Effect of aluminum speciation and pH on in-line coagulation/diatomite microfiltration process: Correlations between aggregate characteristics and membrane fouling

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ABSTRACT

Impacts of aluminum speciation and water pH on coagulation/diatomite microfiltration (DMM) process were investigated in this study. Three commonly used Al-based coagulants, aluminum sulfate (AS), poly-aluminum chloride (PACl), and Al_{13} ($[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$), were employed to explore the role of Al speciation. Floc characteristics, including particle size and fractal structure under different coagulants and water pH levels, were investigated using a laser diffraction particle sizing device. The results indicated that in the dosage range of 1.0–11.0 mg/L, coagulation/DMM could effectively remove particles (97–100%) and DOC (40–80%), and as pH increased from 3.0 to 10.0, its purification efficiency was higher and more stable than separate coagulation. AS contributed to large and loosely structured flocs and thus alleviated the flux declines most effectively, leading to a flux reduction of about 50%, while the reductions for PACl and Al_{13} were 71% and 73%, respectively. Neutral pH was found most conducive to the hybrid process and alkaline pH (9.0) led to relatively larger flux than strong acidic pH (3.0), especially for AS coagulation system. As pH changed, Al_{13} led to the least variation in flux declines while both the removal efficiency and filtration flux fluctuated most obviously for AS coagulation system.

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1. Introduction

Membrane fouling that causes the declines of membrane permeability, elevation of energy consumption and cleaning frequency, and reduction of membrane lifetime still remains a major obstacle to wider application of microfiltration (MF) and ultrafiltration (UF) processes in drinking water treatment. Natural organic matter (NOM) has been considered to be a detrimental foulant in low-pressure membrane processes used for drinking water treatment since it contains a complex mixture of humic acid (HA), fulvic acid (FA), proteins, and function groups, which can either stick to the surface of membrane or leading to the development of microbiological fouling [1,2]. Hence, it is of essential importance to interpret the removal of NOM and its fouling behavior on membrane process for the sustainable application of membrane technology.

Pre-coagulation with Al-based coagulants, including alum, poly-aluminum chloride (PACl), etc., has been shown to be an effective way to control membrane fouling and improve water quality, especially by in-line chemical coagulation [3–5]. Aluminum coagulation destabilizes and agglomerates the colloidal and particulate foulants, increasing

their size and thereby mitigating pore constriction and blockage and the formation of a porous cake layer. It has been claimed that membrane fouling decreases with an increase in particle size and even becomes relatively insignificant when filtering particles larger than 1 μm [6,7]. However, membrane fouling is still not completely avoided since some fractions of NOM cannot be removed, which cause fouling by narrowing or blocking membrane pores, and substances retained on the membrane that form a gel or a cake layer still contribute resistance.

Many previous literatures have proved the relationship between membrane fouling and the chemical, physical, and morphological properties of flocs [8,9]. Cho et al. [8,10] claimed that flocs with a high fractal dimension (D_f) had low compressibility, leading to low membrane permeability. Other studies, however, reported that aggregates of relatively low D_f were highly compressible after their deposition on the MF membrane surface, resulting in pronouncedly increase in the specific cake resistances (higher than 50 kPa as trans-membrane pressure) [9,11]. Up to now, findings on the relationship of floc characteristics to membrane performance are not consistent, although it is believed that the structure of the cake layer plays an important role in membrane permeability. Additionally, the severity of fouling depends not only on the foulant characteristics but also on the solution chemistry [12] and coagulant characteristics [13], which essentially determine the floc properties [14]. For example, our previous study [15] proved that pre-hydrolyzed

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Al_{13} polycation ($[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$), which is claimed as the most active species in PACl, generally resulted in smaller but more compact NOM flocs than commonly used alum and PACl. Therefore, the UF membrane permeability deteriorates more severely during Al_{13} coagulation than during alum/PACl coagulation due to the higher specific resistance of the cake layer. This is consistent with the previous study of Wang et al. [16], demonstrating pre-hydrolyzed PACl was inferior to alum when exploited in coagulation/UF combined process. On the other hand, pH plays an important role in interaction between NOM and aluminum species, leading to formation of aggregates with various properties, which display obviously different fouling effects on membrane filtration. Membrane fouling has been proven in previous study [17] to decrease with increasing pH as a result of the increasingly negative surface charge of the particles and the development of great colloid–colloid repulsive force. Semmens and Field [18] reported an optimal alum coagulation pH of 5.0 for the removal of natural organic substances and proposed that the coagulation mechanism was pH dependent, while it has been claimed that aggregates formed under charge neutralization conditions were less compressible and produced lower hydraulic resistance than those under sweep coagulation conditions [19]. Thus, pH is believed to have crucial influence on membrane behaviors.

To date, however, a clear understanding of the interaction of aluminum coagulants with NOM during membrane filtration as well as the impact of different aggregate properties and resulting adsorption behavior on membrane fouling is still lacking, especially the correlation between membrane fouling degree and solution pH or aluminum species. The study reported here systematically investigated the effects of aluminum Al speciation and pH on the purification ability and membrane fouling of the coagulation/MF process. Besides, diatomite microfiltration membrane (DMM) was applied in the hybrid process instead of commercial organic membrane, such as polyethersulfone (PES) and polyvinylidene fluoride (PVDF) membranes. That was because the diatomite has a unique combination of stable physical and chemical characteristics, such as high porosity, good hydrophilicity, bulk volume, high purity, large specific surface area, high adsorption capacity, and good adsorptive properties. Yet limited information is available regarding the treatment of drinking water using coagulation/DMM combined process. Three kinds of Al-based coagulants with different Al species distributions were employed for coagulation unit under varying pH conditions, followed by a DMM process in dead-end mode and the relationship between floc properties and diatomite membrane performance were explored.

2. Materials and methods

2.1. Water sample

All chemicals were AR grade unless otherwise mentioned and experiments were conducted at room temperature ($15 \pm 3^\circ\text{C}$). Fulvic acid (Shanghai, China) stock solution was prepared by dissolving 5.0 g of FA into 1 L of deionized (DI) water, with 1.0 g of NaHCO_3 to provide a certain buffer capacity and ion strength. Then, the solution was stirred for 24 h and filtered through a $0.45\text{-}\mu\text{m}$ membrane to remove residual non-dissolved FA. In order to represent a micro-polluted surface water that might be used as a drinking water source, the synthetic test water was prepared by dissolving 10.0 mL of FA stock solution in tap water of Jinan and meanwhile, kaolin suspension, prepared similar to Yukselen and Gregory [20], was used to adjust the initial turbidity of synthetic water to 5.0 ± 0.6 NTU. The pH of the raw synthetic water is 8.0 ± 0.05 , and characteristics of the test water samples are summarized in Table 1.

2.2. Coagulant preparation and characterization

Three Al-based coagulants, aluminum sulfate (AS), poly-aluminum chloride (PACl), and Al_{13} polymer, were used in this study. AS was

Table 1

Properties of synthetic test water and effluent after diatomite membrane filtration (DMM).

Quality parameter	Raw water	Effluent of DMM
Temperature($^\circ\text{C}$)	15.0 ± 3.0	15.0 ± 3.0
Turbidity (NTU)	5.0 ± 0.6	0.52–0.62
UV ₂₅₄ (cm^{-1})	0.092–0.101	0.056–0.061
Zeta potential (mV)	-13.45 ± 0.50	-13.41 ± 0.45
DOC (mg/L)	3.87 ± 0.15	2.19–2.65

prepared by directly dissolving $\text{Al}_2(\text{SO}_4)_3$ into deionized water. PACl and Al_{13} were prepared using solid–solid blending and ethanol–acetone methods, respectively, and more details could be found in our previous studies [21]. The total Al concentration was measured by ICP-OES (Perkin Elmer, Model Optima 7000 DV, USA). Al species distributions of coagulants were determined by the ^{27}Al NMR (nuclear magnetic resonance) spectroscopy to provide speciation based on structure symmetry of species and Al-Ferron timed complexation spectrophotometer with ferron reagent to provide speciation based on chemical reactivity. As listed in Table 2, AS and Al_{13} are mainly composed of monomeric species (Al_a) and medium polymer species (Al_b), respectively, while all the Al_a , Al_b , and Al_c species (sol or gel $\text{Al}(\text{OH})_3$) could be detected in the PACl solution.

2.3. Integrated coagulation/DMM process

A programmable jar-test apparatus (MY3000-6F, Wuhan Meiyu Instrument Co., Ltd., China) with 1.2-L cylindrical Plexiglas beakers was used for coagulation experiments. Jar tests were conducted in a sequence of 1.5 min of rapid mixing at 200 rpm (rpm) ($G = 87.8 \text{ s}^{-1}$) and 15 min of flocculation at slow-mixing rate of 40 rpm ($G = 10.1 \text{ s}^{-1}$) to allow aggregates growth. A pre-determined amount of coagulant was added into the test water at the beginning of the rapid stirring phase.

Afterward, the coagulation suspension without sedimentation was gently discharged from the coagulation tank to the DMM device, as shown in Fig. 1. Seven slices of diatomite membranes (Jilin Guibao Co., Ltd., China) with the average pore size of $0.1 \mu\text{m}$ were installed in the cylindrical membrane filtration vessel, and the effective membrane area is 0.04 m^2 for each module. The applied pressure of the filtration system was generated using the high pressure pump and controlled at 22 kPa. Data of permeate mass were collected by an electronic balance (MSU520IS-000-D0, Sartorius AG Germany) over the filtration time, and the permeate flux (J) was determined according to the following equation:

$$J = V/At \quad (1)$$

where J is the permeate flux, V is the permeate volume, A is the membrane effective surface area, and t is the time taken to collect the permeate. Schematic diagrams of the experimental setup for the coagulation/DMM hybrid process are shown in Fig. 1.

Table 2

The Al species distributions of AS, PACl, and Al_{13} coagulants.

Method	Coagulants	Al_a (%)	Al_b (%)	Al_c (%)
^{27}Al NMR	AS	94.3	0.4	5.3
	PACl	13.2	40.2	46.6
	Al_{13}	2.5	92.7	4.8
Al-Ferron	AS	93.8	0.6	5.6
	PACl	14.3	39.7	46.0
	Al_{13}	3.2	91.5	5.3

Fig. 1. Schematic diagram of the coagulation/microfiltration setup.

2.4. Water quality analysis and on-line measurement of floc size

Coagulated water sample was collected from 2 cm below the surface and passed through a 0.45- μm glass filter paper for DOC measurement (Tekmar-Dohrman Co., Phoenix, AZ). Besides, the feed and permeate water samples through coagulation/DMM process were also collected for DOC analysis. A small amount of sample was taken immediately after the 1.5 min of rapid mixing to determine the zeta potential (Malvern, Zetasizer 2000, U.K.).

A continuous laser diffraction instrument (Mastersizer 2000, Malvern, U.K.) was used to measure the dynamic particle size as the floc formation and growth proceeded. The suspension was monitored through the optical unit of the Mastersizer and transferred back into the jar by a peristaltic pump (LEAD-1, Longer Precision Pump, Baoding, China) with a 5-mm internal diameter tube at a flow rate of 10 mL/min. The size measurements were taken every 30 s for the duration of the jar test. Additionally, the inflow and outflow tubes were placed opposite one another at a depth just above the impeller in the holding ports.

2.5. Floc fractal structure

Flocs are mass fractal objects as both the internal and surface structures of the aggregates exhibit fractal properties. The structures of flocs can be simply described by fractal dimension (D_f), which could be described as the exponent of relationship of floc mass (M) and size (L) [22]:

$$M \propto L^{D_f} \quad (2)$$

Recently, small-angle laser light scattering (SALLS) using Masterizer 2000 has been extensively employed in fractal dimension determination in various systems, such as kaolin, latex, and aluminum suspension [23–25]. During the SALLS, a laser light beam with the wavelength of 632.8 nm was passed through the suspension, which was then scattered by the sample. There are 52 photosensitive detectors in the Mastersizer 2000 to receive the scatter light within the angle of 0.01–40.6°. For independently scattering aggregates, the total scattered light intensity I is related to the scattering vector Q and the fractal dimension D_f , which is shown as [26]:

$$I \propto Q^{-D_f} \quad (3)$$

where Q is the difference between the incident and scattered wave vectors of the radiation beam in the medium, which is given by:

$$Q = \frac{4\pi n \sin(\theta/2)}{\lambda} \quad (4)$$

n , θ , and λ are the refractive index of the medium, the scattered angle, and the wavelength of radiation in vacuum. On a log–log scale there should be a straight line, and the slope of which is D_f . Commonly, a higher value of D_f means more compact structure of floc, whereas aggregate with loose structure exhibits lower D_f .

3. Results and discussion

3.1. Comparison of coagulation and coagulation/DMM performances

A series of preliminary tests were comparatively conducted to investigate the effect of aluminum dosage on coagulation and coagulation/DMM hybrid processes. Three coagulants, i.e., AS, PACl, and Al_{13} , with varying Al species distributions were employed in the coagulation unit, and the removals of residual turbidity and DOC were applied to reflect the coagulation and coagulation/DMM efficiencies in the case of fulvic-rich water (Fig. 2) treatment. It was found for separate coagulation process (Fig. 2(a) and (b)) that turbidity and DOC removals increased rapidly first with aluminum dosage, and then the increment became gentle after the Al concentration reached 4.0 mg/L and above. When the dose increased from 5.0 to 10.0 mg/L, AS only improved the turbidity removal efficiency from 78% to 80%, and the curves for PACl and Al_{13} kept nearly flat. Similar trends were also found in the cases of DOC removals. Additionally, it should be noticed that an unsatisfactory DOC removal efficiency of 11–28% was obtained at low dosage of 1.0 mg/L for all the coagulation systems. It has been claimed that zeta potential is in excellent correlation with the coagulation behavior and the optimal removal should be achieved at the isoelectric point if the charge neutralization was the only mechanism involved in coagulation [27]. However, the optimum dosages for AS, PACl, and Al_{13} in this study were found to be 5.0, 4.0, and 4.0 mg/L, where the zeta potentials displayed in Fig. 2(c) turned out to be -5.6 , -5.2 , and -4.9 mV. The data proved that the optimal dosage was less than traditional optimum dosage at the isoelectric point, which should be 6.0–7.0 mg/L. This could be probably ascribed to the mutual coagulation mechanisms besides charge neutralization, such as adsorption, bridge, and entrapment

Fig. 2. Turbidity, DOC removal efficiencies, and zeta potentials of the coagulation systems with different coagulants (AS, PACI, and Al₁₃) in the dose range of 1–11 mg/L. The initial pH of synthetic water was 8.0 ± 0.05 .

occurred between fulvic acid and hydrolyzing poly-aluminum products, including metal precipitates [28,29].

Comparatively, purification efficiencies of the coagulation/DMM hybrid process were always kept at high efficiency of 97–100% and 40–80% for turbidity and DOC removals (Fig. 3) in the whole chemical dosage of 1.0–10.0 mg/L. It was observed that the optimal coagulant dosage in conventional coagulation process for water treatment was not

Fig. 3. Turbidity and DOC removals by the coagulation/microfiltration hybrid process with various dosages (1–11 mg/L) of AS, PACI, and Al₁₃. The initial pH of synthetic water was 8.0 ± 0.05 .

necessarily the optimal dosage for in-line coagulation/microfiltration system. This could be attributed to the interception performance of diatomite membrane following coagulation process. All the three coagulants led to similar efficiencies except the DOC removal at 1.0 mg/L, where Al₁₃ was found to contribute to the best DOC removal (60%), followed by PACI (50%) and AS could only remove about 40% of DOC as shown in Fig. 3b. The data imply a positive correlation between the low-dose DOC removal rate and the Al₁₃ content of coagulant (Table 1), which could be ascribed to the best charge neutralization ability of Al₁₃ coagulant as shown in Fig. 2(c). This is consistent with the published literature, which indicates that the active Al₁₃ species in the pre-hydrolyzed aluminum salts is the most highly charged [30]. Charge neutralization was generally believed to be the major mechanism in pollutant removal at low coagulant concentration. Al₁₃ could effectively destabilize the FA molecules and form fine particles even at the dose of 1.0 mg/L and then, the formed aggregates could easily be removed by the microfiltration. When the dosage increased (4.0–11.0 mg/L), where adsorption, sweep, and co-precipitation played important roles in coagulation, Al₁₃ exhibited no superior efficiency than the other coagulants. It has been recognized that monomeric Al readily forms a large amount of amorphous aluminum hydroxide [31], and consequently when AS solution, consisting of most monomeric Al, was dosed into the solution at a sufficiently high concentration, organic matters could be efficiently enmeshed in the amorphous precipitates, resulting in large flocs. At AS dosage of 1.0 mg/L, an insufficient amount of AS in

synthetic water failed to enmesh the FA molecules in the suspension and thus resulted in extremely low turbidity and DOC removal rate.

In order to clearly verify the performances of coagulation and diatomite membrane in water purification, the qualities of effluents treated by a separate diatomite membrane cell were measured and the results are also listed in Table 1, showing DMM alone removed 86–91% and 34–41% of the turbidity and DOC, respectively. The data indicate that although diatomite filtration exhibited a high efficiency for solid–liquid separation, the DOC removal efficiency was much lower than both the sole coagulation and hybrid processes. Overall, coagulation/DMM hybrid process in this study managed to contribute to more effective and stable removals for both particles and dissolved organic matters as well as to save chemical dosage than single coagulation process.

3.2. Membrane filtration of synthetic waters with and without pre-coagulation

Membrane fouling is usually considered as the most challenging factor in coagulation/microfiltration process due to uncertain impact of coagulated flocs on membrane permeability. In this study, coagulated suspensions by different coagulants were subjected to the DMM unit (Section 2.2), and the extents of membrane foulings were evaluated. Besides, it could be observed by referring to Fig. 2 that the improvement of coagulation efficiency slowed down at the AS dosage of 5.0 mg/L and above, while the corresponding values for the pre-hydrolyzed coagulants, i.e., PACl and Al_{13} , turned out to be 4.0 mg/L. However, taking into account chemical consumption and to avoid coagulant concentration discrepancy, the dosage of the three coagulants for the following coagulation/DMM process was fixed at the same concentration of 5.0 mg/L as Al, where the DOC removals by AS, PACl, and Al_{13} were 58%, 62%, and 65%. Moreover, the effects of aluminum speciation on coagulation/DMM performances could also be accurately evaluated with the same Al concentration.

Normalized permeate fluxes (J/J_0) versus filtration volume for AS, PACl, and Al_{13} coagulation systems are shown in Fig. 4. As seen, the permeate flux decreased severely reaching only about 19% of its initial value in the absence of pre-coagulation. A favorable outcome was seen in this study that coagulation was effective for mitigation of membrane fouling. Pre-hydrolyzed PACl and Al_{13} led to improvements of final fluxes to 29% and 26% of the initial value, respectively, and an even better result was obtained for traditional AS coagulation, which enhanced the flux to 50% of the initial value. Referring to Table 1, it could be deduced that the higher the proportion of pre-hydrolyzed Al_{13} species in

coagulant, the severer the membrane fouling. Raw FA water led to the most severe membrane fouling due to the high concentration of NOM, which is thought to be mainly responsible for membrane fouling [32]. Turbidity (particulate matter) can also cause membrane fouling, mainly reversible fouling. However, for the coagulated waters, no clear correlation was found between DOC/turbidity and the permeate flux. Al_{13} and PACl at 5.0 mg/L led to the slightly higher of particulates and DOC removal efficiencies than AS (Fig. 2), while the fluxes, however, were proved decline more severely for the pre-hydrolyzed coagulants (Fig. 4). The result implies other factors, including floc size and structure in the coagulation system might be critical in the evolution of membrane fouling. It has been claimed that enmeshment into $Al(OH)_3(s)$ precipitates form large flocs reducing penetration into membrane pores and increase cake permeability compared to MF of untreated water [33,34]. That is to say, coagulation majored by enmeshment mechanism, which might be the dominant mechanism of AS coagulation in this study, could reduce both internal pore fouling and external cake resistance effectively.

3.3. Floc size and structure analyses

Changes in floc particle size and fractal structure due to the addition of different coagulants are expected to evidently affect membrane fouling. In this study, particle sizes during the whole coagulation with 5.0 mg/L of different coagulants were monitored by a laser diffraction instrument, Mastersizer 2000. As illustrated in Fig. 5(a), the particle size in raw synthetic water presents a small mean size (d_{50}) of 2.8 μm . This was due to the presence of electrostatic repulsion among FA molecules corresponded to the negative charges of carboxyl functional groups, which tended to stabilize the FA molecules in suspension. Thus, there was less or no tendency for FA molecules to approach and agglomerate. It was noticed that aluminum salts played important roles in changing the particle size distribution of the coagulation systems. Once the coagulants had been injected into the test water, small and fluffy flocs started to form in the suspension. During the slow stirring process, those flocs collided with each other and entangled into larger flocs. Results present in Fig. 5(b) show the final floc size distributions for different coagulation systems and obvious shifts in the major peak to larger sizes were observed. AS led to the largest d_{50} value of 419 μm , followed by PACl with the mean size of 385 μm , and Al_{13} gave rise to the smallest floc size of 351 μm . This could be ascribed to the different coagulation mechanisms involved in coagulation processes. In AS coagulation, monomeric Al would undergo a hydrolysis reaction when it was dosed in synthetic water and eventually formed amorphous Al precipitates when organic molecules were incorporated in the hydroxide matrix; therefore, large agglomerations were formed [35]. By contrast, Al_{13} was more stable than other Al species and generally played an active part in coagulation by way of charge neutralization or/and complexation [36,37]. With the addition of Al_{13} , FA molecules started to lose stability in water suspension, as the repulsion forces between negatively charged molecules were reduced and consequently resulted in coagulation and particle precipitation. This postulation is supported by the zeta potential results, as depicted in Fig. 2(c). The results present in this study agreed well with the findings of Jarvis et al. and Kim et al., claiming that the flocs formed by charge neutralization are smaller compared to sweep coagulation flocs [38,39].

Since particle diameter is inversely proportional to specific cake resistance as stated in the well-known Carman–Kozeny equations [40], the resultant permeate flux for raw water with the tiny particle size was responsible for the severe flux decrease and in contrast, large flocs in the AS coagulation system were found to substantially decrease the membrane fouling. PACl was observed to lead to aggregates with modest sizes as well as a modest effect in mitigating the membrane fouling. Besides, fractal structure analysis using SALLS was conducted to further explore the correlation between properties of aggregates and membrane fouling. It is obvious from Fig. 5(c) that Al_{13} contributed

Fig. 4. Normalized flux decline of raw water and systems pre-coagulated by different coagulants. Feed suspensions were prepared by the jar tests in Section 2.1 and the coagulant dose was fixed at 5.0 mg/L as Al.

Fig. 5. Particle size distribution of (a) synthetically prepared feed water and (b) coagulated water in the AS, PACl, and Al_{13} coagulation systems, and (c) the fractal dimension of flocs formed during different coagulation processes.

to the largest D_f (2.31) of flocs, followed by PACl (2.16), and AS gave rise to the most fluffy aggregates with the lowest D_f value of 2.04. The loosely structured flocs have been stated to produce less resistance for membrane filtration, and in contrast, compact flocs lead to cohesively

structured cake layer with high level of resistance [16]. This is also the reason why pre-coagulation by AS contributed to the least membrane fouling.

3.4. Effect of pH on coagulation and coagulation/DMM performances

Raw synthetic water pH was adjusted to predetermined value by 0.1 mol/L HCl and 0.1 mol/L NaOH solutions and the turbidity and DOC removals by separate coagulation as a function of pH are shown in Fig. 6. It could be seen that pH imposed a strong influence on coagulation efficiencies, which improved with pH from 3.0 to 6.0. When the pH further increased to 10.0, coagulation efficiencies were found decline for all the three coagulants. Maximum removal was achieved around pH range of 6.0–8.0 in order of Al_{13} > PACl > AS. In particular, AS led to obviously lower turbidity and DOC removals than pre-hydrolyzed PACl and Al_{13} coagulants in the acidic and basic pH regions. Considering the speciation of the Al-based coagulants (Table 1), it is indicative that the higher the proportion of Al_{13} in coagulant, the more stable and efficient pollutant removal exhibited when imposed to varying pH levels. Even at pH 10, DOC removal by Al_{13} decreased slightly. The influence of pH on NOM removal could be interpreted from two aspects. One was that charge neutralization mechanism was significantly impacted by pH changes, and this could be confirmed by the increasing zeta potentials with decreasing pH as illustrated in Fig. 6(c). It seemed that particle restabilization occurred for the aluminum coagulants resulting in the decrease of organic matter removal as pH was decreased to 6.0 and below. On the other hand, pH would affect the speciation transformation of various aluminum coagulants after dosing. Previous investigations [41,42] have proved that at acidic and basic pH conditions, hydrolysis products of Al-coagulants were mainly medium polymers or monomers, which had an ability to remove DOC by complexation. However, it was observed that the flocs formed would not settle as efficient as those formed through bridging or sweep flocculation, occurring in the neutralized and weakly alkaline pH range of 7.0–8.0 or so. Another point deserved to be noted is that the Al_a fraction in the primary coagulants is the most unstable species, which would quickly transform into Al_b , and finally into Al_c ; while the pre-polymeric and colloidal species, in contrast, once preformed, they turned out to be much more stable. This was also the reason that the coagulations employing hydrolyzed PACl and Al_{13} present more stable and efficient when exposed to various pH conditions.

In case of coagulation/DMM process, the effect of feed water pH was found relatively insignificant. As demonstrated in Fig. 7, the combined process could remove nearly all the particulate matters in pH range of 5.0–10.0 and even at the acidic pH of 3.0–4.0, a favorable outcome of above 85% of turbidity removal for all the coagulants was achieved. Although the colloidal products formed under the acidic pH conditions were rather difficult to be removed by sedimentation alone as mentioned above, it was possible to be removed by diatomite microfiltration. For the coagulants applied in this study, the maximum DOC removals achieved at around pH 7.0–8.0 for separate coagulation and the hybrid process were 57%–65% and 71%–76%, respectively. And even at pH 3.0, the combined process managed to remove 30%–50% of DOC, while the corresponding value for separate coagulation was only 6%–24%. Still, the coagulation/DMM process using Al_{13} coagulant present more stable in NOM removals with the flocculated pH, which was ascribed to its stable structure during coagulation, producing flocs with more stable characteristics.

3.5. Effect of pH on floc properties and filtration performance

Solution pH is usually an important factor in membrane fouling because it affects the charge of ionizable foulants and surface charge of membranes. In this study, fluxes of the coagulated suspensions by AS, PACl, and Al_{13} under various pH conditions, i.e., the initial water pH of 3.0, 5.0, 7.0, 9.0, and 11.0, were measured and in all cases, the flux was

Fig. 6. Turbidity, UV₂₅₄ removals, and zeta potentials by coagulation and coagulation/diatomite microfiltration hybrid processes under various pH conditions. All the coagulant dose was fixed at 5.0 mg/L.

found decrease gradually along the filtration time until a relatively constant value was achieved. Fig. 8 displays the changes of terminal J_0/J versus pH employing different coagulants. It could be found that for all the three coagulation systems, the terminal fluxes depicted similar trend with varying pH, which increased with pH in the acidic range and then declined with pH further increasing from pH 7.0 to pH 10.0. The most satisfactory fluxes occurred at the neutralization pH and the final J/J_0 values at alkaline pH were generally higher than those at acidic pH condition. Fluxes obtained at pH 3.0 were observed to be the least, implying the most severe membrane fouling by the feed water pre-coagulated at pH 3.0. This could be ascribed to the changes of floc zeta potentials involved in different coagulation systems. It has been

evidenced that the surfaces of diatomite are negatively charged in the wide pH ranges of 2.0–12.0 [43] and when the water pH decreased from 6.0 to 3.0 in this study, zeta potentials of flocs involved in the three coagulation systems became positive and increased progressively to 6.7–9.9 mV at pH 3.0 (Fig. 6(c)). Therefore, the charge repulsive strength of diatomite membrane to the generated flocs was weakened in which the foulant had a great chance of attaching to the membrane surface. However, an opposite correlation was observed when the pH was beyond 6.0, where fluxes declined with the increasing pH, although the zeta potentials decreased from the zero point to negative value range of -5.9 mV to -9.4 mV at pH 10.0. This is postulated that not only electrostatic interaction was responsible for the membrane fouling.

Fig. 7. Turbidity and DOC removals by the coagulation/microfiltration hybrid process under different pH conditions. (The coagulant concentration was fixed at 5.0 mg/L)

Fig. 8. Terminated normalized permeate flux (J/J_0) for pre-caugulated FA waters by AS, PACl, and Al_{13} coagulants under different pH conditions. All the coagulants doses were fixed at 5.0 mg/L.

Different floc characteristics generated under various coagulation mechanisms might also play remarkable roles in influencing the membrane fouling buildup.

Changes of particle size data from continuous monitoring of FA coagulation with different aluminum coagulants and varying pH levels are shown in Fig. 9. In most cases, the average floc size (d_{50}) grew rapidly after the coagulant addition and then further increase in the sizes was restricted, resulting in a steady-state floc size, usually assumed to represent a dynamic balance between shear-induced aggregation and breakage. However, AS coagulation at the water pH 3.0 and 11.0 as well as PACl at pH 11.0 could hardly achieved the plateau stages according to Fig. 9(b) and (c). Varying pH caused appreciable change in the floc

formation phase and consequently the plateau sizes, which could evidently impact the following membrane filtration process, so, the focus of these data should be on the relative differences between the flocs sizes formed under different pH conditions. The acidic and alkaline conditions, especially pH 3.0 and 11.0, caused most of small particles that were not able to aggregate into large flocs and still remained in water system. Comparatively, flocs formed at pH 5.0–9.0 were apparently with larger sizes. Since particle diameter is inversely proportional to specific cake resistance, the smaller size of flocs and residual fulvic substance might be the factors resulting in higher resistance in DMM process and, therefore, the severer declines in fluxes. This seems to be consistent with the results shown in Fig. 8, where coagulated samples at acidic and alkaline pH levels caused severe membrane foulings than those in neutralized pH range, regardless of the coagulant applied.

It is evident from the data of Fig. 5(c) that the flocs under investigation exhibited scattering behavior typical of mass fractal objects. The D_f of flocs formed under different pH levels are listed in Table 3. For the three coagulants, D_f values generally increased with pH, demonstrating flocs had more compact structures when formed at alkaline acidic ranges. Wang et al. [16] reported that the aggregates formed by charge neutralization were looser than those by sweep mechanism, and it was mentioned above that charge neutralization was predominant mechanism at acidic pH while adsorption of organic matters onto amorphous precipitates played an important role at alkaline pH ranges. As a result, it may be expected that acidic pH was benefit to alleviate the membrane fouling. Nevertheless, from a size effect standpoint, the reduced floc sizes at pH 3.0 over those at pH 11.0 (Fig. 9) were considered to result in lower fluxes. The two contradictory conclusions could be validated by the results of microfiltration test as shown in Fig. 8, indicating that the severity of flux decline under alkaline condition was slightly reduced over that at acidic pH condition. It therefore appears that floc

Fig. 9. Growth profile of FA flocs formed from three different coagulants (AS, PACl, and Al_{13}) under various pH levels. The coagulants doses were fixed at 5.0 mg/L.

Table 3
Floc fractal dimension (D_f) by different coagulants under different initial pH levels.

Initial pH of waters	AS coagulation	PACl coagulation	Al ₁₃ coagulation
3.0	1.74 ± 0.05	2.05 ± 0.03	2.21 ± 0.02
5.0	2.01 ± 0.06	2.13 ± 0.03	2.27 ± 0.03
7.0	2.06 ± 0.04	2.18 ± 0.05	2.32 ± 0.05
9.0	2.24 ± 0.04	2.34 ± 0.04	2.53 ± 0.04
11.0	2.21 ± 0.05	2.40 ± 0.02	2.49 ± 0.05

size played a more important role in membrane fouling than fractal structure.

However, although charge neutralization was believed to play a more significant role in Al₁₃ coagulation than the other coagulations as discussed previously, it was interesting to observe that under the same pH condition, Al₁₃ tended to develop flocs with the highest D_f , followed by PACl and conventional AS resulted in the most fluffy aggregates, especially in the acidic pH range (Table 3). A possible explanation for this inconsistencies is that in acidic pH, positively charged Al₁₃ could destabilize the organic molecules more effectively over the other coagulants, helping to bind the tiny particles together and therefore led to relatively more compact flocs over the other floc types. In alkaline pH range, the resulting floc structure by Al₁₃ seemed to be related to the effective interparticle bridging mechanism due to the formation of Al₁₃ aggregates [44]. Javies et al. [45] has claimed that bridging gives rise to the most compact structures, although further work is required in this field in order to adequately quantify this. Consequently, it is not surprising to observe that flocs produced by AS at pH 5.0 present a mean size of around 356 μm , which was comparable to those formed by Al₁₃ at pH 7.0 (about 345 μm), while the steady-state normalized permeate fluxes caused by the flocs with similar size were statistically different, which were 37% and 26% for the AS (pH 5.0) and Al₁₃ (pH 7.0) coagulation systems, respectively. On the whole, the results of this work have shown that pH changes imposed least impacts on coagulation/DMM process involved Al₁₃ in terms of floc size, compact degree and thus membrane permeability, and the process with AS fluctuated most obviously when exposed to different pH levels. Therefore, it could be concluded for the coagulation/DMM process, traditional AS could be applied when treating waters at neutral pH, while when the treated waters are acidic or alkaline, pre-hydrolyzed PACl/Al₁₃ could more efficiently promote pollutants removals and alleviate membrane foulings.

4. Conclusions

This study contributes to understanding of the effects of aluminum speciation and water pH on FA coagulation process and the diatomite microfiltration foulings as a result of flocs generated during coagulation. The DMM fouling mechanism is related to particle size and structure, which are largely dependent on the coagulation conditions. This research focused on the correlation between coagulation mechanisms with varying Al-based coagulants and pH levels, floc properties and membrane foulings, and the main findings of the study are as follows:

- In general, coagulation/DMM performed effectively in FA water treatment, even at low coagulant concentration. Al₁₃ contributed to the best DOC removal efficiency at the low dose over the other two coagulants due to its best charge neutralization ability.
- The flux declines of DMM could be considerably alleviated by pre-coagulation and AS, which consists of most Al_a species, was observed to be the most effective. And this should be ascribed to the large and loosely structured agglomerations formed through the adsorption and sweep mechanisms during AS coagulation. By contrast, Al₁₃ was found to contribute to smaller and more compact flocs and thus aggravated the flux decline when compared to the other coagulants.
- For both coagulation and coagulation/DMM processes, best purification efficiency was obtained around the neutral pH, while acidic and

alkaline pH seemed not conducive to the synthetic water treatments. Coagulation/DMM process involving Al₁₃ presents the least sensitive to the pH variation in terms of more stable water quality of effluent and membrane fouling buildup process, while the treatment efficiencies and fluxes of the process employing AS fluctuated most as the original pH changed.

- Flocs formed under acidic and alkaline pH levels were evidently smaller than those under neutralized pH, and consequently, flux declines were more severely, especially for the acidic pH. Additionally, floc size played a more important role in membrane fouling than fractal structure, and this is the reason why acidic pH gave rise to more severe flux decline than alkaline pH, although aggregates at acidic pH were more loosely structured.

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