Influence of coagulation process on the ultrafiltration performance – The roles of Al species and characteristics of algae-laden water

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ABSTRACT

The aim of this study was to investigate the coagulation performances in different algal systems, and effects of algal morphology and composition of extracellular organic matter (EOM) on membrane flux were also investigated. The results indicated that Al_{13} generated the largest flocs, and strength factor and recovery factor were also largest. The results of ultrafiltration experiments also showed that the floc size and the concentration of Soluble Microbial Products (SMP) may be the main decision factors in the membrane fouling process. Al species distribution was important in removing EOM in the coagulation process. SMP in EOM could be effectively removed by Al_{13} and Al_{30} , so the membrane fouling could be alleviated due to the larger removal efficiency of SMP. The roughness of the sediment layer formed by Al_{13} was largest, and the sediment layer would adsorb and intercept more algae organic matter.

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1. Introduction

Former studies had showed that the algal cells and pollutants caused by algae would affect the drinking water quality [1–4]. The production of unpleasant tastes and odors [5], formation of disinfection by-products (DBPs) [6], and toxins from cyanobacteria [7] were the most important problems. Membrane technology had gradually shown its important role and bright prospects in water treatment process, and ultrafiltration (UF) technology could remove a broad range of impurities almost completely [8,9]. Although the membrane technology had developed rapidly, membrane fouling was always a challenge for the development of membrane technology. Especially for the algae-laden source water, algal cells could secrete extracellular organic matter (EOM) and mucilaginous slime material, which could cement particulates on the membrane surface and increase the resistance to filtration [10,11]. Some researches had demonstrated the influence of different hydrophobic/hydrophilic fractions of EOM on ultrafiltration membrane fouling [12–14]. In the membrane fouling process, the deposited layer formation, pore plugging and hydrophobic adhe-

sion were the main mechanisms for the membrane fouling caused by algal EOM [15]. In order to solve these problems, amounts of studies conducted on the removal of algae have been mainly concentrated on effects of organic matter of algae (AOM) and the disinfection by-products (DBPs) [16,17]. In different algal growth phases, the concentration and composition of EOM may be different [18]. Some researches investigated the flux decline and fouling potentials from different algal growth phases, with fouling for the stationary > late exponentially phase > early exponential phase [19]. However, few studies referred to the morphology of algal cells prior to entry into the UF system. It was therefore not clear whether the morphology of algal cells could influence membrane fouling of UF, particularly when the algae-laden water was treated using different Al-based coagulants.

Amount of pretreatment technologies had been conducted to improve the membrane performances, and the results showed that pretreatment technology could greatly expand the use of UF membrane system [20]. Although these pretreatment steps could improve the coagulation performances and decrease the amount of the algal cells, they could deteriorate disinfection process by changing the nature of the water and cause the formation of trihalomethanes (THMs) and haloacetic acids (HAAs). Coagulation, which is regarded as an economical and efficient pretreatment method, has been widely used in drinking water and wastewater treatment. The actual effect of pre-coagulation on the permeability

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of the membrane depends on coagulation conditions, including coagulant types, dosage and mixing condition [21]. The coagulant directly affected the coagulation performance, and the coagulation performance directly determined the efficiency of water treatment [22]. Aluminum salt is the most commonly used coagulant in water treatment plant, and a large amount of scientific researches and the applications results showed that the concentration of Al_{13} could reflect the coagulation behavior and performance of polyaluminum chloride (PACl) products. The Al_{13} structure is stable and carry large amounts of positive charges, so the Al_{13} molecules could directly been adsorbed on the surfaces of particles and a strong electrical neutralization process could be exerted [23]. Thus, production of PACl with a high concentration of Al_{13} has become the main target of the PACl research and production industry [24]. Al_{30} is another polycation with Keggin structure in hydrolysis polyaluminum solutions, and it is composed of two Al_{13} molecules connected by four Al monomers. Former studies showed that Al_{30} molecules performed better bridging effects in coagulation process [25]. Although the coagulation mechanisms for Al_{13} or Al_{30} had been investigated well, few researches focused on the treatment of different algae-laden water, and the membrane fouling process was also not investigated well. Thus, study focused on membrane fouling in treatment of different algae-laden water with Al-based coagulants is necessary.

The purpose of this study is to understand the role of Al species in membrane fouling when coagulation technology was used as pretreatment in treatment of algae-laden water. In this study, different algae-laden waters samples were generated by coagulated with different Al-based coagulants. The water samples were varied by an important operating conditions: with or without sedimentation after the coagulation process. Membrane fouling and flux decline associated with different algal systems, and the effects of Al species distribution on flux decline are described.

2. Materials and methods

2.1. Algae cultivation

The following freshwater algae cultures were obtained from the Institute of Hydrobiology, Chinese Academy of Sciences: *Microcystis aeruginosa* (cyanobacteria), *Chlorella* (green algae) and *Cyclotella* (diatoms). Axenic cultures were carried out in batch mode in 10 L and growth conditions have been described, regularly observed their growth and counting [26]. All algae were harvested for experiments in the early stationary phase.

2.2. Preparations of water samples and coagulant

The relationship between the density of algae cells and suspension absorbance will coincidence with linear relation. Thus, This study choose the algal cell suspension absorbance at 680 nm as a measure of algae cell density. The experimental water sample were prepared by algal cell suspension diluted with deionized water. To facilitate comparison between algae, adjusting the absorbance of the three algae was 0.300 under 680 nm. The reagents used in experiments were purchased from China National Pharmaceutical Group Corporation (Beijing). 5.0 mmol/L $NaNO_3$ and 4.0 mmol/L $NaHCO_3$ were added to provide a ionic strength and a contain buffer capacity. The pH of water sample was adjusted to 8.5 with NaOH (0.1 mmol/L) and HCl (0.1 mmol/L) solutions. Three Al-based coagulants were used in this study: $Al_2(SO_4)_3$, Al_{13} and Al_{30} . Their preparation methods as stated in the literature [25]. The total aluminum concentration in this paper was determined by titrimetric method according to National Standard of China. Al-species distributions of three coagulants were measured by

Al-Ferron complexation timed spectrophotometry method [27], and the results are summarized in Table 1.

Results (Table 1) indicated that the Al species distributions of three coagulants used in this study were different, and these three coagulants could be used to investigate the effects of Al species distribution on the membrane fouling process in algal system.

2.3. Jar tests and UF membrane tests

A programmable Jar tests were performed on a Flocculator (MY3000-6F, Wuhan Meiyu, China), which enabled mixing speed and time to be preset. Coagulation test was consisted of 4 steps: (1) Stirring the suspension at a speed of 250 rpm for 0.5 min to mix the solution evenly. (2) Adding certain amounts of coagulants and simultaneously stirring the solution at 200 rpm for 1.5 min to uniformly disperse the coagulant; (3) Stirring the solution at a reduced speed at 40 rpm for 10 min to allow floc growth to occur; (4) The coagulated water sample was sedimented for 30 min to measure the residual turbidity and the amount of residual algal cells. The coagulated water was treated with membrane without sedimentation, and the coagulated water which was sedimented for 30 min was used to be compared.

The previous series on algae removal by coagulation experiments had determined the optimum dosage of coagulant (Fig. S1), and results of optimum dosage of the coagulants were summarized in Table 2. With colony counting method, the residual cells in the treated water samples were calculated and summarized in Table 3, and the results indicated that the coagulation process could significantly decrease the amount of algal cells (cells/mL). After the coagulation process, the treated water samples were transported into filtration cells (without or after sedimentation) which was purchased from Millipore (Amicon 8400, USA). The flat sheet ultrafiltration membrane (100KDa) made of Polyvinylidene fluoride (PVDF) was purchased from Ande Membrane Separation Technology & Engineering Co., Ltd (Beijing). Under the process of ultrafiltration, the coagulation effluent always needs to provide in order to prevent membrane surface drying. Normalized flux J/J_0 as a function of time was shown for the flux decline results from the stirred cell experiments, and J_0 was the initial membrane flux. In order to facilitate the comparison, the fixed ultrafiltration time is 1800 s and the feed solution was driven to penetrate across the membrane by nitrogen gas at a constant pressure of 0.1 MPa. The membrane after filtration were taken out to be dried in natural conditions, and FE-SEM analysis (JEOL Ltd., Tokyo, Japan) and AFM analysis (Nanoscope, IIIa, Multimode) were used to investigate the mechanism for membrane fouling, respectively.

2.4. EOM analysis

The algae organic matter (AOM) comprises both extracellular organic matter (EOM) and intracellular organic matter (IOM). In order to study the effect of EOM on the fouling of ultrafiltration membrane, Fluorescence EEMs of EOM was measured on a Varian Eclipse fluorescence spectrophotometer (Hitachi F7000, Japan) in scan mode. The spectrums were gathered with scanning emission: Em spectra from 220 nm to 550 nm at 5 nm increments by varying the excitation; Ex wavelength from 200 nm to 400 nm at 5 nm increments. The spectra were recorded at a scan rate of 12,000 nm/min, using excitation and emission slit bandwidths of 5 nm. The voltage of the photomultiplier tube PMT was set to 500 V for low level light detection.

2.5. Characteristics of flocs formed in the coagulation process

Generally, floc size, strength factor (S_f), recovery factor (R_f) and fractal dimension (D_f) were some basic parameters to describe the

Table 1

Al species distribution in coagulants used in this study.

Coagulant	Al _T (mol/L)	Al _a (%)	Al _b (%)	Al _c (%)
Al ₂ (SO ₄) ₃	0.025	96.83	2.18	0.99
Al ₁₃	0.025	4.92	93.74	1.34
Al ₃₀	0.025	5.98	7.14	84.88

Table 2

Optimum dosage for coagulant in treatment of different algae-laden water.

Algae	Al ₁₃ (mmol/L)	Al ₃₀ (mmol/L)	AS (mmol/L)
<i>M. aeruginosa</i>	0.06	0.08	0.08
<i>Chlorella</i>	0.04	0.06	0.08
<i>Cyclotella</i>	0.10	0.10	0.12

characteristics of flocs. And flocs with larger S_f and R_f values were considered to have stronger and better re-growth capacity. The methods for investigating these characteristics of flocs were summarized in former studies [28]. Floc breakage and re-growth experiments were carried out as follows: a regular coagulation process (without sedimentation) followed by a breakage phase at 200 rpm for 5.0 min and a re-growth phase at 40 rpm for 10.0 min. A small-angle light scattering instrument (Malvern Mastersizer 2000, Malvern, UK) was used to measure dynamic floc size and fractal dimension (D_f) as the coagulation process proceeded.

2.6. Other characteristics for source water or membrane

Turbidity was measured by a turbidity meter (2100P, Hach, USA). DOC was determined using a total organic carbon. Solution pH value was measured by pH meter (pHS-3C, Shanghai, China). Contact angle was measured by Optical Contact Angle Measuring Device (Contact angle system OCA20, Dataphysics, Germany). Membranes were first gently dried and then fixed on the stage. Water (2.0 μ L) was dropped carefully onto the dried membrane surface using a microsyringe. The static water contact angle was determined from a magnified image of the drop taken by a digital camera and analyzed using image software.

3. Results and discussion

3.1. Characterization of the EOM in these three algal systems

EEM for the three raw water samples were summarized in Fig. 1.

EEM spectrum (Fig. 1) indicated the composition of EOM, and four peaks had been detected. A peak (Peak T) is present at $\lambda_{ex} = 240\text{--}250$ and emission $\lambda_{em} = 280\text{--}380$. A second peak (Peak A) is observed at $\lambda_{ex} = 240\text{--}250$ and emission $\lambda_{em} = 400\text{--}450$. A third fluorescence centre (Peak C) is observed at $\lambda_{ex} = 330\text{--}340$ and emission $\lambda_{em} = 400\text{--}450$. A fourth fluorescence centre (Peak S) is observed at $\lambda_{ex} = 270\text{--}330$ and emission $\lambda_{em} = 280\text{--}380$. Peak T is identified as tryptophan-like. Tryptophan-like fluorescence may be exhibited by natural waters where tryptophan is present

as free molecules or bound in proteins, peptides or humic structures. It is related to microbial activity and may be transported into the system (allochthonous) or be created by microbial activity within the system (autochthonous). Peak A and C are related to humic-like (mainly humic and fulvic acids) derived from the breakdown of plant material. These two components are the most common fluorophores in natural surface waters. These four organic compounds can be summarized to three major organics, i.e. humic substances, aromatic proteins and SMP-like substances. As stated by Chen et al., the beneath EEMs within selected regions could represent the cumulative fluorescence response of EOM with similar properties. Therefore, quantification of the EEM spectra could be achieved by the fluorescence regional integration (FRI) method [29].

The chemical characteristics of these three raw water samples and the composition of organic matter were summarized in Table 4.

Results in Table 4 showed that the *Cyclotella* system had largest concentration of organic matter (DOC = 2.345 mg/L), and the smallest SUVA indicated that the most amount of organic matter was hydrophilic. The quantification of the EEM spectra showed that the composition of organic matter was different, and the fraction of SMP was always the largest in all these three algal systems.

3.2. Membrane fouling and flux decline

The flux decline in different algal systems under different conditions was summarized in Fig. 2.

Results in Fig. 2 indicated that the membrane flux was improved obviously after the water samples were treated by the coagulants, and some researches had demonstrated that coagulation as pretreatment technology could improve the flux of ultrafiltration membrane [30]. NOM is ubiquitous in natural surface waters, and it is often claimed as an important factor for both reversible and irreversible fouling in water filtration process. In the coagulation process, the organic matter existed in the suspension would be effectively removed, so the water flux decline was improved. These results also indicated that the membrane flux without sedimentation was larger than the membrane flux after the coagulated water was sedimented. Possible reason is that flocs could form a deposited layer on the membrane surface, and these layers could absorb and intercept organic matter [31]. So the deposited layer could effectively prevent organic matter from reaching the surface of the membrane. When the coagulated water was sedimented, the organic matter in coagulation effluent would directly contact the membrane surface or plug in the membrane pores due to few flocs existed on the surfaces of membrane [32].

The improvements of membrane flux after filtration process (1800 s) were summarized in Table 5. Results in Table 5 indicated that Al₁₃ could significantly alleviate the flux decline, and the improvement of AS was not significant in all these three algal systems. This might be caused by the larger amount of positive charges of Al₁₃, which could effectively remove organic matter and algal cells from source water through charge neutralization ability [33]. Furthermore, in terms of these three kinds of algae systems, the membrane flux decline rate was not the same. *M. aeruginosa* caused the fast rate of membrane fouling. At the beginning of

Table 3

The residual cells in the treated water samples using different coagulants.

	<i>M. aeruginosa</i>	<i>Chlorella</i>	<i>Cyclotella</i>
Raw algae	$1.2 \times 10^6 \pm 0.8 \times 10^5$	$5.06 \times 10^5 \pm 3.96 \times 10^4$	$1.24 \times 10^4 \pm 1.61 \times 10^3$
Al ₁₃	$2.4 \times 10^4 \pm 1.6 \times 10^3$	$1.62 \times 10^4 \pm 1.26 \times 10^3$	$0.78 \times 10^3 \pm 1.01 \times 10^2$
Al ₃₀	$1.32 \times 10^4 \pm 0.88 \times 10^3$	$0.51 \times 10^4 \pm 0.40 \times 10^3$	$1.12 \times 10^3 \pm 1.45 \times 10^2$
Al ₂ (SO ₄) ₃	$1.32 \times 10^4 \pm 0.88 \times 10^3$	$0.61 \times 10^4 \pm 0.48 \times 10^3$	$0.33 \times 10^3 \pm 0.43 \times 10^2$

Fig. 1. EEM spectra for raw water samples.

Table 4

Characteristics of raw water samples used in this study.

Algae	UV ₂₅₄	DOC (mg/L)	SUVA	Protein (%)	HA (%)	SMP (%)
<i>M. aeruginosa</i>	0.0323	1.451	2.22	19.70	22.69	57.62
<i>Chlorella</i>	0.033	1.139	2.89	23.07	31.69	45.24
<i>Cyclotella</i>	0.031	2.345	1.32	28.65	19.57	51.78

180 s period in the UF stirred cells experiment without being treated by coagulation process, *M. aeruginosa* system caused the membrane flux decline of 79.0%, *Chlorella* system was 59.9% and *Cyclotella* system was 74.2%, respectively. In the next 180 s, the decline changed to 88.0%, 71.9% and 85.7%. Many researches had suggested that the humic substances fraction of natural organic matter (NOM) is a major foulant which controlled the rate and extent of fouling [34,35]. But some other researches had showed that hydrophilic (non-humic) NOM might be a more significant foulant [36]. However, the organic matter in the feed water was important in the membrane fouling process. According to the results of DOC, there are larger amount of NOM in *Cyclotella* system (2.345 mg/L). But the membrane flux decline in *M. aeruginosa* system was the largest in all these three algal systems. This phenomenon could be explained by the morphology of each algal cell and the composition of algogenic organic matter (AOM). Some previous study had described that *M. aeruginosa* cell was small,

ellipse and population distribution, *Chlorella* cell was large, spherical and dispersed single, and *Cyclotella* cell was irregular shape, variety sizes and dispersed single, respectively [10]. Therefore, gaps of their deposited layer formed on the surface of the membrane are different, which directly affect the membrane flux. The gaps in the layer formed by *M. Aeruginosa* system and *Cyclotella* system were small, and the gaps of *Chlorella* system were larger, thus, *Chlorella* system has the smallest rate of flux decline. However, the morphology of algal cells is only part of reason for membrane flux decline, and some other characteristics (such as the composition of AOM) also have great influences on the membrane decline. Some researches showed that the significant organic fouling that is contributed by polysaccharides and/or proteins in macromolecular and/or colloidal forms depends on molecular shape as well as size [37]. In the filtration process, the NOM molecules were adsorbed both inside pores and on the membrane surface, and forms a gel layer. Xiao et al. found that aromatic protein

Fig. 2. Flux decline as a function of time in different algal system under different conditions. Where A represent C-UF process without sedimentation and B represent C-UF process with sedimentation.

Table 5
Improvement of membrane flux after filtration process.

Algal system	Treatment process	Al ₁₃	Al ₃₀	Al ₂ (SO ₄) ₃
<i>M. aeruginosa</i>	After sedimentation	27.4 ± 1.58%	17.7 ± 1.47%	11.6 ± 1.49%
	Without sedimentation	35.1 ± 1.38%	28.0 ± 1.09%	14.9 ± 0.78%
<i>Chlorella</i>	After sedimentation	43.8 ± 2.17%	34.4 ± 1.37%	18.5 ± 0.89%
	Without sedimentation	46.2 ± 1.14%	38.2 ± 1.43%	20.4 ± 1.55%
<i>Cyclotella</i>	After sedimentation	49.8 ± 1.96%	26.9 ± 0.58%	7.2 ± 1.69%
	Without sedimentation	52.2 ± 2.07%	33.5 ± 0.96%	8.0 ± 0.78%

had a highly correlation with irreversible fouling. Humic substances were not found to be important in the formation of the combined fouling layer [36]. And some other studies had showed that the concentration of SMP had a key role in membrane irreversible fouling, while humic substances were not found to be important in the formation of the combined fouling layer [38]. Effects of composition of AOM would be described in Section 3.3.

3.3. Characteristics of flocs and algogenic organic matter (AOM)

3.3.1. Characteristics of flocs formed in the coagulation process

The Floc size (D_{50}), strength factor, recovery factor and fractal dimension are used to characterize the flocs, and the coagulation

performances using different Al-based coagulants are shown in Fig. 3.

Results in Section 3.2 indicated that the morphology of algae cells and composition of algogenic organic matter in raw water had significant effects on the membrane filtration, and these results also showed that the filtration process was different after the raw water was treated by different Al-based coagulants. The former studies had indicated that the coagulation process had significant effects on the flocs, and the filtration process may be different due to the different characteristics of flocs [39]. Results (Fig. 3) showed that Al₁₃ could produce largest flocs (larger than 800 μm in all these three algal systems), and the floc size had significant correlation with the concentration of Al_b. Compared with

Fig. 3. Coagulation performances using different coagulants in different algal systems.

membrane flux showed in Table 5, Al_{13} had the largest ability to improve the membrane flux. Thus, it seemed that floc size had significant effects on membrane flux, and the largest flocs could produce the largest membrane flux. The flocs formed by three coagulants in *M. aeruginosa* system were slightly larger than in *Chlorella* system, but the improvement of membrane flux in *Chlorella* system was much more significant than in *M. aeruginosa* system. That is to say, floc size was an important role in the membrane fouling, but there were other characteristics of flocs which could affect the filtration process.

In order to quantitatively evaluate the process of floc breakage, re-growth and fractal properties, the S_f , R_f and D_f were calculated and summarized in Table 6. It could be observed that algal flocs formed by Al_{13} (S_f are 35.9%, 42.2% and 59.0%, respectively) and Al_c (S_f are 35.2%, 39.7% and 56.7%, respectively) were more difficult to be broken and exhibited larger flocs strength. Similar standpoint has been previously proposed by P. Jarvis and B. Jefferson, who observed that Al_b and Al_c aggregates had much more branched structure and the bridging of particles onto Al_b or Al_c aggregates could markedly enhance the flocs strength [40]. Flocs formed by coagulants with larger amount of Al_b or Al_c were more resistant to the increased shear and exhibited the least variation in properties. Therefore, the flocs formed would remain the same characteristics in the filtration process. The deposited layer formed by AS would become more dense, and the membrane flux declined more

obviously. Furthermore, the changes of R_f using AS, Al_{13} and Al_{30} as coagulants seems to follow same trend. R_f for Al_{13} were 17.9%, 26.4% and 32.1%, and these results for Al_{30} were 15.0%, 23.0% and 30.8% and for AS were 13.6%, 8.0% and 25.3%, respectively. The flocs formed by Al_{13} had largest recovery factors, and these results may be caused by the larger positive charges of Al_{13} molecules which was thought to promote floc re-formation [41].

Fractal dimension is another important parameter to describe the structure of aggregates. As can be clearly seen in Table 6, *M. Aeruginosa* system produced flocs with larger D_f than *Chlorella* system and *Cyclotella* system. Former studies had indicated that when the flocs had larger fractal dimension, the flocs would be more compact [40]. The particle size increased with increasing the concentration of Al_b in three algal systems, and these results indicated that the charge neutralization was probably occupied to some extent. The aggregates formed by charge neutralization are looser than that by sweep coagulation for extended structure [42]. The flocs which were more compact would had a larger gap when they formed the deposited layer on membrane surface, and these gaps would affect the membrane flux. Normally, the deposited layer which had larger amount of gaps would alleviate the membrane flux decline, but the membrane flux decline was obviously in *M. aeruginosa* system. The membrane flux decline was obviously in *M. aeruginosa* system especially when Al_{13} or Al_{30} were used as coagulants compared with other two algal systems. Former studies

Table 6
Strength factor, recovery factor and fractal dimension for flocs formed by Al₁₃, Al₃₀ and Al₂(SO₄)₃ in different algal systems.

Algae	S _f (%)			R _f (%)			D _f		
	Al ₁₃	Al ₃₀	AS	Al ₁₃	Al ₃₀	AS	Al ₁₃	Al ₃₀	AS
<i>M. aeruginosa</i>	35.9	35.2	32.3	17.9	15.0	13.6	2.04	2.13	2.16
<i>Chlorella</i>	42.2	39.7	37.6	26.4	23.0	8.0	1.618	1.75	1.87
<i>Cyclotella</i>	59.0	56.7	44.9	32.1	30.8	25.3	1.288	1.526	1.808

Fig. 4. EEM spectra for different water sample, Where D represent ultrafiltration effluent without coagulation process.

had showed that the compact flocs would increase the adsorption and cake layer resistances in membrane fouling and thus resulted in severe flux decline [43]. These results may be caused by the larger amount of SMP molecules in the raw water. The deposited

layer had larger amount of gaps, and more SMP molecules could transport through the deposited layer. There would be more organic matter could reach the surface of membrane, and the membrane flux decline was obviously in the *M. aeruginosa* system.

Fig. 5. SEM images for the membrane surface.

It is interesting that when AS was used as coagulant in *Cyclotella* system, the membrane flux declined more quickly, and these results may be caused by the larger amount of organic matter. It has been reported that EOM had a high affinity to metals in coagulant induce the reduction of coagulation efficiency due to the formation of complexes between metals of EOM, which could bring about the excess consumption of coagulant. In the *Cyclotella* system, there were larger amount of organic matter, but the effects of EOM on the coagulation performances using Al_{13} and Al_{30} as coagulants were not significant (The EOM molecules had significant effects on the coagulation performances using AS as coagulant, but the removal efficiency for organic matter using Al_{13} and Al_{30} as coagulant could remain larger).

3.3.2. Characteristics of organic matter in the treatment process

Three Dimension Fluorescence excitation emission matrix (3D-EEM) spectroscopy is a highly sensitive and selective tool, which

had been extensively utilized to characterize natural organic matter (NOM). The 3D-EEM spectroscopy for different water samples were summarized in Fig. 4.

SMP were found to be dominant in all these three raw algae-laden water samples (Fig. 1). When raw algae-laden water was filtered by 100 kDa membrane, the intensity of SMP dramatically decreased. However, the peak intensity of humic-like substances did not decrease as dramatically as that of SMP substances. The humic-like substances of algal EOM concentrated in low-MW portion. And more detail fluorescence information of ultrafiltration effluent after coagulation process (without sedimentation and after sedimentation) could be found in Fig. S2. Results (Fig. 4) also showed that the fluorescence intensity of EOM decreased obviously after the coagulation process, especially for SMP (The intensities of SMP in different water samples were summarized in Table S1). It was reported that the high MW organic materials comprised of soluble microbial products (SMP) were the major cause of membrane

Fig. 6. AFM images for the membrane surface.

fouling when low pressure membrane was applied. As great parts of algal EOM were high-MW organics, the formation of cake layer due to size exclusion was inevitable during UF. Therefore, cake layer formation might be one of significant mechanisms for membrane fouling caused by EOM. In the coagulation process, the size of organics dramatically increase. When transport towards the membrane, these aggregates could form porous cake layer. Therefore, improved permeability was found after the addition of coagulants. The results showed that Al_{13} had larger removal efficiency for these organic matter in all these three Al-based coagulants. So the residual EOM could cause less impact on the ultrafiltration process, and that could be attributed to the larger amount positive charges of Al_{13} which played an important role (charge neutralization and electrostatic patch) in coagulation process. Similarly, Al_{30} decreased the amount of algal particles through bridging effects and electrostatic

patch in coagulation process, and the removal of organic matter also may be large. The highest peak of 3D-EEM of 280/350 in Fig. 4 indicated that a number of SMP remained in the supernatant after the coagulation test no matter what coagulants were used. Removal efficiency using $Al_2(SO_4)_3$ was the smallest for organic matter such as SMP, so there would be larger amounts of SMP molecules remained in the system, which could cause a certain effect on ultrafiltration process. These results were consistent with Babel et al., who found that EOM caused the serious membrane fouling and chemical pretreatment technology could effectively reduce EOM and thus improve membrane flux [4]. However, humic substances could be found little contribution to the fouling. Furthermore, the concentration of SMP was decreased to least after coagulated by Al_{13} , and these results indicated that the Al_{13} had the best ability to improve flux decline.

Table 7

The roughness of the membrane surface.

	Without coagulation (nm)	Al ₁₃ (nm)	Al ₃₀ (nm)	AS (nm)
<i>M. aeruginosa</i>	49.353	71.362	66.581	66.338
<i>Chlorella</i>	62.306	103.701	97.849	75.896
<i>Cyclotella</i>	61.556	110.296	90.502	71.907

Table 8

The average contact angle of the membrane surface with different kinds of algae after coagulation/ultrafiltration process. Where A represent bare membrane, B represent raw solution directly across the membrane, C represent coagulation without sedimentation and D represent coagulation with sedimentation, respectively.

Algae	A	B	C	D	C	D	C	D
			Al ₁₃		Al ₃₀		AS	
<i>M. aeruginosa</i>	67.3°	89.1°	72.5°	75.2°	76.7°	78.4°	83.7°	84.9°
<i>Chlorella</i>	67.3°	86.3°	70.5°	71.7°	72.5°	73.6°	78.6°	79.1°
<i>Cyclotella</i>	67.3°	87.5°	71.3°	71.9°	74.8°	75.6°	85.2°	85.9°

3.4. Scanning electron microscope (SEM) and atomic force microscope (AFM) analysis

SEM was used to reflect the deposition layer on the surface of the membrane. The results were summarized in Fig. 5.

Results (Fig. 5) showed the morphology of the deposited layer on the membrane surface after three kinds of algal cells directly crossing the membrane without being coagulated. Obviously, *Chlorella* cell was larger and more close to the ball, *M. aeruginosa* cell was small and high density, and the shape of *Cyclotella* cell was irregular. Furthermore, the deposited layer of *Chlorella* system has larger gaps than in *M. aeruginosa* system and *Cyclotella* system, and the three kinds of algae cells were uniform distribution in the deposited layer. This phenomenon just confirms our previous explanation in Section 3.3.1. Other SEM images showed the membrane surface in three algae systems after coagulation process by Al₁₃, Al₃₀ and Al₂(SO₄)₃, respectively. It was obvious that all membrane surface has become more rough and nonuniform distribution than raw suspensions. The coagulation process had two important effects in the coagulation-ultrafiltration process. One is the removal of EOM especially SMP from raw suspension, and another effect is the formation of deposited layer on the membrane surface.

The AFM images for different membrane were summarized in Fig. 6, and the roughness of membrane was summarized in Table 7.

The fouled membrane surfaces became more rough than the clean membrane surfaces, and exhibited a surface coverage with a “higher topography”. The AFM images of UF membranes clearly support the notion of surface coverage as a fouling mechanism. AFM analyses elucidate that the membrane roughness of each membrane is very different and may be more influential in membrane fouling by controlling interaction between fouling components and the membrane surface/pores. Compared with SEM, atomic force microscope (AFM) could better reflect the real situation of the overall membrane surface. And the deeper the color represents the deeper the bottom of the sediment layer. Table 6 showed the roughness of the deposited layer formed by Al₁₃ are 71.362 nm (*M. aeruginosa*), 103.701 nm (*Chlorella*) and 110.296 nm (*Cyclotella*), respectively. The roughness of the deposited layer formed by Al₃₀ are 66.581 nm (*M. aeruginosa*), 97.849 nm (*Chlorella*) and 90.502 nm (*Cyclotella*), respectively. The roughness of the deposited layer formed by Al₂(SO₄)₃ are 66.338 nm (*M. aeruginosa*), 75.896 nm (*Chlorella*) and 71.907 nm (*Cyclotella*), respectively. Some previous study had indicated that the greater roughness of the ultrafiltration membrane, the easier to intercept

pollutants [44]. The roughness of the sediment layer formed by Al₁₃ was the largest, which could absorb and intercept more algae organic matter, and then obtained the least EOM reach the surface of the membrane. The coagulation effluent by Al₁₃ had the least content of EOM, meanwhile, its deposited layer could absorb and intercept largest EOM. Thus, Al₁₃ with the best ability to reduce membrane fouling than Al₃₀ and Al₂(SO₄)₃.

3.5. Contact angle analysis

The contact angle could reflect the changes in hydrophobicity of the membrane surface. The larger the contact angle, the higher the hydrophobicity of the membrane.

Table 8 listed the results of contact angle of membrane surface under different conditions. It was showed that the average contact angle of bare membrane was 67.3° and the average contact angle for membrane after being filtrated (three raw suspensions) were 89.1° (*M. Aeruginosa* system), 86.3° (*Chlorella* system) and 87.5° (*Cyclotella* system), respectively. All the average contact angle of membrane surface after coagulation process decreased compared to raw suspensions, thus the membrane flux was improved. Furthermore, the trends of contact angle changes were consistent with the trends of membrane flux decline, and the average contact angle of membrane surface (After the suspension was treated by Al₁₃) was smaller than using Al₃₀ and Al₂(SO₄)₃ as coagulant. NOM has been characterized into three fractionations: (1) Hydrophobic acids including strong (Fulvic and humic) and weak (alkyl mono and dicarboxylic acid); (2) Hydrophilic acids including hydroxy and sugar acids and (3) Strongly hydrophilic species including polysaccharides, alkyl alcohols, amides and bases. The results of composition of EOM (Fig. 1) indicated that the concentration of SMP was largest in all these EOM. These SMP molecules were hydrophilic molecules, so the contact angle decreased when using Al₁₃ or Al₃₀ as coagulant (which could remove larger amount of SMP molecules).

4. Conclusion

In this study, the mechanism of ultrafiltration membrane fouling caused by coagulation/ultrafiltration process between Al-species coagulants and three different kinds of algae were investigated, including floc size, the removal rate of EOM and characteristics of the membrane surface. The main conclusions are as follows:

- (1) The membrane flux was improved obviously after the water samples were treated by the coagulants, and Al_{13} could alleviate the flux decline more significantly.
- (2) Flocs formed by Al_{13} were larger and more resistant to breakage, and Al_{13} could effectively remove EOM from algae-laden water.
- (3) The flux decline in C-UF hybrid process was mainly determined by the content of residual SMP in EOM, and the removal of EOM in coagulation process was mainly aimed at the SMP.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2017.04.004>.

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