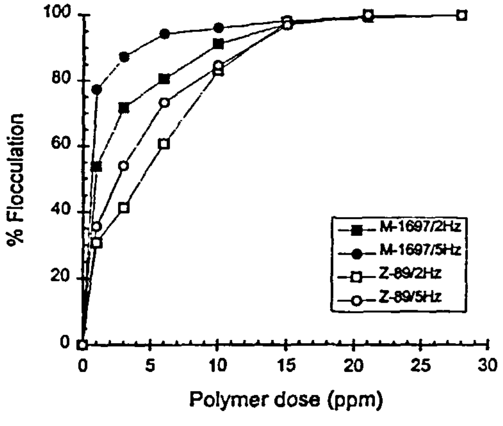

FIG. 10 Effect of polymer dosage on flocculation for both Magnafloc 1697 and Zetag 89. Oscillation amplitude = 8 mm, polymer addition mode = slug.

achieved under slug addition. Not only could this be due to better mixing being associated with oscillation intensity, but also increased rates of polymer adsorption and particle collisions (1). This suggests that a different mechanism of flocculation in an oscillatory baffled column could be expected. We are further investigating these factors.

A comparison of the percentage of flocculation vs polymer dosage for both Magnafloc 1697 and Zetag 89 polymer was also made, which is shown in Figs. 9 and 10 for the incremental and slug additions, respectively. It can be seen that for the same oscillation intensity, the polymer with a low molecular weight induced a sharper and higher increase in the percentage of flocculation for the range of polymer dosage investigated in the oscillatory baffled column. This is expected as the polymer with a high molecular weight requires a longer time to be dispersed within the column. Overall, the increase in the oscillation intensity gave a better rate of flocculation.

CONCLUSIONS

We have reported, for the first time, the experimental results of particle flocculation in a batch oscillatory baffled column. We identified 40 minutes as the optimal settling time for measurements of the percentage of flocculation. Investigation on the effect of mixing intensity on the percentage of flocculation showed that there exists an optimal oscillation intensity at which a maximum percentage of flocculation is obtained. The mixing mode also affects the degree of flocculation; it was shown that the two-stage mixing mode produces a higher percentage of flocculation than the single-stage mode for low polymer dosages, but is more or less unchanged for high polymer dosages. Experiments on the effect of polymer addition methods have shown that incremental addition is better than slug addition, and there was no evidence of overdosing for both low and high molecular weight polymers at a combination of high polymer dosage and slug addition. This is an interesting finding, and a different mechanism of particle flocculation may be expected in the oscillatory baffled column. We are currently setting up a particle image velocimetry device which will enable us to quantify the local shear rate within the column and monitor the growth of flocs. This could then allow us to compare our work with those reported in stirred tanks, correlate the percentage of flocculation and floc size with the measured shear rate and power consumption, and gain further insight into the mechanism of flocculation in the oscillatory baffled column.

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