The role of shear conditions on floc characteristics and membrane fouling in coagulation/ultrafiltration hybrid process- The effect of flocculation duration and slow shear force

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Complete List of Authors:	nan, jun; Harbin institute of technology, Yao, Meng; Harbin institute of technology, School of Municipal and Environmental Engineering Li, qinggui; Harbin institute of technology, School of Municipal and Environmental Engineering Zhan, Dan; Harbin institute of technology, School of Municipal and Environmental Engineering Chen, Ting; Harbin institute of technology, School of Municipal and Environmental Engineering Wang, Zhenbei; Harbin institute of technology, School of Municipal and Environmental Engineering Li, haoyu; Tianjin University,
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The role of shear conditions on floc characteristics and membrane fouling in coagulation/ultrafiltration hybrid process- The effect of flocculation duration and slow shear force

Jun Nan[a,*], Meng Yao[a], Qinggui Li[a], Dan Zhan[a], Ting Chen[a], Zhenbei Wang [a], Haoyu Li[b]

Abstract:

Impacts of shear conditions during coagulation on ultrafiltration permeate flux in coagulation-ultrafiltration (C-UF) process were investigated. Different flocculation durations and slow shear forces were applied to explore the impact of shear condition on the C-UF process. Floc characteristics, including floc average size, fractal dimension and flocs size distribution under different coagulation conditions were studied. Besides, the normalized flux and reversibility of membrane fouling were also analyzed to investigate the membrane fouling. The results indicated that flocs formed under shorter flocculation duration with small fractal dimension, which easily developed cake layer with larger pores and fluffy structure on membrane surface. But, the higher frequency of small size flocs still remained at 5 min flocculation time attributing to the inadequate collision among particles, which could cause severe membrane fouling. As a result, appropriately shorten slow stirring time (for 10 min) and reduction of low-shear force (G=8 s^{-1}) are conducive to form flocs with loose and porosity structure without the occurrence of more small particles in water, which seemed to be effectively improved the membrane permeability.

Keywords: Flocculation duration; Slow shear force; Floc characteristic; Cake layer; Membrane fouling;

1. Introduction

In drinking water treatment process, membrane technology is an attractive alternative for providing high quality water that can satisfy the requirements of more strict water quality regulations. [1] However, fouling is one of the main disadvantages with membrane ultrafiltration process, attributing that the decline of flux resulted in higher water treatment cost and the deterioration of membrane. [2]Different pre-treatments before ultrafiltration have been widely applied as methods to lower membrane fouling, such as coagulation, adsorption and oxidation. The combination of powder active carbon (PAC) adsorption and UF has been reported to more effectively mitigate the membrane fouling. [3] The oxidation before ultrafiltration can decrease the density of organic matter of effluents and remove oxidation intermediates, which could reduce the severity of membrane fouling by the removal of foulants on membrane surface.[4, 5]

Pre-coagulation before UF, especially by “in-line” chemical coagulation, can significantly improve membrane fouling.[6, 7] The effects of pre-coagulation on membrane permeability are mainly related the coagulation conditions, including coagulants types, dosages and mixing mode.[8, 9] Pikkarainen et al [10] has stated that the Fe- and Al-based coagulants caused similar hydraulic resistance properties in membrane filtration, but Fe-based coagulant would result in strongly colored on surface water. Choi and Dempsey [11] investigated the influence of alum concentration

[a] State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, PR China, Tel.:+86 451 86084169; Fax: +86 451 86283001; Email: nanjun_219@163.com.

[b] School of Science & Technology, Tianjin University, Taijin 300072,PR China

on polyethersulfone flat-sheet ultrafiltration membrane fouling, and found "in-line" coagulation can improve hydraulic removal of filter cake. Flocs formed under charge neutralization lead to lower hydraulic resistance than that of sweep floc condition.[12] Significantly, the properties of aggregates formed under different coagulations could affect the membrane fouling. [13-15] It should be worthwhile to note that the structure of particle aggregates also closely bonds to the flocculation duration and shear conditions involved in the coagulation/flocculation process.

In various mechanical aquatic systems, particles and flocs in suspension are highly dependent on the varying flocculation durations and flow conditions. In pre-coagulation/ultrafiltration process, the circulation of suspension induced by different coagulation conditions most likely influence the characteristics of flocs and further the structure of cake layer on membrane surface. Rossini et al investigates the influence of the rapid mixing time on final coagulation efficiency, and found that a short duration of rapid mixing was helpful to produce the lower residual turbidity [16]. Eric J. Wahlberg [17] have shown in his work that the activated sludge flocculated by mechanical means rapidly grow by 99% within 10 minutes under batch conditions. With same condition, the properties and configuration of flocs formed in the whole flocculation process could intensively change under different flocculation time. Nevertheless, few attentions have been paid for the flocculation duration on the performance of coagulation-UF process. Biggs and Lant [18] considered that the large shear force, the smaller average size of flocs aggregated under steady-state conditions. Other literatures have reported that the morphology of flocs was strongly depended on how the shear rate (G) was applied when a polymeric flocculant was used. [19, 20] Weipeng has investigated the evolution of floc size and structure in low-shear force.[21] Klimpel and Hogg [22] thought that higher mixing speed caused large fractal dimension of floc structure. Up to now, previous studies were mainly focus on the relationship between flocs characteristics and conventional coagulation/flocculation process. But, there was lack of insufficiently comprehensive and thorough understandings of the relationship between floc characteristics formed under different pre-coagulation conditions and the subsequent membrane behaviors and fouling mechanisms in coagulation-ultrafiltration process. Our previous paper investigated the influence of flocs breakage process on membrane fouling in coagulation/ultrafiltration process, which was concentrated on the effect of additional coagulant of poly-aluminum chloride and polyacrylamide. Other articles are specialized on the comparisons of flocs characteristics formed by different coagulants as well as their distinct effects on membrane fouling. [23, 24] Little research has been done on the effects of different flocculation durations and low-shear force during coagulation and membrane performances.

This work aimed to investigate the impact of different flocculation duration and low-shear force on coagulation process, in order to give a better mechanism understanding of the change of aggregates properties on membrane fouling in the subsequent ultrafiltration process. A series of modified flocculation tests were conducted under different flocculation durations and slow mixing speeds prior to UF. The main investigation focused on flocs size, structure and surface characteristic in pre-coagulation combined with UF membrane process. The reversibility of membrane fouling was still investigated.

2. Methods and materials

2.1 Suspension

Kaolin clay (Tianjin, China) and humic aicd (shanghai, China) were used as testing water sample. Kaolin clay was prepared by dissolving 50.0 g of kaolin clay in 1 L deionized water with continuous magnetic stirring for 24 h. After sedimentation for 1 h, 800 ml supernatant was the stock suspension of kaolin clay.

10 g of humic acid (Shanghai, Jufeng, China) was dispersed in 0.1 mM/L NaOH, and mixed for 24 h by a magnetic stirrer. The suspension was filtered by a 0.45 μm fiber filter membrane. The pH of the filtered solution was adjusted to 7.5 using 0.01 mol/L NaOH or HCl and the solution diluted to 1000 mL in a measuring flask. [25]The solution was stored in the dark.

Harbin tap water, China, has alkalinity of 15 mg/L as $CaCO_3$ and a pH of around 7.2. A small dosage of humic acid was added in the testing water to diminish the disturbance of divalent metal ions, like Ca^{2+} and Mg^{2+} in tap water. [26] For flocculation tests, the stock solution was diluted in the tap water, containing 100 mg/L of clay and 2 mg/L of humic acid. The initial turbidity was about 90 NTU. During the experimental program, the temperature of the solution was 22±2℃.

2.2 Coagulants

Polyaluminum chloride (PACl) (28% quality calculated as Al_2O_3), the basicity of which was 72.3%, was prepared as a concentration of 1 % by dissolving 5 g reagent in 500 mL deionized water. [27] This coagulant solution renewed 24h, for the flocculation tests, directly pipetted in the testing water without further dilution.

2.3 Apparatus

A modified version of the jar-test process was used in this research. A non-intrusive optical sampling technique was applied to capture digital images of particles from the moment of coagulant addition, which were then analyzed to form particle size distributions, geometrical properties, and calculations of the fractal dimension. [28] This basic procedure was similar as the work of Chakraborti et al, and has been widely used by our research fellows.[21, 26, 29] Because of no sample handling during measurements, there is no concern for destroying the floc characteristics. This coagulation setup, which was introduced in detail in our previous sturdies, [30, 31] included an in-site recognition system, a rectangular stirred tank (homemade) and a R1342-type impeller (IKA, Germany). The schematic diagram of this setup was shown in Fig. 1.

2.4 Coagulation procedure

As added the optimal dosage of PACl (around 0.08mM Al) in the reactor, testing water sample was mixed rapidly at 400 rpm ($G \approx 175 s^{-1}$) for 60 s. [21] Then, followed by a slow stirring at 90 rpm ($G \approx 20 s^{-1}$) for different flocculation durations, to allow flocs to grow. After 30 min sedimentation, the turbidity of supernatant was measured by an online turbidimeter (100AW, WTW, Germany). After 400 rpm for 60 s to break, stirring speed back to 90 rpm for 15 min to allow flocs re-grow. To investigate the effect of different slow mixing speeds, the rapid mixing speed was also set at 400 rpm for 60 s, then at shear rates from 8 to 20 s^{-1} for 15 min, 400 rpm for 60 s to break the flocs and then reduced to 90 rpm for the flocs to re-grow.

2.5 Analysis on floc morphology

The size, d_p, of irregular shape of a floc can be calculated in terms of the equivalent diameter by

$$d_p = \left(\frac{4A_P}{\pi}\right)^{\frac{1}{2}} \quad (1)$$

Where A_p is the projected area of a floc. Then, average size and size distribution of flocs in more than 20 images within a minute were used to reflect floc size at the corresponding moment.[21]

For a 2D projected particle image, the value of fractal dimension (D_f) reflects the surface morphology of aggregate in two-dimensional projection according to

$$A_p \sim P^{D_f} \quad (2)$$

Where P is the perimeter of an aggregate, and D_f is the two-dimensional fractal dimension of the objective. The values from D_f = 1 indicating the projected area of a linear structure, to D_f = 2 for a circular structure. As the object area is getting larger, the perimeter increases more quickly than for Euclidean objects means that the boundary of the objects become more convoluted and the shape of more irregular. In our study, flocs in more than 10 images within a minute were applied to calculate the value of D_f at the corresponding moment.

2.6 Ultrafiltration procedure

A dead-end batch ultrafiltration unit with a 400mL- capacity cylindrical beaker (Amicon 8400, Millipore, US) was applied for ultrafiltration experiments, and the schematic diagram was also shown in Fig. 1. Ultrafiltration membrane (Mosu, shanghai, China) with cut-off molecular weight (MWCO) of 100 kDa was used for ultrafiltration after it was "wetted" to its optimal operating condition. The membrane material was polyethersulfone (PES) and the effective membrane area was 50.24 cm^2. The membrane pore size is about 0.005 – 0.01 μm. A fresh piece of membrane was used in every ultrafiltration experiment. The coagulation effluent solution (after different flocculation duration and slow stirring speed) was gently decanted from the coagulation tank without sedimentation to the dead-end filtration unit and filtered through ultrafiltration membrane. Constant pressure at 0.15 MPa was kept by nitrogen gas. Instantaneous mass of cumulative permeate was measured by electronic balances (SI-2002, Denver instrument, China) with recorded via a personal computer equipped with a data acquisition system.

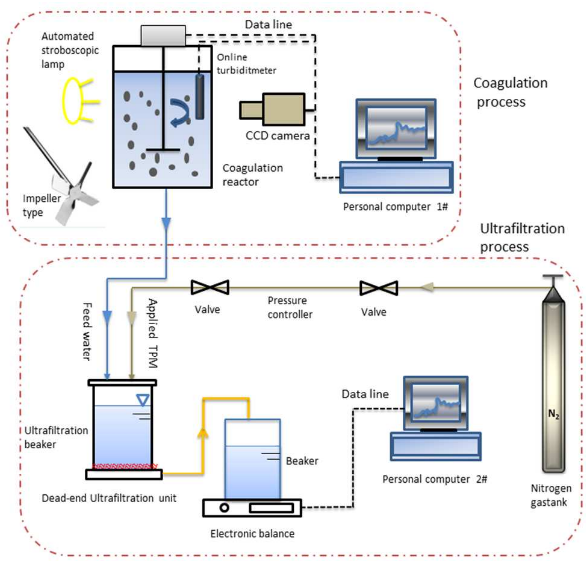

Fig.1 Schematic diagram of pre-coagulation/ultrafiltration experiments.

Every ultrafiltration test contains three periods, and each period includes three steps, and the operation sequences are shown in Fig. 2. 1) 400 mL coagulation effluent solution filtrated through the UF; 2) turn the ultrafiltration membrane over and put the opposite face on, then back washing with 50 mL ultrapure water; 3) Re-position the ultrafiltration membrane and put the positive face on, then filtrated 100mL ultrapure water for sake of membrane flux after back washing. The flux of membrane (*J*) is used as critical indicator to evaluate membrane fouling. The initial membrane flux of ultrapure water is represented as $J_{p\,(0)}$. The initial flux and final flux of each period are represented as $J_{i(n)}$ and $J_{f(n)}$, respectively. In here, n (1-3) is the cycle number. Based on this, normalized permeate fluxes of ultrafiltration process is represented as $J/J_{p(0)}$. The value of $J/J_{p(0)}$ is decreased, means fouling of membrane become severe.

If pollutant on membrane surface could be removed by hydraulic backwash process, this pollutant is noted as Reversible fouling (RF), while remaining contaminant on the surface of membrane is named as Irreversible fouling (IF). Both of the two kinds of fouling are total fouling (TF). Jermann et al .[32] has reported that RF, IF and TF can be calculated as the following equations:

$$IF_n = \frac{J_{p(n-1)} - J_{p(n)}}{J_{p(0)}} \tag{3}$$

$$TF_n = \frac{J_{p(0)} - J_{f(n)}}{J_{p(0)}} \tag{4}$$

$$RF_n = TF_n - IF_n \tag{5}$$

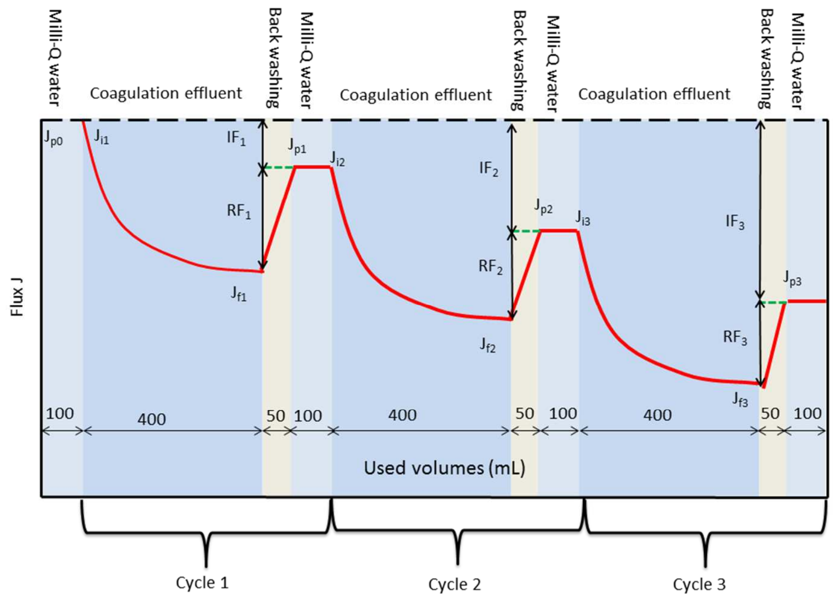

Fig.2 Schematic diagram of ultrafiltration operating sequences

3. Results and discussion

3.1 Effect of flocculation duration on the coagulation-ultrafiltration

3.1.1 Effect of flocculation duration on the evolution of floc characteristics

The flocculation duration is expected to have a major effect on the size and shape of flocs. Additionally, floc characteristics, such as floc size, compaction degree are very important for continuous membrane filtration. Thus, the average floc size and fractal dimension (D_f) were explored, and results shown in Fig. 3. The general shape of the curves is broadly similar in all cases. Average size of the flocs increased with coagulation time during the floc aggregation process, regardless of the specific duration. When the stirring rate is increased to 400 rpm, there is a rapid reduction in average size, as a result of floc breakage. After the breakage period, there is different degree recovery of average size, showing that the agglomeration time has significantly impact on the reversibility of broken flocs. Specifically, with shorter flocculation time, floc has smaller average size at the end of the aggregation stage. The similar growing tendency was found for flocculation time of 10 min, while average size of floc is larger than that of 5 min. After coagulation with 15 and 20 min, average size of flocs still continuously increased. Yet, both of them attained to the maximum value nearly simultaneously after 10 min, then, slightly fluctuated near the plateau. It can be seen that there needed to be adequate time for suspended particles aggregating to clusters, but the sizes of flocs are not persistent as increasing time. The traditional coagulation process is preferred to large size of flocs due to the following sedimentation unit. But for coagulation-ultrafiltration process, particles size larger than membrane pore size could be rejected on the membrane surface and further removed by hydraulic or chemical backwashing. [33] Therefore, there is no necessary to produce flocs with too large size, and shorter flocculation time has more research significance.

Howe and Clark [34] stated that the remaining dissolved organic matter (DOM) caused very little fouling for ultrafiltration membrane after the colloidal fraction was removed. As a result, the external membrane fouling of cake layer should be investigated deeply. Cake layer are consist of flocs formed during coagulation process, hence flocs structure directly influenced on the membrane fouling. [35] The floc fractal dimension was widely used to evaluate the morphology of flocs. [21, 36] In this study, the evolution of flocs fractal dimension (D_f) with different flocculation duration was investigated to identify the degree of floc compaction. D_f of the flocs increased with the coagulation time during the floc aggregation process under different flocculation time, suggested that much compacter flocs were developed. However, the value of fractal dimension in the steady state was increasing with increment of flocculation time, and was in the order of 20 min> 15 min> 10 min> 5 min. The large value of D_f indicated that the higher development degree and compaction degree of flocs began to produce as increase of reacted time. Densely packed aggregates had a higher D_f which are good at settling, while lower D_f resulted from large, high branched and loose bound structures are benefit of reducing membrane fouling. From the results in Fig. 3, it can be seen that flocs formed at 5 min has the smallest fractal dimension, which deserved to the best one to alleviate membrane fouling. However, shorter flocculation time would provide an incomplete reaction process for scattered particles to aggregate large flocs. Thus, small particles, especially the size of nano-scale primary particles are still existence in water system, which may be one of the main factors determining the density of cake layer and improve the membrane resistance. Therefore, except for floc size and fractal dimension, the particle size distribution is also the significant factor to impact the membrane fouling.

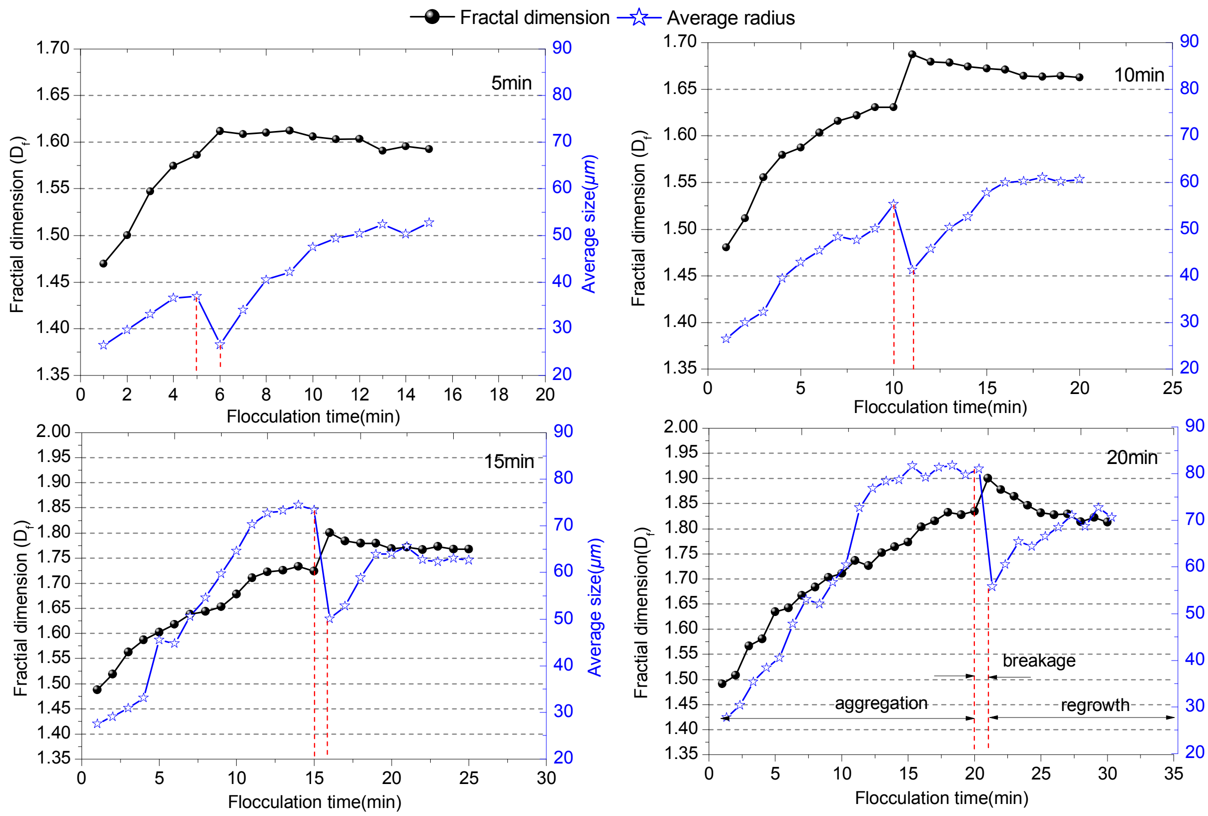

Fig.3 Variation of average size and fractal dimension for different flocculation durations

3.1.2 Particles (flocs) size distribution with different flocculation durations

In order to investigate the coagulation-ultrafiltration in more details, the size distribution of flocs with different durations of flocculation were investigated. Four samples of flocs with different durations of slow stirring time (5 min, 10 min, 15 min and 20 min) were taken at the end of flocculation stage. The images of flocs were captured by in-situ recognition system and analyzed by the software, as described in section 2. Fig. 4a shows flocs size distribution of the steady state under different flocculation durations. Firstly, the major peak of flocculating 5 min was on the left of all the other conditions, implying that frequency of small size flocs notably reduced with flocculation time increase. But at 10 min, even average size of flocs is not large enough, the probability of small particles are dramatically decreased. Considering slow stirring duration of 15 and 20 min, the flocs reached a large size, which was expected as longer slow stirring duration would promote aggregation procedure of particles. For longer slow stirring duration, floc average size rapidly increased at the initial stage, and then further increase in the size was restricted, resulted in a steady-state floc size and represent a dynamic balance between shear-induced aggregation and breakage. [30] It can be speculated that too long slow stirring time mainly contribute to further improve the compactness of flocs, instead of promotion for distribution of flocs size. As a result, longer flocculation duration is seemed more conducive to the traditional coagulation-sedimentation process. However, different from the traditional coagulation process to form large and tight flocs, the main purpose was decrease the amount of small particles and changed the structure of cake layer on membrane surface. Cho et al has also reported that higher probability of small particles could intensify the membrane fouling.[37] Therefore, it can be seen that properly shorten the flocculation duration has much more potential to retard membrane fouling.

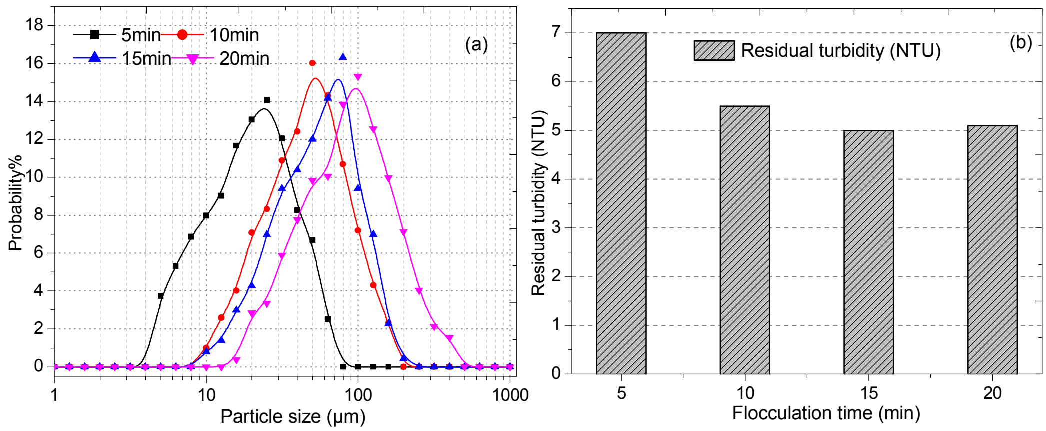

Fig.4 Effect of flocculation duration on (a) flocs size distribution and (b) residual turbidity

As shown in Fig. 4b, residual turbidity after static sedimentation of flocs gradually decreased after 10 min, and stayed around 5 NTU with flocculation duration increase. Owing to the residual turbidity after settling is mainly determined by the small particles, especially for nano-scale particles, the probability of small particles are compared with the residual turbidity. [38] The lower proportion of small particles, the lower was residual turbidity. Larger average size did correspond to lower frequency of small particles and lower residual turbidity. (Fig.3 and 4) But compare the slow stirring time of 10 min and 20 min, twice increase of flocculation duration did not dramatically lessen the amount of small particles and the residual turbidity (Fig.4), instead promote the compactness of flocs (Fig. 3). As well known, higher density of flocs caused the voidless cake layer on membrane surface and further strengthened the membrane fouling. Therefore, the flocculation duration can significantly influence the characteristics of flocs, such as floc average size, floc structure and floc size distribution, which could further influence the efficiency of the subsequent ultrafiltration process.

3.1.3 Effect of flocculation duration on membrane flux

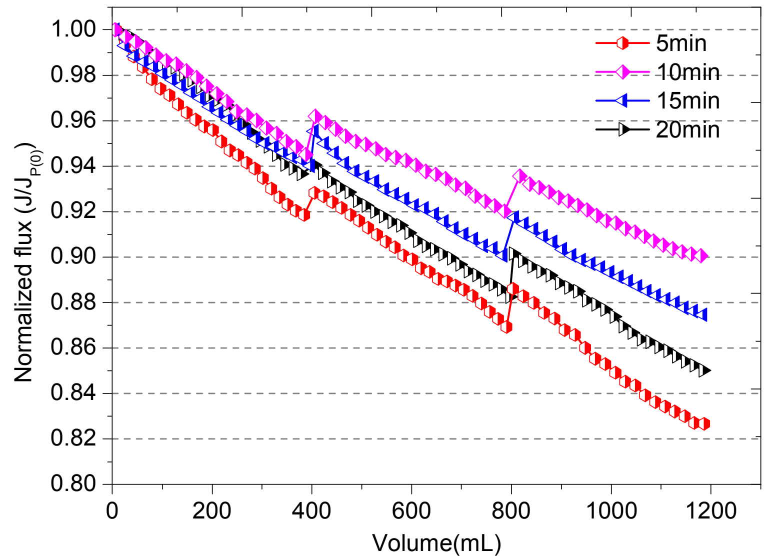

Fig. 5 Normalized UF permeate flux profiles of different flocculation durations

The UF experiments were performed by filtering the pre-coagulation suspensions under different flocculation durations. The normalized permeate fluxes ($J/J_{P(0)}$) versus filtration volume are demonstrated in Fig. 5. In our previous study [15], the same raw water was used and the normalized permeate fluxes declined dramatically from 1 to 0.4 in the end. In contrast, it could be observed that the pre-coagulation significantly improved the permeate fluxes, independent on flocculation duration. Specifically, the flux improvement was followed with flocculation time increase. At slow stirring 5 min, the final value of $J/J_{P(0)}$ was about 0.8, whereas the final normalized flux increased to 0.9 at 10 min slow stirring. Inversely, this value tends to be declined with flocculation time further increase. This somewhat implied that flocculation time could influence the performance of ultrafiltration. Coagulation effluents, the feed water of ultrafiltration, contained different size of flocs formed under various flocculation durations. According to the results from Fig. 4, there are more small particles remained in coagulation effluent at flocculation 5 min, and those particles are proved to be difficult to remove by sedimentation. The several hundreds nano-scale particles are transported by drag force and stay on the surface of membrane to develop membrane fouling. It seemed that membrane fouling mainly relied on the number of small particles in water solution. However, the results shown that flux ratio are declined with small particles amount decrease. The flocs fractal dimension was increased with slow stirring time extension (Fig. 3), meant higher density of flocs formed. Normally, the higher fractal dimension of flocs, the higher density of cake layer developed by flocs.[13] As a result, cake layer on membrane surface formed by flocs with lower density may have higher porosity and looser structure. These cake layer plays as another filter shield, more fine colloids and other pollutants could adsorbed and plugged into the cake layer of pore structures, which further confirming that the characteristics of coagulated flocs played an important role in membrane filtration process. For longer flocculation time, flocs with higher effective density are preferable for traditional coagulation process because of their better settleability in the subsequent settling unit. Nevertheless, such aggregates were compressed easily by external pressure and build up compact cake layer to cause a higher specific resistance on the water flow. Based on the discussion above, rather shorter slow stirring time (for 10 min) was much more adequate to improve the permeability of water through cake layer on the membrane surface to reduce membrane fouling.

3.1.4 Effect of different flocculation durations on reversibility of membrane fouling

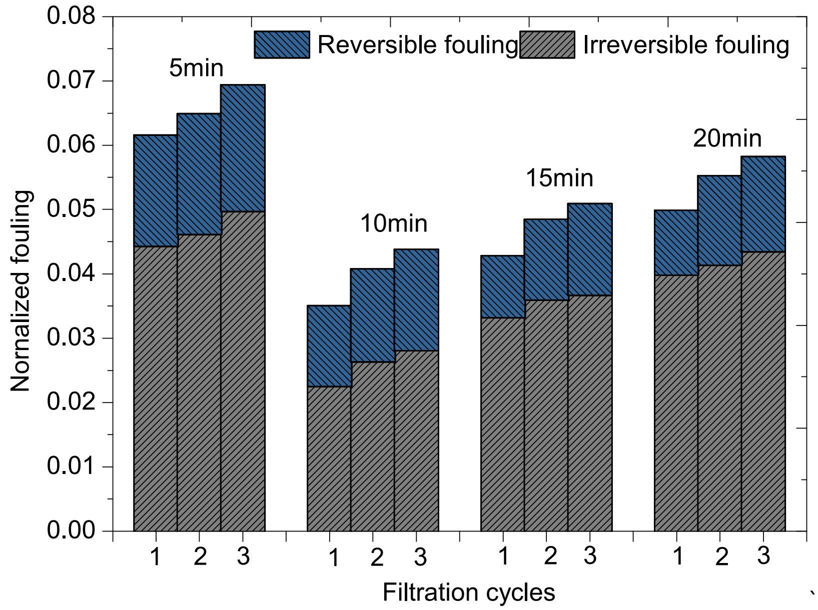

Fig. 6 Effect of different flocculation durations on the reversibility of membrane fouling

Previous literature has shown that particle size smaller than about 3 nm caused very little membrane fouling [39]. In our study, the results meant that nano-scale particles retained on the membrane surface would not lead to inner membrane fouling, instead of external fouling. A part of external fouling could be removed by the hydraulic back wash was considered as reversible fouling (RF), while the remaining part on membrane surface was irreversible fouling (IF). Both RF and IF, which occurred during filtration of different flocculation time of membranes, are shown in Fig.6 The total fouling and irreversibility fouling continued to rise with filtration cycle increase regardless flocculation duration, indicated that foulants constantly accumulated on membrane surface. For shorter flocculation time, the proportion of reversibility was larger than that of longer slow stirring time. From the results in Fig. 3, flocs fractal dimension are relatively smaller at shorter flocculation duration than that of longer slow stirring time, suggested that cake layer composed with lower fractal dimension has relative larger pores and fluffy structure. Loose enough cake layer could be removed by the hydraulic backwash to reduce membrane fouling, while the relatively compact cake layer was still on the surface of membrane resulting in a continuous increase of membrane resistance and flux decrease. Especially for slowly stirring 5 min, cake layer permeability decreases resulted from incomplete particle aggregation and more number of residual small particles. It was more difficult for smaller particles to be removed by backwash and further causes sever irreversible fouling. The higher irreversible membrane fouling may mainly cause by the tight cake layer and small particles number, which could be improved to properly shorten the flocculation duration.

3.2 Effect of low-shear force on coagulation-ultrafiltration process

3.2.1Effect of low-shear force on the evolution of floc characteristics

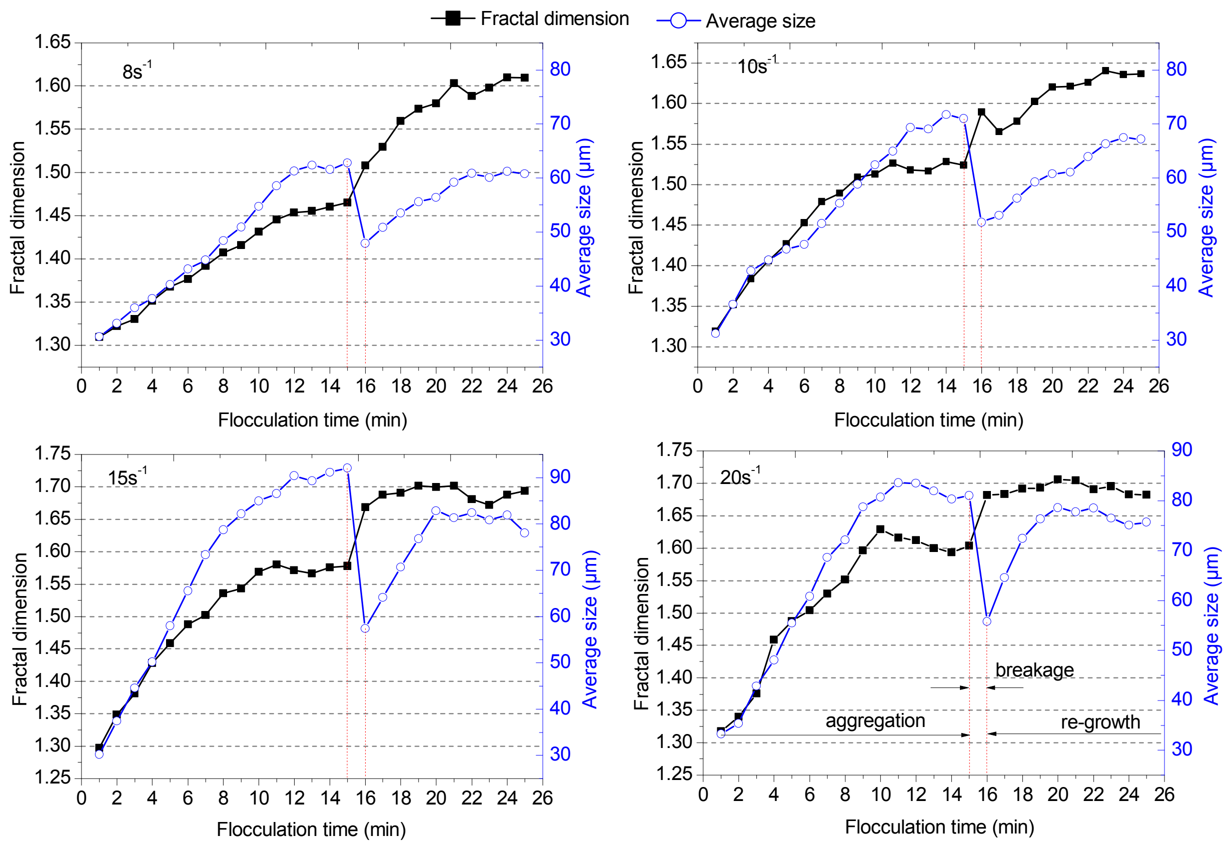

Fig.7 Variation of average size and fractal dimension for different low-shear forces

Except for flocculation duration is very important for optimizing the coagulation/ultrafiltration hybrid process, the slow stirring force can also influence the filtration efficiency. Fig.7 shows the evolution of floc size and structure under varying low-shear forces (G<20 s^{-1}), for a flocculation time of 15 min. The average size of flocs before breakage firstly increased as the slow stirring speed increased. As well known, there is a limiting floc size under the given slow stirring conditions.[40] At lower shear force (G=8 s^{-1} and 10 s^{-1}), flocs average size reached rather larger steady state size. It was expected as sufficient stirring time would promote particles collision and aggregation. At G=15 s^{-1}, the flocs evolved to the largest size at the steady state, and then shows a slightly decline at the shear force of 20 s^{-1}. With increasing shear rate, more sufficient collisions were produced to make larger particles, while floc breakage could occur as well due to more frequent visits of particles in more vigorous stirring and representing a dynamic balance between floc growth and breakage. Serra et al [41] found that latex flocs and floc size formed under steady state conditions was always reduced at larger shear rates (G>20 – 30 s^{-1}). Although particle diameter is inversely proportional to specific cake resistance as stated in the well-known Carma-Kozeny equations [7], the resultant permeate flux most likely affected by other factors.

Floc fractal dimension, which is closely related to aggregate structure and ultrafiltration efficiency, was measured under different shear rates as flocculation time and the results were also provided by Fig. 7. It was obviously that flocs fractal dimension increased as flocs formation with different shear conditions adopted. Basically, dispersed particles rapidly aggregated as the result of shear conditions at the initial of experiment, simultaneously, some pores are formed in the inner of flocs. With the growth of flocs, micro-clusters agglomeration gradually plays a significant role in the development of flocs. Small but compact flocs could have chance to enter into the inner holes of large flocs, and then the fractal dimension of flocs will be increased as the growth of flocs. Based on the results of flocs average size, the higher shear force leads to the more breaking probability of large flocs. The large shear rates (G=15 and 20 s^{-1}) are apt to the conventional sedimentation process for better settleability of high density flocs, while low-shear forces (G=8 s^{-1}) are seemed to be more appropriate for the ultrafiltration process for porosity and loose flocs. After the breakage stage, fractal dimension of flocs are higher than that of flocs before breakage, which is consistent with previous studies.[19, 42] This is probably that the surface bonding around the periphery are destroyed owing to higher shear force, some inner pores hidden by aggregates were re-available to other small but compact clusters or particles, which improve the compactness degree of flocs.

3.2.2 Effect of low-shear force on particle size distribution

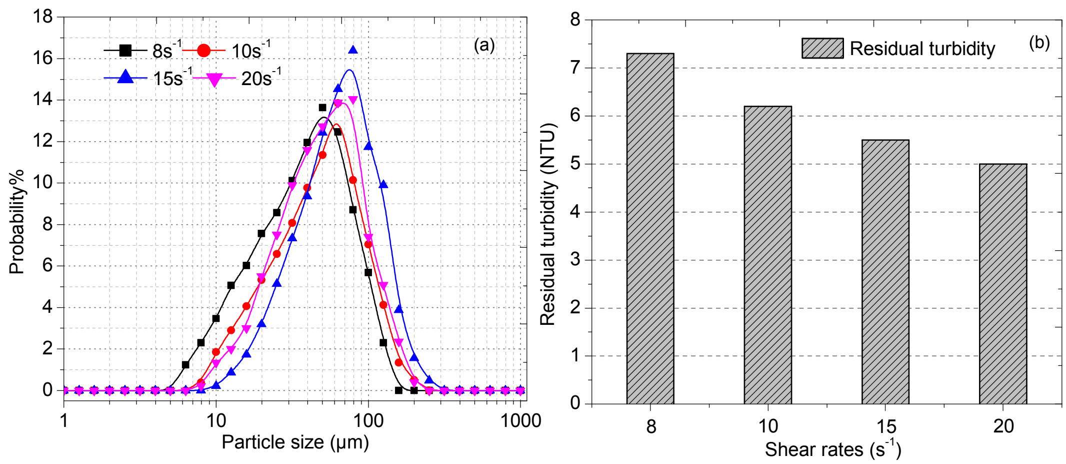

Fig.8 Effect of different low-shear forces on (a) flocs size distribution and (b) residual turbidity

The size distribution of flocs with different shear forces was shown in Fig.8. With the shear force increase, the probability of small particle numbers was slightly decreased. Nevertheless, the size distribution of flocs with higher applied shear (G=20 s^{-1}) was shift towards smaller size, and the average size of flocs are also decreased. It is most probably that particles are able to collision and aggregation to larger flocs with gentle stirring, while breakage possibly occurred under the larger shear force and lead to the increase of small particle numbers. Since the frequency of small flocs was a little higher for the higher slow mixing speed, it is expected that these would give higher residual turbidities. However, this is not the case and the results shown in fig. 8b. For the shear force was 8 s^{-1}, the residual turbidity was around 7 NTU. There was a steady decrease in residual turbidity as the slow stirring speed increased to 20 s^{-1}. The results may be that floc density increases with increased stirring speed, giving higher settling rates, regardless the smaller floc sizes.[38] The higher shear rates during the slow stirring process could produce flocs with higher effective density, which was beneficial of sedimentation process. In contrast, flocs formed under low-shear force have loose and porosity structure without the occurrence of more small particles in water, which seemed to be effectively improve the membrane permeability.

3.2.3 Effect of low-shear force on membrane filtration

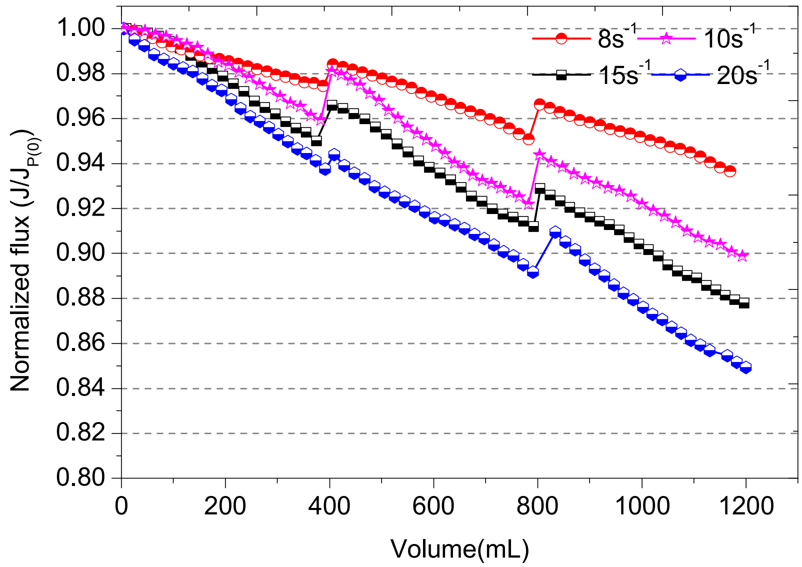

Fig.9 Normalized UF permeate flux profiles of different low-shear forces

Coagulation with different shear force was performed to investigate the effect of different slow stirring conditions on ultrafiltration performance. The associated normalized permeate fluxes with filtration volume were plotted in fig.9. It could be found that the flux decline trends varied depending on shear rates applied in the system. As for raw water without coagulation, the final membrane flux was about 0.4 and the result could be found in our previous study[15]. It could be observed that pre-coagulation with low-shear force significantly improve the permeate fluxes. Specifically, the flux improvement by shear rate of 8 s^{-1} was the most effective because of the largest eventual permeate flux. The largest slow stirring speed was found to contribute to the smallest improvement in membrane flux. On basis of discussion above, it was concluded that different floc morphology formed under different shear forces could impact on the C-UF hybrid system in terms of membrane permeability. Even if the flocs average size produced with lower shear force are smaller than that of intensive slow stirring condition, the flocculation duration was enough for dispersed particles collision and aggregation, since the probability of small particles in the end of flocculation process was not distinctively different. Therefore, there may be another factor to influence the ultrafiltration efficiency except the particle size distribution. It is obviously from the results that increased shear force resulted in aggregates with higher fractal dimension, indicating more compact floc structure. Previous study has been stated that the aggregates with loosely structure produce less resistance for membrane ultrafiltration, while the tight flocs contributed to cohesively structured cake layer could augment the UF resistance and aggravate the flux declines.[43] For low-shear force, it tends to form fluffy cake layer and definitely help alleviate flux declines. Therefore, the application of low-shear force (G=8 s^{-1}) is more significant research and feasible meaning.

3.2.4 Effect of low-shear force on reversibility of membrane fouling

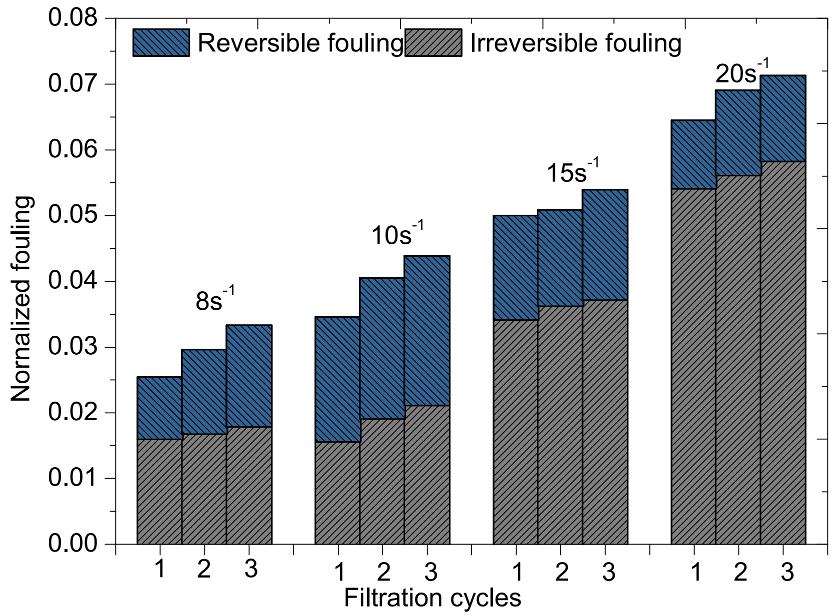

Fig.10 Effect of different low-shear forces on the reversibility of membrane fouling

Both reversible fouling and irreversible fouling, occurred under various slow stirring speeds, are presented in Fig. 10. There were dramatically improvements of RF and IF with increase the shear force in the slow stirring procedure. This was probably because mild stirring condition could cement the small particles together to form floc aggregates, then a smaller quantity of small size substances deposited in membrane pores. Besides, intensified shear rates would force large size flocs to break at the end of the flocculation stage, which is attributing to the deterioration of floc structure and the occurrence of more micro-particles. This result may lead to small particles lock in the membrane pores and did not remove by the hydraulic backwashing easily. The higher fractal dimension indicates a higher effective density, resulting in a faster floc settling velocity, which is preferable in a conventional coagulation-sedimentation process for water treatment but not in a coagulation-UF system. Flocs with a lower density could form a higher porosity cake layer., while flocs with higher fractal dimensions resulted in more severe fouling in a hybrid coagulation and UF filtration systems due to relatively regular shaped flocs being more easily compressed by external pressure [44, 45]. In our study, the structure of flocs formed at low-shear force became incompact and porous, which decreased the irreversible fouling. The irreversible fouling was strengthened at the shear force 20^{-1}, even though the probability of small particles was lower than that of shear rate 8 s^{-1}. The results indicated that the reversibility of fouling after hydraulic washes during the multiple filtrations of the coagulated water was mainly governed by the morphology of flocs, and low-shear force of slow mixing stage in the pre-coagulation process could effectively retard the total and irreversible fouling through ultrafiltration process.

4 Conclusions

The main conclusions of this work are as follows:

1. Coagulation/ultrafiltration process was conducted under different flocculation durations. Longer flocculation duration will produce flocs with large average size and fractal dimension, while shorter flocculation time form small size of flocs with small fractal dimension. Flocs with small fractal dimension have loose and porous properties, which easily developed cake layer with larger pores and fluffy structure on membrane surface. Comprehensive consideration the flocs

size distribution, the higher frequency of small size flocs still remained at 5 min flocculation time attributing to the inadequate collision among particles, which would cause severe membrane fouling. Therefore, rather shorter slow stirring time (for 10 min) was much more adequate to improve the permeability of water through cake layer on the membrane surface to reduce membrane fouling.

2. The slow shear force was also an important factor deserved to be investigate during coagulation/ultrafiltration process. The average size of flocs increased as the slow stirring speed increase, and the same as the flocs fractal dimension. Nevertheless, the size distribution of flocs with higher applied shear (G=20 s^{-1}) was shift towards smaller size, and the average size of flcos are also decreased owing to the breakage. As a result, flocs formed under low-shear force (G=8 s^{-1}) have loose and porosity structure without the occurrence of more small particles in water, which seemed to be effectively improved the membrane permeability.

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