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INVESTIGATION OF THE SHEARING EFFECTS ON THE FINES FLOC SIZE AND FLOCCULATION PARAMETERS IN FINES FLOCCULATION USING COFACTOR-POLYETHYLENE OXIDE RETENTION AID SYSTEM

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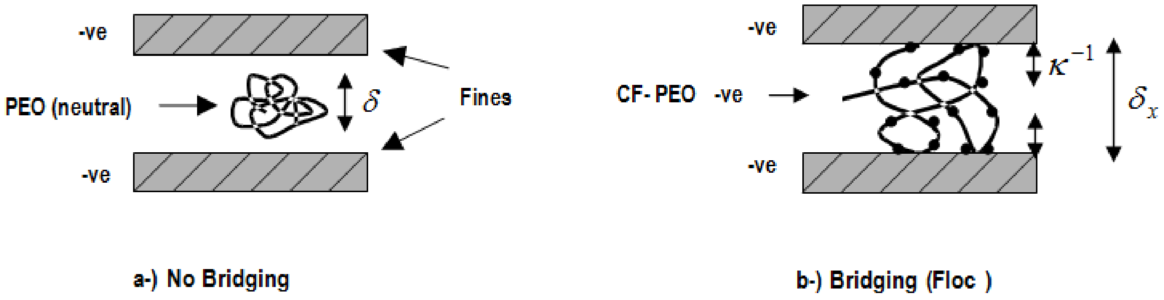
ABSTRACT

In industrial applications confirmed with research work, the particles are wanted in some required specific properties; one is the particle size. In fines flocculation, the cofactor (CF)- polyethylene (PEO) dual system is essential and conventionally used. The fines comprise more than half the raw pulp. For this, we have investigated the effect of the shearing on the resulted flocs after flocculation. Results have shown that increases in the shear rate caused the floc size, the flocculation rate, and flocculation rate constant to decrease. In other hand, increases in shear rate enhanced deflocculation, causing the deflocculation rate, the deflocculation rate constant, and the reverse equilibrium rate constant to increase. For more, as with shear rate increase, the flocculation rate constant has decreased and deflocculation rate constant has increased, they approach each other and expected to be equal at a value of (0.4 s^{-1}) , while reverse equilibrium rate constant equals to 1 when the shear rate approach 700 s^{-1}. Since the flocs are easily affected by shearing, which changes the required flocs specifications, this study becomes important and as a guide to mills in the field and research.

KEYWORDS: Polyethylene oxide, Cofactor, Flocculation, Deflocculation, Floc Size, Shear rate, Rate constant, reverse equilibrium rate constant.

INTRODUCTION

In many industrial applications, specific characteristics of particles and flocs are required. Number of factors in process affect the characteristics and parameters that specify the process change with the changes in the factors. One application is papermaking, where specific values of paper sheet strength, permeability, opacity and density are needed (Brecht, W. and Klemm, K., 1953; Norman, 2008). Large fibrils are unwanted as they change the wanted properties, and work to return them to the wanted sizes are recommended (Hubbe, M. A., et. al. 2002; Hubbe, M. A. 2007). Number of processes like flocculation, dispersion, attachment, detachment, and deflocculation are reported in literature. Deflocculation was reported after floc production, where the resulted floc dissipate and the retention aid becomes no more capable to keep the floc (Abdallah, Mohammad. R. 2002; Carignan, A. et al. 1998; van de Ven, T.G.M. 1994). We studied number of factors that affected flocculation in which all the mentioned processes took place (Dr. Mohammad Raji Abdallah Qasaimeh, 2024; Mohammad Raji Abdallah Qasaimeh, 2022; Abdallah/Qasaimeh, M. R., et. al., 2014; Abdallah Qasaimeh, M. R., 2011; Abdallah/Qasaimeh, M. R., et. al., 2011; Abdallah, Mohammad. R. 2002). In previous studies we investigated the factors affecting the fines flocculation using the cofactor CF- polyethylene oxide (CF-PEO) retention aid system (Abdallah/Qasaimeh, M. R., et. al., 2014). For their importance, we studied the effect of CF concentration and analyzed the affective parameters (Mohammad Raji Abdallah Qasaimeh, 2024; Mohammad Raji Abdallah Qasaimeh, 2022;). We are also going to study the effect of fines consistency on flocculation, since consistency showed important effects on suspensions and their behaviors (Martin A. Hubbe, et. al., 2017). In the past, we investigated the deflocculation phenomenon in fines flocculation using the CF-PEO retention aid system, and attributed the causes to parameters in PEO (Abdallah Qasaimeh, M.R., 2011). In literature a lot of work studied flocculation using polymeric retention aids (van de Ven, T.G.M. and Allince, B. 1996; van de Ven, T.G.M., 1994; De Witt, J.A. and van de Ven, T.G.M., 1992) and dual systems with cofactors (van de Ven, T.G.M. and Allince, B., 1996: van de Ven, T.G.M., 1997). The polyethylene oxide PEO was recommended as neutral retention aid not interfering with ions that spoil the retention aid (Pelton, R. H., et. al., 1980; Pelton, R.H., et. al., 1981). Different types of cofactors were used with PEO to enhance it activity (van de Ven, T.G.M. 1997). The CF-PEO mechanism to bridge particles was studied by number of theories (Abdallah, Mohammad. R. (2002) and the dominant one was the association-induced polymer bridging proposed by van de Ven and Alince (van de Ven, T.G.M., and Alince, B., 1996), who explained the mechanism and argued the transient network mechanism (Lindström, T. and Glads-Nordmark, G., 1984). Van de Ven and Alince confirmed that PEO and phenolic CF used alone, do not adsorb on most pulps and showed bridging of fillers occurred in two ways (van de Ven, T.G.M. and Alince, B. 1996). In first way, the CF segments adsorbed on PEO coils (of size δ) and acted to expand these coils forming a larger CF-PEO complex (of size δ_x), which adsorbs on the surfaces and bridges the particles. In this state, the negative CF segments in the complex rebel each other and act to stiffen and expand the PEO coils into a size larger than the thickness of the electrostatic double layer (κ^{-1}). This large size stiffened complex facilitate and bridge with two conditions $\delta_x > 2\kappa^{-1}$ and $\theta(=\Gamma/\Gamma_m) < 1$. Here, θ is the PEO fractional coverage on the surfaces, the Γ is the PEO quantity covering the surfaces, and Γ_m is the PEO quantity needed to maintain the full coverage on the surfaces (De Witt, J.A. and van de Ven, T.G.M. 1992). In the second way (van de Ven, T.G.M. and Alince, B., 1996), the CF segments adsorbed on PEO coils work to reduce the PEO coil entropy and the heat of adsorption into adsorption zone facilitating for PEO coil adsorption on the surfaces.



a-) No Bridging

b-) Bridging (Floc)

Fig. 1: PEO Induced Bridging Mechanism.

The PEO bridging induced by CF (Fig 1) also works in fines flocculation (Abdallah, Mohammad. R. 2002; van de Ven, T.G.M. 1997). The CF segments and the fines have negative charges and rebel each other, thus CF does not adsorb on fines nor the PEO. In a combination of CF with PEO, the CF induces the PEO coils to adsorb on the fine's surfaces as a CF-PEO complex that bridges the fines. PEO coils in entanglement, its size δ and configuration before addition to flocculation are important to satisfy the $\delta > 2\kappa^{-1}$ (Abdallah, Mohammad. R. 2002; Kratochvil, D., et. al., 1999: De Witt, J.A. et. al., 1992). The shape along with the size δ are restricted to factors in PEO preparation unit such as concentration, dilution, dissolution, aging and delivery

(Abdallah, Mohammad. R. 2002). A contradictive to induced polymer bridging is the asymmetric bridging. Here, although PEO alone doesn't adsorb on fines (Lindström, T. and Glads-Nordmark, G. 1984), it adsorbs on one class of fines (Kraft pulp fines), acquires the ability to adsorb on other fines and bridge fines with asymmetric bridging mechanism (Carignan. et.al. 1998; van de Ven, T.G.M. and Alince, B. 1996; Abdallah/ Qasaimeh, M.R. et.al., 2011). Comparing fines flocculation using PEO alone (asymmetric bridging) with fines flocculation using the CF-PEO complex (induced PEO bridging), it was found that CF addition enhanced flocculation efficiency and floc sizes to several times. Similar results were reported in a second work (Abdallah Qasaimeh, M.R. 2011). For more, the bridging mechanism with CF-PEO to flocculate fines was reported to apply Longmuir equation and Smoluchowski isotherm (van de Ven, 1994). In collision theory, Smoluchowski proposed the collision rate constant (k_{sm}) as the rate of collision between two spherical particles of radii a_1 and a_2 subjected to a process shear rate (G_p) and stated it as $(k_{sm} =) \frac{4}{3} G_p \left(a_1 + a_2\right)^3$ (Smoluchowski, M., 1917). When particles are identical having same radius a, the process becomes homoflocculation and the rate constant becomes $k_{sm} = \frac{16}{3} G_p a^3$ (Abdallah, Mohammad. R. 2002; Petlicki, J. and van de Ven, T.G.M. 1992). For a suspension having C number of particles in a unit volume, or particle consistency (C), the actual flocculation rate of the successful collisions will be $r_f = r_{att} = -k_{att} C^2 = -\eta k_{sm} C^2$. Here the rate r_f is negative as it is in term of the particle disappearing rate, the k_{att} is the attachment rate constant, and η is the flocculation efficiency denoting the ratio of the collisions leading to successful attachments to the total performed collisions (Abdallah, Mohammad. R. 2002).

In previous work (Abdallah, Mohammad. R. 2002), Longmuir models were derived for possible interactions among the particles at the headbox in papermaking. To verify these models, the kinetics of fines-fibers heteroflocculation and fines-fines homoflocculation were investigated in flow loop at high shear rate near to mill condition and found to apply Longmuir equation and Smoluchowski isotherm. According to Longmuir, the flocculation rate $r_f\ (= r_{att} - r_{\det})$ is a resultant of the two opposing attachment rate (r_{att}) and detachment rate ($r_{\det}$). At equilibrium, the rate $r_f\ (= 0)$, denoting equal attachment and detachment rates ($r_{att} = r_{\det}$). To enhance r_f, workers directed their work to enhance r_{att} and reduce $r_{\det}$ (Abdallah, Mohammad. R. 2002). At initial flocculation, attachments among the particles are dominants as flocs are not yet initiated with no detachment, resulting in a maximum initial rate of flocculation (Abdallah, Mohammad. R. 2002). One important phenomena, which contradict Longmuir equation was the deflocculation reported in most works using PEO alone and CF-PEO, shown as transient flocculation after equilibrium (Abdallah, Mohammad. R. 2002; Abdallah Qasaimeh, M.R. 2011; Meng, R.Wu. and van de Ven, T.G.M. 2009). In further study, we measured the deflocculation rate (r_d) (Abdallah Qasaimeh, M.R. 2011). Based on Longmuir equation, the flocculation rate r_f should be zero at equilibrium and after where $r_{att} = r_{\det}$, but in case of deflocculation the $r_{\det} > r_{att}$ and the difference is the r_d (Abdallah Qasaimeh, M.R. 2011; Meng, R.Wu. and van de Ven, T.G.M. 2009). Reviewing the factors and mechanisms important to flocculation in literature; the PEO entangle state; the role of different cofactors CF; the bridging mechanisms; the attachments; the detachments; the Smolochowski isotherm and Longmuir equations; the PEO addition; the CF concentration effect, and the effect of shearing on flocs are needed to investigate. All mentions factors are to be controlled to produce the flocs at required characteristics; these flocs can be spoiled by the effect of shearing. Based on these data, the object of this work is to study the effect of floc shearing on the resulted flocs. Shearing is expected to disperse flocs and enhance detachment and deflocculation. Detachment will reduce the flocculation rate r_f, while deflocculation will increase the rate r_d, and getting new parameters are expected.

Experimentation

Materials

The materials used were fines obtained from a mixture of pulps taken from Masson Maclaren Mill (Canada), disintegrated and washed to remove the fibers and other colloids before use. Flocc 999 (the neutral PEO of a 7 million molecular weight) and the cofactor (Interac 1323), the negative phenol material were the retention aids supplied by I.Q.U.I.P Inc, (Canada). These materials were used in previous works (Abdallah, Mohammad. R. 2002; Abdallah Qasaimeh, M.R. 2011; Abdallah/Qasaimeh, M.R. et al. 2011; van de Ven, T.G.M. et al. 2004), but with different conditions based on the factors to be studied.

Experimental Setup

The fines were added to the beaker (flocculation vessel) (Fig 2) at consistency $C (= (0.1\%)$ to run flocculation experiment. These fines were mixed at a constant low stirring rate $N = 206$ (rpm), at sufficient low G_p to maintain homogeneous fines suspension (steady state 1). The sufficient low

G_p was kept to run flocculation to maintain large flocs that significantly be affected by the shear rate (G_t) exerted by a peristaltic pump at the exit of flocculation vessel. Fines were first circulated by the pump via the transparent tube at G_t to get homogeneous fines at steady state 1 that pass the photo cell of the Photometric Dispersion Analyzer (PDA) to measure its flocculation intensity (Gregory, J. 1984; Rank Brothers Ltd.). After steady state 1 maintenance, CF was first added followed with PEO. Flocculation intensity was shown after the PEO addition and recorded by PDA readings to estimate floc size (A), flocculation rate r_f, and rate of deflocculation r_d at different tube G_t values to study and analyze the effect of shear rate G_t. This setup (Fig. 2) was the same used in previous works where all factor were constants except the factor under study. (Abdallah, Mohammad. R. 2002; Abdallah Qasaimeh, M.R. 2011; Abdallah/Qasaimeh, M.R. et al. 2011; van de Ven, T.G.M. et al. 2004; Abdallah Qasaimeh, Mohammad et al 2010).

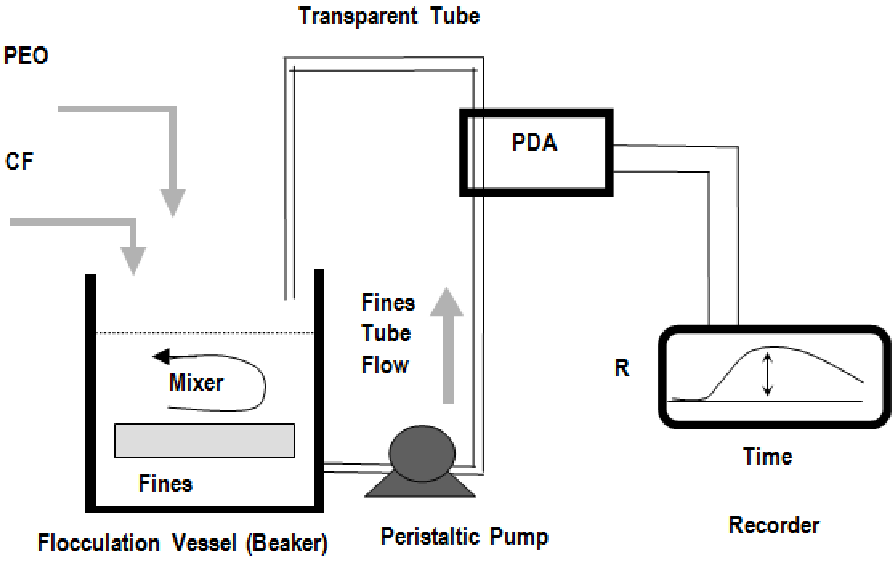


Fig. 2: Experimental Set up of Fines flocculation.

Flocculation and Deflocculation Intensity Readings

The main PDA output signal is the ratio reading (R), taken as the vertical distance the pen of the recorder moves with time (t). The reading R at time t, the flocculation amplitude denotes the particle size (A) at time t (Gregory, J. 1984; Rank Brothers Ltd.), where larger the particle is the larger R. In flocculation process, the reading R starts increasing with time after CF and PEO additions, reaching a maximum, and then starts to decrease showing

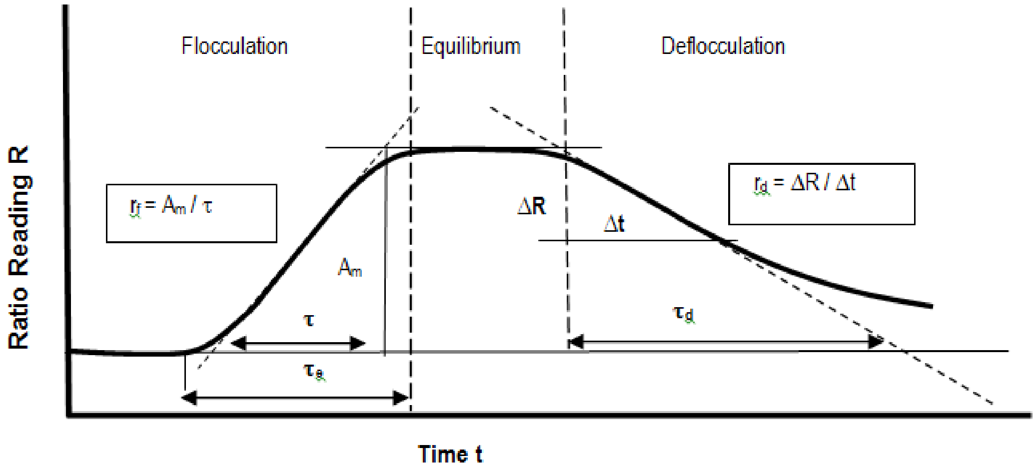


Fig. 3: Flocculation and Deflocculation Intensity Readings.

deflocculation. The recorder plots the reading R versus the time t (Fig 3), where the maximum R indicates the maximum floc size (A_m) in arbitrary unit (A.U.). From the curve, the initial rate of flocculation $r_f\ (= A_m / \tau)$ in A.U. is the slope of the curve at initial flocculation (Abdallah, Mohammad. R. 2002). The time needed to get A_m at initial rate r_f is the characteristic time of flocculation (τ) that indicates flocculation speed (Abdallah, Mohammad. R. 2002). The time needed to reach equilibrium is equilibrium time (τ_e). Initial rate of deflocculation (r_d) is the slope of the curve at initial deflocculation. The time needed to reach the zero amplitude at r_d is characteristic time of deflocculation (τ_d) that indicates deflocculation speed (Abdallah Qasaimeh, M.R. 2011). In this work, the flocculation rate constant is taken using $k_f\ (=1/\tau)$, the deflocculation rate constant using $k_d\ (=1/\tau_d)$, and the reverse equilibrium constant using $K_{-equ}\ (=k_d/k_f)$ as in previous work (Dr. Mohammad Raji Abdallah Qasaimeh, 2024; Mohammad Raji Abdallah Qasaimeh, 2022).

RESULTS AND DISCUSSION

The second significant factor to be considered is the hydrodynamic forces. Based on literature, the increase in G_p in flocculation process caused the resulted flocs to break (Jacquelin, G. 1968; Bjorkman 2003; Healy, T. W. and La Mer, V.K. 1964; Spicer, T.P. and Pratsinis, S. E. 1996;

Klomogorov, A. N. 1949; Higashitani, K. et al. 1989). In PEO dissolution unit prior to flocculation, the increase in the shear rate caused the PEO entanglements to dissociate (Abdallah, Mohammad. R. 2002; van de Ven, T.G.M. et al. 2004). In flocculation, some workers have investigated the multimodal effective particle size distributions (EPSDs) due to the particle breakage as an alternative to the reported previous distributions in coastal and estuarine waters. This breakage was dynamically resulted in a fluid shearing as an alternative to the reported previous distributions in coastal and estuarine waters (R. Maltauro, et. al. 2023). In another work, the effects of hydrodynamic breakage on floc size, fractal dimension, and floc morphology were investigated with an in-situ recognition system. Results indicated that the hydrodynamic conditions significantly influenced the floc destabilization and the restructuring processes (Xinran Zhang, et. al. 2022). For more, the effects of shear-induced breakage and reflocculation of the floc, settling, and dewatering of coal tailings were investigated. They showed that the settling velocity of flocculated tailings decreased with the increase in the shear strength, and at high dosages, the shear rate enhanced the floc dewatering performance by reconstructing the filter cake (Yuping Fan, et. al. 2020).

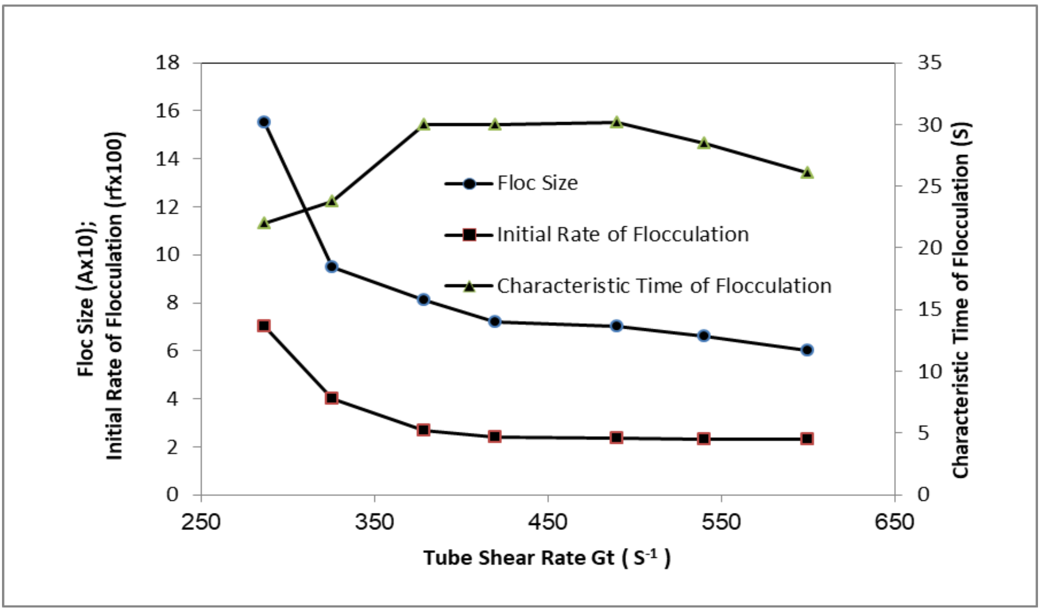


Fig. 4: The effect of tube shear rate G_t at the exit of flocculation vessel on floc size, initial rate of flocculation rate and characteristic time of flocculation.

In our previous work, fines flocculation was performed at process shear rate $G_p = 130\, s^{-1}$ that gave lower characteristic time of flocculation τ or the maximum speed (Abdallah, Mohammad.

R. 2002). At lower process shear rate $G_p = 75\, s^{-1}$ higher characteristic time of flocculation τ or lower speed with higher floc size were obtained. These works showed the effects of the process shear rate G_p. In this work, we have studied the effect of shearing on the floc in tube after its formation in the flocculation vessel by increasing the shear rate G_t at the exit of flocculation vessel. This increase in G_t (Fig. 4) has shown significant decreases in floc size and flocculation rate. Characteristic time of flocculation τ showed slight increase followed with a decrease in values between 20 and 25 seconds. In this paper, the effects of shear-induced breakage and reflocculation of the floc, settling, and dewatering of coal tailings were investigated. The results show that as shear strength increases, the settling velocity of flocculated tailings decreases. At high dosage conditions, shear could enhance the dewatering performance of flocs by reconstructing the filter cake.

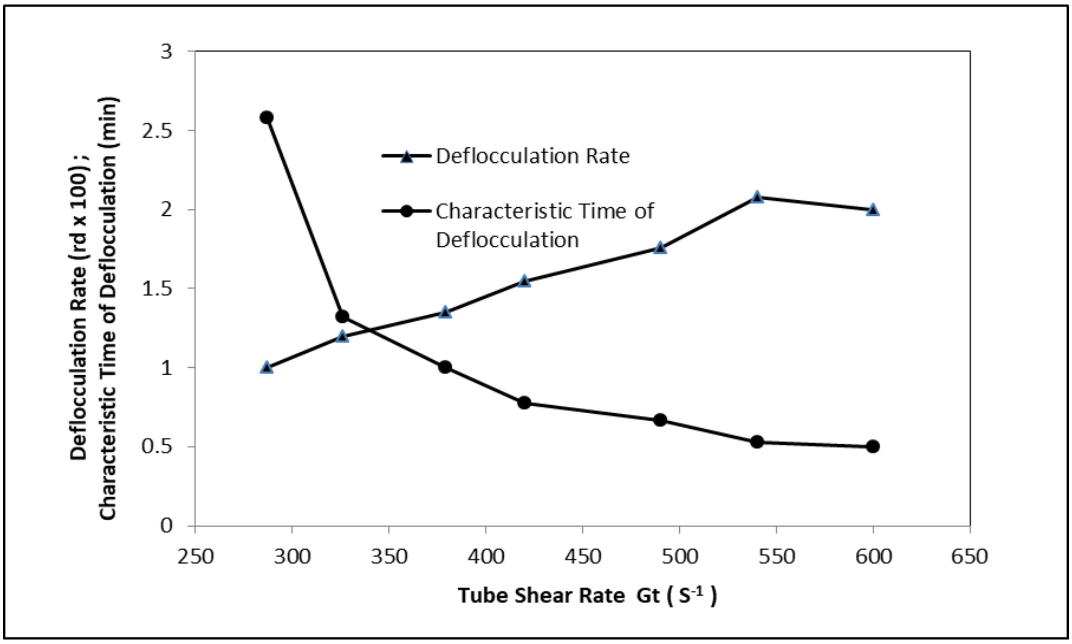


Fig. 5: The effect of tube shear rate G_t at the exit of flocculation vessel on flocculation rate and characteristic time of deflocculation.

Defloculation, as occurred in flocculation experiment, has been investigated (Fig. 5) with the increase in G_t, where significant increase is shown in deflocculation rate r_d, and drastic decrease in characteristic time of deflocculation τ_d. To investigate more, and to find out the combined effect of flocculation and deflocculation, we have found out the rate constants (Fig. 6) and plotted their values versus the increase in tube shear rate G_t. The rate constant is found in a method similar to that used in previous work (Dr. Mohammad Raji Abdallah Qasaimeh, (2024); Mohammad Raji Abdallah Qasaimeh, (2022).

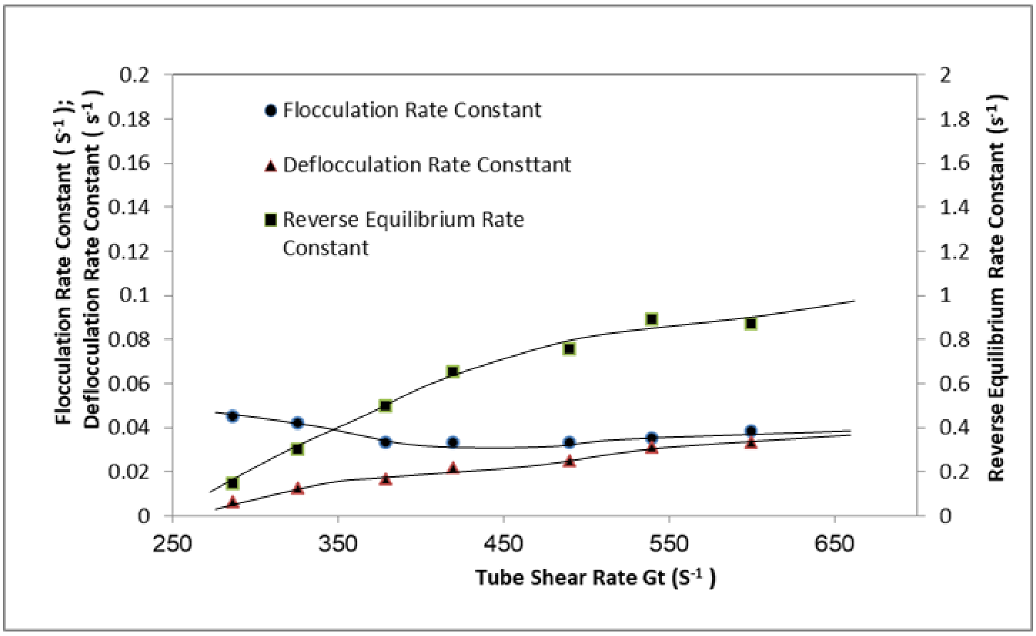


Fig. 6: The changes of the flocculation rate constant, deflocculation rate constant, and reverse equilibrium constant with the increase in tube shear rate G_t.

The flocculation rate constant k_f decreases with the increase in the shear rate G_t indicating a decrease in flocculation rate r_f, while the deflocculation rate constant k_d increases with the increase in G_t. The two curves are expected to intersect at same values at 0.4 when G_t reaches the value around 700 s^{-1}. The reverse rate constant K_{-equ} increases with the increase in G_t and is expected to reach a value of 1 when G_t reaches around 700 s^{-1}. From these results, we can conclude that flocculation is always faster than deflocculation, but with increasing the flocs shearing, deflocculation speeds up after equilibrium and approaches the flocculation speed. In this work, we have extrapolated the shear rate to a value that flocculation and deflocculation speeds become equal at around $G_t = 700\, s^{-1}$, where the $k_f = k_d = 0.4\, s^{-1}$, and $K_{-equ} = 1$. Further study is recommended to investigate the shearing effect at higher values.

CONCLUSION

In this work we have investigated of the effect of shearing fines floc, which can occur when the shear is changed at the exit of flocculation vessel and during the processes after flocculation such as delivery and storage. This shearing is found to change all the characteristics of flocculation and flocs. With the increase in shearing the floc size and the flocculation rate constant decreased, The deflocculation rate constant increased, thus resulting a significant increase in reverse equilibrium constant. All flocculation results showed in previous work and in this work higher flocculation rate constant than deflocculation rate constant, but with shearing the floc the difference between their values decreases and they become equal at definite high shear rate. These results are important to control fines flocculation at the required settings.

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