Influence of floc structure on coagulation–microfiltration performance: Effect of Al speciation characteristics of PACls

Bingqing Zhao^{a,*}, Dongsheng Wang^{a,*}, Tao Li^a, Christopher W.K. Chow^{a,b}, Chihpin Huang^{a,c}

^a State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, No. 18, Shuangqing Road, Haidian District, Beijing 100085, China

^b Australian Water Quality Centre, 250 Victoria Square, Adelaide, SA 5000, Australia

^c Institute of Environmental Engineering, National Chiaotong University, Hsinchu, Taiwan, ROC

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ABSTRACT

Microfiltration performance in coagulation–microfiltration hybrid systems (without settling process) has strong correlation with the floc structure. This study investigated the effect of Al speciation distribution (Al_a , Al_b and Al_c) of PACls (polyaluminum chlorides) on floc structure and the overall membrane performance. The floc properties, analyzed with small angle laser light scattering (SALLS), of different aluminum based coagulants, $AlCl_3$ (PACla, with high Al_a species), polyaluminum chloride (PAClb, with high Al_b species), commercial polyaluminum chloride product (PAClp, with similar amount of each Al species) were compared using synthetic waters with added humic acid and kaolin particles. The coagulated waters were then fed through a dead-end microfiltration system using an unstirred batch cell with 0.22 μm PVDF flat sheet membrane. The results show that the property of flocs, largely depended on aluminum species, is the most influencing factor for membrane filtration behaviors. The floc sizes from different coagulants are in the following order PACla > PAClp > PAClb, which is consistent with the amount of Al_a species in the PACls. The fractal dimension values are very similar for each PACls. The floc strength follows the order of PACla > PAClb > PAClp. Cake made of PACla-flocs shows a noticeable flux advantage followed by PAClp-flocs and PAClb-flocs, which agrees well with the order of floc size. However, the flux decline of PAClp-flocs is much worse than PACla-flocs although both of them have similar final steady-state floc size. The difference between the flux of PAClb-flocs and PAClp-flocs is not as significant as the difference between their floc sizes. This can be explained that the PAClp-flocs are much more fragile than PAClb-floc due to its weak floc strength. These results also suggest that floc strength is another very important factor influencing the filtration performance.

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1. Introduction

Combined coagulation and membrane filtration has become an attractive alternative to conventional water treatment. Indeed, it is now very common to use coagulation as pretreatment of microfiltration (MF) and ultrafiltration (UF) to increase the removal of natural organic matter [1], improving membrane flux and even mitigate irreversible membrane fouling [2]. The hybrid coagulation–microfiltration process such as submerged membrane systems or direct membrane filtration processes which do not require to include settling processes are becoming more popular in the water industry [3]. There is also a tendency to use dead-end MF or UF systems rather than pumped cross-flow systems to reduce energy consumption [4]. However, membrane fouling in dead-end mode has been known as the major problem.

Research effort to overcome this issue in hybrid membrane process is needed.

Floc characteristics, such as floc size, floc strength, fractal dimension, play an important role in reducing membrane fouling in the coagulation–membrane filtration hybrid process. There is a great amount of literatures supporting the importance of floc properties in coagulation–MF or UF hybrid process. In early research, the classical Carman–Kozeny relationship which correlated the specific resistance to floc size has been widely recognized and used. Then, Guan et al. [5] first described a modified Carman–Kozeny relationship which incorporated fractal dimension and related the specific resistance with both floc size and fractal. As indicated by the modified Carman–Kozeny relationship, specific resistance would increase with decreasing floc size and increasing fractal dimension. Lee et al. [6] investigated the effect of floc size and structure on specific cake resistance and compressibility in dead-end microfiltration. They concluded that larger flocs produced filter cakes of lower specific resistance and floc structure effects were more significant for smaller floc, with higher specific resistance for cakes

* Corresponding author. Tel.: +86 10 62849138; fax: +86 10 62849138.
E-mail address: wgd@rcees.ac.cn (D. Wang).

formed from more compact flocs. Cho et al. [7] reported that coagulated flocs of lower fractal dimension can improve membrane permeability due to its higher porosity and relatively loose aggregation. Until recently, reports began to highlight the importance of floc strength or the floc resistant ability to shear stress. Choi et al. [3] reported flocs of high humic water, small and regular in shape represented by the low flocculation index (FI) and high fractal dimension, have higher specific cake resistance and can be more compressible than those of low humic natural water. Barbot et al. [8] reported that the effect on the permeate flux depended on the ability of flocs resistant to shear stress. Flocs which do not resist shear stress have no influence on permeate flux. Very large flocs, which are highly resistant to shear, lead to a 20% increase in permeate flux because flocs were not easily broken. While large flocs but with less resistant to shear leads to a decrease of 50% in permeate flux. These results imply that the size is not sufficient to explain membrane performance. An optimum balance was quantified for large flocs, resistant enough to shear stress facilitating flow between aggregates.

However, the physical and chemical properties of flocs are strongly related to other parameters in the coagulation process including coagulant type [9,10]. Recently, polyaluminum chloride (PACl) has been widely used in water and wastewater treatment to remove contaminants. Polyaluminum chloride (PACl), partially hydrolyzed products of Al(III), has been reported by many investigators to be superior to the traditional Al-based coagulants in performance of particulate and/or organic matter removal under some conditions [11–14]. According to the Al(III) hydrolysis/polymerization, Ferron assay has been used extensively to differentiate Al species of PACls into three categories [15–17]: Al_a , monomeric (possibly some oligomeric) species such as Al^{3+} , $Al(OH)^{2+}$, and $Al(OH)_2^{+}$. Dimer ($Al_2(OH)_2^{4+}$), trimer ($Al_3(OH)_4^{5+}$), some small polymers, and instantaneous reacted species are usually classified into this category; Al_b , intermediate polymeric species with molecular weight in the range of 500–3000 Da; Al_c , larger polymer or colloidal species, no reaction species. The dependence of PACls' performance on their Al speciation characteristics has also been recognized [15]. However, knowledge about the effect of Al speciation characteristics on floc structure is still limited. Its indirect influence on membrane performance is also rarely reported. Therefore, the goal of this study is to investigate the effect of Al species distribution of PACl on the properties of flocs such as size, fractal dimension and floc strength, and its role in the membrane filtration characteristics. Three kinds of PACls with different Al species distributions were used for coagulation of simulated water including humic acid and kaolin particles to evaluate the formation of flocs and their properties with small angle laser light scattering (SALLS). After coagulation, microfiltration in dead-end mode was conducted to explore the relationship between floc properties and filtration performance such as flux decline rate, cake resistance and specific cake resistance.

2. Experimental

2.1. Coagulants

All the reagents used were of analytical grade, except for being specified. Three aluminum chloride-based coagulants – PACla

Table 1

Speciation of PACls as characterized by the Ferron assay.

Coagulant	Al_a (%)	Al_b (%)	Al_c (%)
PACla	90.7	9.3	0
PAClb	4.1	93.0	2.9
PAClp	33.5	33.1	33.4

($AlCl_3$, Beijing Chemical Regent Company, China); PAClb (prepared in laboratory using $AlCl_3$), PAClp (a commercial PACl product, Wanshui Water Cleaning Agent Co., China) – were used in this study. A detailed procedure for preparing PAClb can be described as follows [18]: the $PACl_{2,2}$ was first prepared by slow-titration of 0.5 mol/L $AlCl_3$ solution with 1.0 mol/L NaOH resulting in the OH/Al ratio of 2.2 to gain high content of Al_b . Then the $PACl_{2,2}$ sample was rapidly mixed with $NaSO_4$ solution according to the target Al/ SO_4 ratio to obtain the Al_b -sulfate amorphous precipitates. After filtration, washing, and aging for further crystal formation, the sulfate in the Al_b -sulfate crystals was permuted through reacting with Ba^{2+} by mixing with certain amount of 0.1 mol/L $BaCl_2$ solution under ultrasonic vibration. The resulted purified Al_b -chloride solution was denoted as PAClb. The coagulants were both diluted into 0.1 mol/L as Al before use.

The Al species distribution in the PACls and $AlCl_3$ samples was analyzed by the Ferron (Sigma, UK) method. Based on the kinetic difference of the reactions between aluminum and Ferron reagent, soluble aluminum species can be differentiated as monomeric, fast-reacting polymeric, or slow-reacting colloidal species, namely, Al_a , Al_b and Al_c . The detailed procedures have been reported elsewhere [17]. The results are shown in Table 1. As shown, Al_a is the dominant species of PACla, Al_b is the dominant species of PAClb, while PAClp is a mixture of various Al species.

2.2. Synthetic water

The humic acid stock solution was prepared by dissolving 4 g of HA (Tianjin, China) into 500 mL 0.01 M NaOH solution. Then, the solution was stirred for 24 h, and filtered through a 0.45 μm membrane to remove residual non-dissolved humic acid. Dissolved organic carbon (DOC) of the stock solution was measured before use (TOC-Vcph, Shimadzu, Japan).

Kaolin was applied as a model suspension. The stock suspension of kaolin was prepared with deionized water. The solid concentration of suspension was determined gravimetrically to be 33 g/L. The average size of particles in suspension was close to 3 μm , measured by a laser diffraction instrument (Mastersizer 2000, Malvern, UK).

The synthetic water was prepared by dissolving the HA stock solution and kaolin stock suspension in deionized water with 0.001 mol/L $NaHCO_3$ to provide ionic strength and pH buffers. A summary of the synthetic water quality characteristics is shown in Table 2.

2.3. Jar testing and floc characterization

Initially, jar tests were performed on a programmable jar test apparatus (Daiyuan Jar Test Instruments, China) to determine coagulation dosage for the optimized flocculation. The sample water was first mixed rapidly at 250 rpm for 30 s. Then the coagulant was dosed by pipettes followed by a rapid mixing at 200 rpm for 1 min and a slow mixing at 40 rpm for 15 min. After another 20 min for

Table 2

Characteristics of synthetic water.

pH	DOC (mg/L)	UV ₂₅₄	Kaolin concentration (mg/L)	$NaHCO_3$ concentration (mol/L)	Zeta potential (mV)	Turbidity (NTU)
7.8–7.9	3.0–3.13	0.400–0.412	50	0.001	–33.2 to –34.3	57

Fig. 1. Coagulation performance varying with PACls dosage: (a) Zeta potential, (b) residual turbidity (RT), (c) pH, and (d) UV₂₅₄.

settling, a sample of the supernatant water is taken for water quality measurement.

Floc size and breakage experiment were performed using the experimental setup similar to those of Jarvis et al. [19]. Briefly, coagulation tests were performed as before; however, after the slow stir phase, increased shear for rpm of 40, 100, 150 and 200 were investigated for a further 15 min. Dynamic floc size was monitored during growth and breakage using SALLS (Mastersizer 2000, Malvern, UK). Size measurements were taken every 40 s for the duration of the jar test and logged onto a PC. The floc properties such as fractal dimension and floc strength were calculated using the above floc size and breakage experiment data.

2.4. Microfiltration procedure

Filtration experiments were conducted using a 50 mL-capacity unstirred batch cell. A 2 L feed reservoir was connected to the stirred batch cell. After the jar test (without sedimentation), each coagulated solution was gently transferred into the feed reservoir and slowly agitated to make a uniform suspension. The constant pressure was provided by nitrogen gas at 50 kPa. Permeate mass was weighed by an electronic balance (PL2002-IC, Mettler-Toledo, Switzerland) and recorded via a personal computer equipped with a data acquisition system. The filtration was terminated when the accumulated permeate volume reached 250 mL. MF membrane used in this study was PVDF flat sheet membrane with an average pore size of 0.22 μm (DURAPORE[®] membrane filters, Millipore). A fresh piece of membrane was used in all the experiment. And the membrane was soaked in deionized water at least 24 h before use. The clean water flux was measured before floc filtration.

2.5. Methods

The pH, suspended solids (SS) were measured using standard methods. DOC was analyzed by a TOC analyzer (TOC-Vcph, Shimadzu, Japan) after filtration through 0.45 μm membrane. UV₂₅₄ was measured by a spectrophotometer (UV-Vis 8500, China) using a 1 cm quartz cell after filtration through 0.45 μm membrane. The turbidity was measured by a turbidimeter (Hach 2100P Turbidimeter, USA). The zeta potentials and floc sizes of particles in raw and coagulated water were evaluated using a zeta meter (Zeta-sizer, Malvern, UK) and a particle size analyzer (Mastersizer 2000, Malvern, UK).

3. Results and discussion

3.1. Coagulation test

Fig. 1 shows the preliminary coagulation test results for dosage optimization of each coagulant. Residual turbidity decreases with increasing coagulant dosage. However, for PAClb, which was consisted of mainly Al_b species, re-stabilization occurred at the dosage higher than 0.12 mmol/L as Al. This is because that Al_b species possesses the highest positive charge and it has the greatest capacity for charge neutralization. The higher the content of Al_b species, the greater the capacity for charge neutralization as indicated by zeta potential curve of each PACl-treatment. The solution pH drops with PACls dosage increases. pH changes are strongly related to the basicity (B -value) of PACls, namely, slighter pH changes for PACl with higher B -value.

As shown in Fig. 1, coagulant dosage of 0.08 mmol/L as Al gave a combined optimum for residual UV₂₅₄ and turbidity after settle-

Table 3

Determination of optimum coagulant doses for each coagulant.

Coagulant	Dose (mmol/L as Al)	pH	Residual UV ₂₅₄ (cm ⁻¹)	Zeta potential of coagulated water (mV)	Residual turbidity (NTU)
PACla	0.08	7.12	0.014	-4.4	1.2
PAClb	0.08	7.64	0.014	-2.5	2.1
PAClp	0.08	7.45	0.020	-3.8	1.2

ment (listed in Table 3). Outside this dose range, the residual UV₂₅₄ and turbidity varied significantly, which would not be suitable for comparison of microfiltration performance for flocs generated by each coagulant treatment. It was therefore decided to use the coagulant dosage of 0.08 mmol/L as Al for all subsequent floc experiments and microfiltration tests.

3.2. Floc properties

3.2.1. Floc size

When coagulating the synthetic water of humic acid and kaolin particles with a set dosage of 0.08 mmol/L as Al with various PACls (different distribution of Al species), different floc growth profiles were obtained, as indicated by the median equivalent volumetric diameter (d_{50}) (Fig. 2). A general trend shows that as the Al_a species increases, floc size is seen to increase following the order of PACla > PAClp > PAClb which is consistent with the results of Wang et al. [10]. A substantial reduction in floc size was seen for PAClb as the maximum size approached only 270 μ m. The formation curves indicate that both floc formation processes can be divided into three regions: lag region, growth region and steady-state region. However, floc formed from different coagulants (different Al speciation) exhibits different growth rate and final floc size. Among them, floc generated by PAClb (with high Al_b species) treatment was the smallest in final size but with fastest growth rate; floc generated by PACla (with high Al_a species) treatment grew to the largest size but required the longest grow time, which meant that it took more time to reach steady-state when AlCl₃ was used as coagulant. In PAClp treatment, the floc grew faster compared to PACla but the floc size was slightly smaller.

Dynamic floc size has been generally accepted as a result of equilibrium between floc formation and floc breakage [20]. Therefore, under the same shear condition and using the same synthetic water, different floc growth profiles are direct reflection of different coagulation characteristics of PACls with different hydrolyzed Al species distribution.

For PACla (AlCl₃), the complexation of monomers with HA (Al_a-HA) is competitive with the general hydrolysis process. Therefore,

the formation of Al_b or Al₁₃ is certainly different from the hydrolysis process without the NOMs. Precipitation is delayed to occur until reaching certain dosage in presence of HA through either absorption of HA with Al-hydroxides or directly aggregation of Al_a-HA. Then the primary aggregates would be joined to the larger flocs by charge neutralization.

For PAClb, the preformed Al_b preferentially co-precipitated with HA in the form of Al_b-HA complexes [21]. Due to the large size of intermediate polymer of Al_b, the precipitate itself can also serve as primary particles which additionally increase the particle concentration and the rate of particle collision. Therefore, the floc growth rate of PAClb treatment is the fastest. However, the Al_b-HA complex has an unstable structure and their adhesions with kaolin particles are also not strong enough to resist the given shear stress, for its limited adsorption sites and thus limited number of bonds holding floc together. The steady-state floc size of PAClb treatment is the smallest.

For PAClp, about one-third of total Al species is Al_c which is large polymer or colloidal species formed during Al(III) hydrolysis of which molecular weight normally larger than 3000 Da. It is not only large in size and easy to precipitate but also has a certain degree of better bridging flocculation capacity. So the PAClp-flocs are also large in final steady-state size.

3.2.2. Fractal dimension (dF)

Floc geometry is now commonly described as fractal, implying that aggregates are self-similar and scale invariant. Fractal dimension is often determined by static light scattering and described by the following relationship between the measured scattered intensity of aggregate clusters ($I(q)$) and the momentum transfer (q) (Eq. (1)):

$$I(q) \propto q^{-dF} \quad (1)$$

When the light intensity is plotted versus the wave vector on a log-log scale, the fractal dimension is calculated in the linear region. Fig. 3 shows the corresponding log-log plots of the flocs concerned in the present studied system. The fractal dimension results showed no much difference between different Al species-dominant PACls.

Fig. 2. Variations of floc size during coagulation with different coagulant. **Fig. 3.** Static light scattering plots for each coagulant.

Fig. 4. Floc strength of different floc.

This is consistent with the understanding that reaction-limited aggregation (RLA, in a low salt environment) leads to compact floc (higher dF , in the range of 2.3–2.5) [4].

3.2.3. Floc strength

After the flocs had reached their steady-state size during the slow stir period, they were exposed to increased shear. When the floc size after 15 min exposure to shear was plotted against G -value, a straight line could be drawn through the data on a log–log scale (Fig. 4). Based on an empirical expression about the relationship between stable floc size and the applied shear (Eq. (2)), the γ -value (the floc strength constant) is considered as an indicator of floc strength [20,22]. The steeper the slope γ , the more prone the flocs are to break into smaller sizes with increasing shear force:

$$\log d = \log C - \gamma \log G \quad (2)$$

Fig. 5. Flux variations of flocs made by different coagulant treatment.

It could be noted from Fig. 4 that the responses of the various PACI-flocs to increases in shear were quite different. The γ -values were 0.3422, 0.4193, 0.6843 for PACla, PAClb, PAClp, respectively. The floc formed by PACla treatment was the strongest and by PAClp treatment was the weakest.

These results can also be easily understood in combination with the floc size analysis. Floc strength is dependent upon the inter-particle bonds between the components of aggregate [20,22]. As reported by Hiradate and Yamaguchi [21], the Al_a -HA is much more stable than Al_{13} -HA complex. Al_{13} in Al_{13} -HA complexes was decomposed into Al -HA complexes with reaction time. Therefore, the floc strength of PACla-floc must be better than that of PAClb-floc. As for PAClp, a relative large portion of Al is in presence of Al_c , larger polymer or colloidal species. It is assumed as no reaction species in the coagulation process [15] and it destabilizes particle or removes NOMs largely through either bridging flocculation or adsorption. The inter-particle bonds within the resultant floc are thus the weakest.

3.3. Membrane performance

A comparison of the flux declines of cakes formed from flocs by various coagulants at TMPs (trans-membrane pressures) of 50 kPa are shown in Fig. 5. Cake made of PACla-floc showed a noticeable flux advantage. The flux for the cases of PAClb-floc and PAClp-floc were both seen to display a substantial decline compared with PACla-floc. The overall order of magnitude of flux decline follow the reverse sequence of floc size, namely, $PAClb > PAClp > PACla$. These results imply that membrane fouling can be greatly affected by floc size which is also reported by Guan et al. [5] that effects of differences in floc size are most significant when floc are more compact.

However, the flux profiles of PACla-floc and PAClp-floc varied significantly although their steady-state floc sizes were very similar. Meanwhile, the difference between the flux of PAClb-floc and PAClp-floc was not as significant as the difference between their floc size. This is because the floc of PACla treatment is largest in size and also the strongest in strength, therefore, cake formed by PACla-flocs is much more porous and also less compressible than the other two cases. The corresponding flux decline must be the slowest which decreases to about 30% of the original pure water flux. While for PAClp, although the steady-state floc size is similar with PACla treatment, the PAClp-flocs are much more fragile than PACla-floc indicated by higher floc strength constant. Cake formed by PAClp-flocs is prone to be more compressible and less porous under the given pressure. This also agrees with the results of Choi

Table 4

Membrane fouling characteristics for different flocs.

Samples	Membrane resistance (R_m , m^{-1})	Total resistance (R_t , m^{-1})	Specific cake resistance (α_c , m/kg)
PACla-floc	5.3×10^{10}	1.9×10^{11}	8.4×10^{12}
PAClb-floc	5.3×10^{10}	3.4×10^{11}	1.7×10^{13}
PAClp-floc	5.2×10^{10}	3.0×10^{11}	1.5×10^{13}

et al. [3]. As for PAClb, the stronger floc strength partly compensates the disadvantage of smaller steady-state floc size. Thus, the floc of PAClb and PAClp treatment exhibit the similar flux profile.

Following conventional cake filtration theory, the membrane resistance, total resistance and the average specific cake resistance, α_c , for cake formed with different flocs generated by various coagulants were calculated using Eqs. (3)–(7):

$$J = \frac{\Delta P}{\mu R_m} = J_0 \quad (3)$$

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu(R_m + R_c)} = \frac{\Delta P}{\Delta P/J_0 + \mu R_c} \quad (4)$$

$$R_c = \frac{1}{\mu} \left[\frac{\Delta P}{J} - \frac{\Delta P}{J_0} \right] \quad (5)$$

$$R_c = \alpha_c \frac{m}{A} \quad (6)$$

$$\alpha_c = \frac{A}{\mu m} \left[\frac{\Delta P}{J} - \frac{\Delta P}{J_0} \right] \quad (7)$$

where J is the flux, ΔP is the trans-membrane pressure, J_0 is the initial flux, μ is the viscosity of permeate, R_m is the intrinsic membrane resistance, R_c is the cake resistance, R_t is the total resistance, A is the membrane area, m is the mass of foulants, α_c is the specific cake resistance. Membrane fouling characteristics determined using the aforementioned parameters are summarized in Table 4. The specific cake resistances of various flocs were ordered as PAClb > PAClp > PACla, agreeing well with the hierarchy of floc size.

4. Conclusions

The experimental results showed that the flocs properties had a strong correlation with aluminum speciation distribution characteristics of the PACl coagulants which will further result in different filtration performance. As for treating high molecule weight humic acid, the floc size, ordered as PACla > PAClp > PAClb, agreed well with the Al_a amount in the PACls. There was no much difference between fractal dimension values for each PACl. Flocs strength followed the hierarchy that PACla > PAClb > PAClp. Cake made of PACla-floc showed a noticeable flux advantage followed by PAClp and PAClb. Although these results suggest that the smaller flocs possess more significant membrane fouling potentials than those larger ones, floc strength is another very importance factor influencing the following filtration performance of flocs.

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