

# Study on mitigating membrane fouling based on precursor and flocculant $Al_b$ matching in EC/O-UF system

Fei Su, Ying-Hua Li, Wen-He Deng, Hai-Bo Li, Lei Yang and Tian-yu Chen

## ABSTRACT

One of the effective ways to remove halogenated disinfection by-products (DBPs) from drinking water is the application of ultrafiltration technology. However, membrane fouling is an important factor affecting the service life and treatment effect. In this study, the electrocoagulation/oxidation-ultrafiltration (EC/O-UF) process was used to remove the precursor substance that produced DBPs, i.e. dissolved organic matters (DOMs). Operating parameters were optimized from the matching of different flocculant morphology to low concentration DOM. The degree of membrane fouling was characterized by analyzing DOMs concentration and membrane flux. The results showed that the optimal conditions for the production of  $Al_b$  were: current density  $10 \text{ A/m}^2$ , hydraulic retention time 10 min, and initial pH 5.0–7.0. Under these conditions, the production of flocculant  $Al_b$  could reach 58–61%, 94–97% DOMs were removed by EC/O-UF.

**Key words** | drinking water treatment, electrocoagulation/oxidation-ultrafiltration membrane, electrolytic coagulation, membrane fouling

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## INTRODUCTION

As one promising technology for drinking water treatment, electrocoagulation/oxidation ultra-filtration (EC/O-UF), has gained rapid development in recent years, especially for the removal of disinfection by-product (DBP) precursors (Sun *et al.* 2018). However, its development and application has always been plagued by membrane fouling (Hosseinzadeh *et al.* 2015; Zhao *et al.* 2019). This is mainly due to the fact that in the presence of low concentrations of dissolved organic matters (DOMs), even if the concentration of DBPs meets the effluent requirements, it is separated from the ionized flocculant. Low degree of bonding, residual DOMs and flocculant in the water will still adhere to the membrane surface, reducing membrane permeability and penetration quality (Bagheri & Mirbagheri 2018). The first method is limited by the low binding degree of DOM to flocculant at low DOM concentrations, while the high manufacturing cost of the ceramic membrane limits its use. Many researchers have found that floc morphology and its binding to DOMs (especially small molecule ones) is one of the decisive factors for membrane fouling (Ly & Hur 2018). Therefore, when the concentration of DOMs is low, regulating flocculation morphology is the most suitable means of controlling membrane fouling. In an EC/O-UF system, the metal electrode aluminum is placed in the treated water as an anode through direct current. The

products released by the reaction in the electrochemical reaction include a hydroxyl group, an atomic hydrogen, and  $Al^{2+}$ . Those free radicals have a strong oxidation ability and react easily with contaminants. Furthermore, those high activated products and numerous galvanic cell reactions lead to redox electro-flocculation and consequently remove contaminants (Zhang 2017). It has been reported that polyaluminium chloride (PACl) is superior to conventional Al coagulants (such as  $AlCl_3$  and alum) in DOM removal, with lower alkalinity consumption, lower cost, reduced sludge production, lower temperature dependence, etc. (Sinha *et al.* 2004). During the hydrolysis of Al-based coagulants, such as  $AlCl_3 \cdot 6H_2O$  and polyaluminium chloride (PACl), many hydrolysed species can be generated through *in situ* hydrolysis, including  $Al(OH)_4^-$ ,  $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$  (Keggin- $Al_{13}$ , also called  $Al_{13}$ ) and aluminium hydroxide ( $Al(OH)_3$  (Jin *et al.* 2019).  $Al_{13}$  is a metastable polycation that can be converted to other Al species through complex reactions (Wang *et al.* 2019). The core of  $Al_{13}$  is tetrahedral coordinated  $AlO_4$ , and the periphery is octahedral coordinated  $12Al(OH)_2$ . In addition to the property of having a high positive charge and a strong binding ability to aggregates, it is temporarily difficult to hydrolyze before being adsorbed onto the surface of the particles. These special properties contribute to the superior

performance of PAC1 in blood clotting. Therefore, they claim that high levels of  $Al_{13}$  are the primary targets of the PAC1 research and production industry. However, there are also some contradictory views. Previous studies have found a negative correlation between DOM coagulant removal and  $Al_{13}$  content (Hu *et al.* 2016). Hu *et al.* (2016) suggested that the  $Al_{13}$  polymer is not an important cation in the removal of humic substances. Studies have also shown PAC1 gives no significant improvement in the removal of DOM compared to alum (Hu *et al.* 2016). Nowadays, whether the  $Al_{13}$  content is positively related to the coagulation effect and electro-flocculation is still a problem worth exploring.

The various forms of aluminum in the hydrolyzed aluminum solution can be divided into three types by the difference in the hydrolyzed complexation of Ferron and the aluminum:  $Al_a$  (monomer form),  $Al_b$  (medium polymerization form) and  $Al_c$  (hydrolyzed polymerized macromolecule).  $Al_c$ , in the form of an alumina sol or gel, does not react with the Ferron reagent or reacts very slowly. Many investigations (Jegatheesan *et al.* 2016; Lee & Gagnon 2016) proved that the  $Al_b$  species could be regarded as the  $Al_{13}$  species, being the main form of electricity neutralization. In the rapid coagulation process of PAC1, the effective collision probability is greatly improved due to the significant neutralization of the surface charge of the particles. The higher the content of  $Al_b$  in PAC1, the stronger the electric neutralization ability and the collision efficiency between particles. Unfortunately, the traditional EC/O ionized aluminum forms are mainly  $Al_a$  monomer and dimer, and few  $Al_b$  polymers exist (Li *et al.* 2016a, 2016b). The purpose of this study is to optimize the electrocoagulation oxidation process, aiming to produce more  $Al_b$  instead of  $Al_a$  and  $Al_c$ . Based on the in-situ morphology of flocculants, their match with DOMs and the removal of DOMs were evaluated. Furthermore, the DOMs of the membrane surface and membrane flux characteristics are comprehensively studied. The results will be helpful to understanding the impact of EC/O-UF floc morphology on fouling mechanism and provide a reliable and practical strategy for sustainable membrane permeability maintenance.

## MATERIALS AND METHODS

### Experimental design

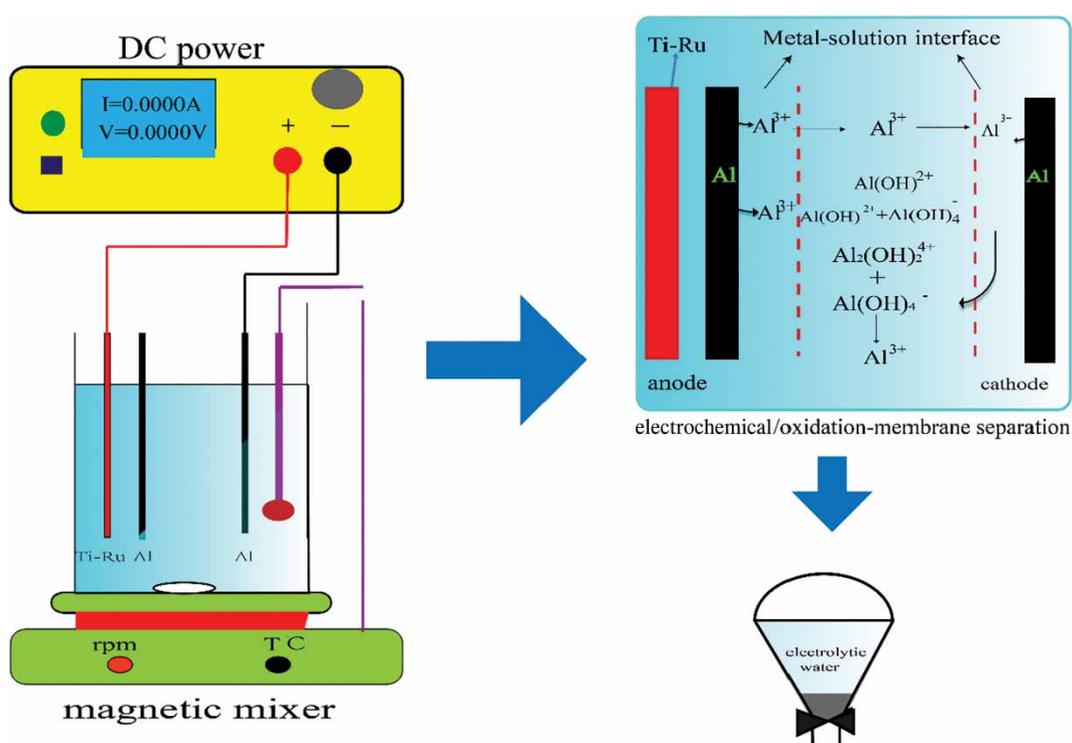
The EC/O-UF reaction device is shown in Figure 1, a 1 L glass was adopted as the electrolytic cell, and the intelligent constant temperature magnetic stirrer (85-2A) stirred the electrolyte and regulated the temperature. Electrolytic

DC power supply (DH1765-1, Beijing, Dahua) was used for electrolysis. The anode was a Ti-Ru electrode and the cathode was an Al electrode that constitutes EO-UF. An additional Al electrode was added between the anode and cathode plates as an induced EC electrode to construct an EC/O-UF, and a membrane module was placed between the electrodes. The 1 L electrolyte was added to the beaker. The magnetic stirrer was turned on and the rotation speed was adjusted to 300 rpm/min, and the current density was adjusted to 2.0, 10.0, 20.0, and 30.0 A/m<sup>2</sup>, respectively. After the start of electrolysis, samples were taken at different time points and the aluminum morphology was immediately analyzed by Ferron colorimetry. After the end of the electrolysis, the total aluminum concentration was determined by inductively coupled plasma-atomic emission spectroscopy.

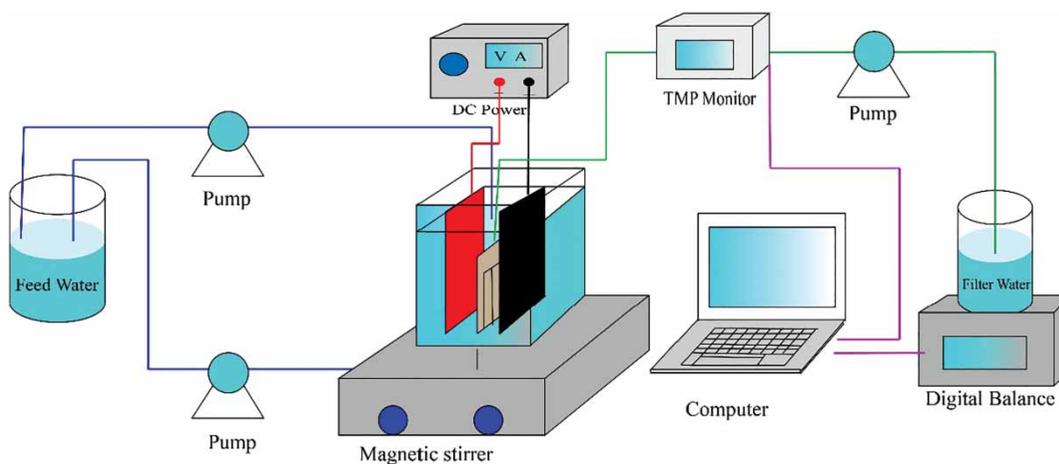
Membrane fouling is an important limiting factor in the development of membrane technology. DOM is the main substance causing membrane fouling. In the third part of this study, the UF membrane was cleaned, and the rinsing liquid was collected for UV-visible absorbance characterization. The mechanism of UM membrane fouling caused by DOM was also discussed. The UF membrane was washed with 20 L pure water, 0.1% hydrochloric acid solution and 0.1% sodium hydroxide solution, respectively. The pure water flow rate was 2 L/min, the cleaning time was 10 min; the flushing rate of the hydrochloric acid solution and the sodium hydroxide solution was 1 L/min with a cleaning time of 20 min.

### EC/O-UF experimental design

The EC/O-UF reaction device is shown in Figure 2. The 1.4 L of synthetic feed water was used in each experiment and was circulated into the reactor tank by two peristaltic pumps (36 mL/min) to create a cross-flow and maintain a constant immersion electrode area for the electrochemical process. The effective volume of the reactor tank was 1,260 mL (14 cm × 6 cm × 15 cm). The effective area of each electrode was 95 cm<sup>2</sup>. Two magnetic stirrers (300 r/min) were applied to keep the feed water and the solution in the reactor tank uniform. A digital balance (AR2202CN, Ahaus, Changzhou, China) connected to the computer was used to collect the quality data of the permeate water as a function of the operating time. The transmembrane pressure was maintained at 30 kPa by a vacuum pump. The top of the membrane module had a small collection tube consisting of ten hollow fibers with an effective membrane area of 24 cm<sup>2</sup>. The average MW cutoff value of hollow



**Figure 1** | Schematic diagram of the electrocoagulation equipment.



**Figure 2** | Schematic diagram of the EC/O-UF system.

fiber membranes (PVDF, Tianjin MOTIMO Membrane Technology Co., Ltd, China) was 100 kDa.

### Raw water

Simulated experimental water: an appropriate amount of humic acid (HA) and fulvic acid (FA) was mixed into deionized water. The pH was adjusted to 12 and the mixture was slowly dissolved on a magnetic stirrer for 24 h, then

filtered with a 0.45  $\mu\text{m}$  filter. The appropriate amount of kaolin was weighed and adjusted with a small amount of deionized water; the pH value was adjusted to 8, and it was stirred for 0.5 h under high shear conditions, then allowed to stand for 24 h. The kaolin reserve liquid was prepared by siphoning the upper part thereof (5 g/L). The HA and FA mixture and kaolin stock solution were added to deionized water to maintain the concentration of the HA and FA mixture and kaolin at 10 and 50 mg/L,

respectively, and the pH was adjusted by 0.1 mol/L NaOH and HCl. 0.5 mmol/L NaHCO<sub>3</sub> was added as a buffer material, and the conductivity of the solution was adjusted with NaCl.

## ANALYTICAL METHODS

### Aluminum characterization

In this experiment, the morphology of aluminum was characterized by Al-Ferron colorimetry. The absorbance was measured by ultraviolet/visible spectrophotometer (HACH, DR6000, Loveland, USA) at a wavelength ( $\lambda$ ) of 370 nm for 120 min. According to the principle of the Al-Ferron method, the relative contents of Al<sub>a</sub>, Al<sub>b</sub>, Al<sub>c</sub>, namely monomers, polymers and Al(OH)<sub>3</sub> colloids (Hu et al. 2012) could be determined.

### Characterization of dissolved organic matter

The DOM was characterized by UV-visible absorbance (Ly & Hur 2018). The organic matter in the effluent after filtration with a 0.45  $\mu$ m microporous membrane was considered to be a dissolved organic matter, and a total organic carbon (TOC) instrument (Multi, N/C3100, Jena, Germany) was used to determine the DOC content (approximately equal to DOM). Four UV-visible absorbances (SUVA<sub>254</sub>, E<sub>253</sub>/E<sub>203</sub>, E<sub>465</sub>/E<sub>665</sub> and E<sub>300</sub>/E<sub>400</sub>) were selected for this experiment.

Among them, SUVA<sub>254</sub>; that is, the UV absorbance of the solution at 254 nm, reflects the level of unsaturated content in the solution to a certain extent, and its ratio with DOC can reflect the unsaturated double bond content and aromaticity of the organic matter. The larger the value of SUVA<sub>254</sub>, the higher the aromatic content of the organic compound in the solution and the higher the aromaticity. E<sub>253</sub>/E<sub>203</sub>, the ratio of the UV absorbance of the solution at 253 nm to that at 203 nm (UV<sub>253</sub>/UV<sub>203</sub>), characterizes the degree of substitution of the aromatic ring and the formation of disinfection by-products, trihalomethanes (THMs). The larger the E<sub>253</sub>/E<sub>203</sub> ratio, the easier the substitution of the aromatic ring is to be replaced and the more likely it is to generate THMs. The ratio of the UV absorbance of the solution at 465 nm to that at 665 nm (UV<sub>465</sub>/UV<sub>665</sub>) characterizes the molecular weight of the organic matter in the solution and is inversely proportional to the molecular weight of the organic matter in the water. That is to say, the smaller the E<sub>465</sub>/E<sub>665</sub> value, the larger the proportion of organic matter

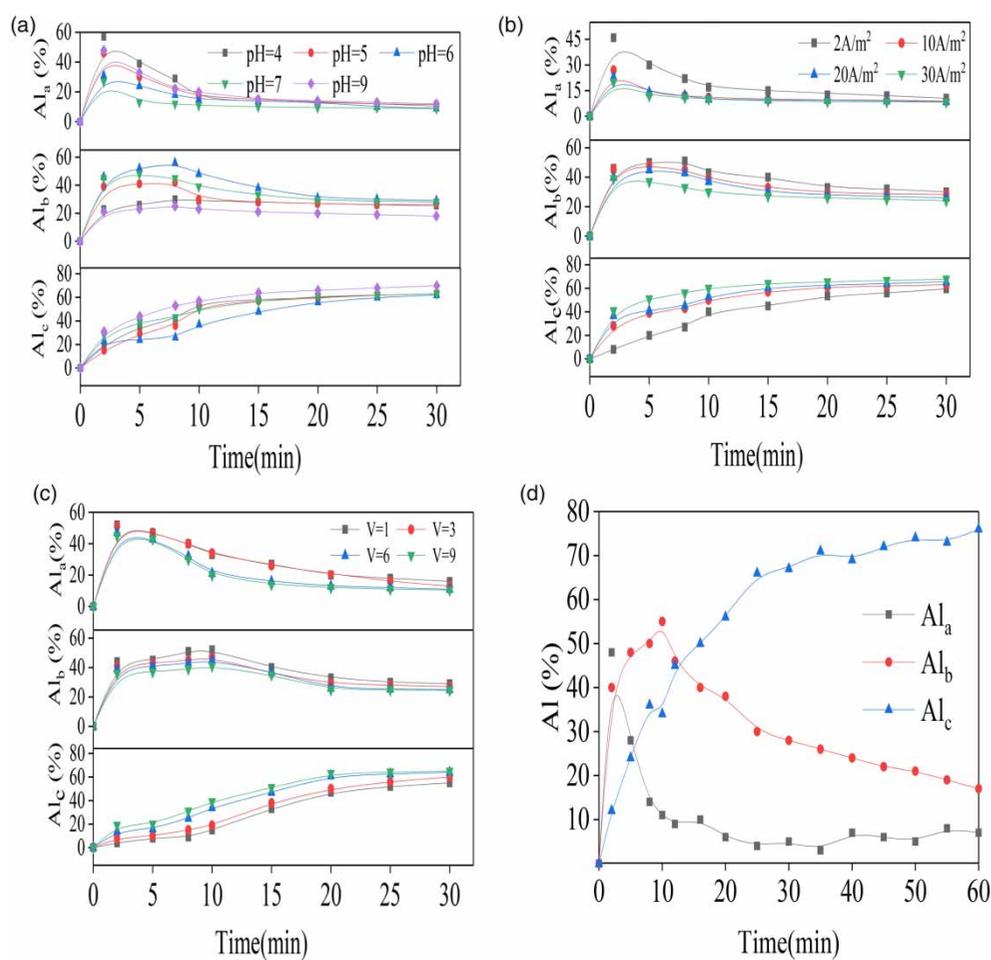
having a large molecular weight in the solution, and the higher the degree of polymerization of the molecular structure. E<sub>300</sub>/E<sub>400</sub>, the ratio of the UV absorbance of the solution at 300 nm to that at 400 nm (UV<sub>300</sub>/UV<sub>400</sub>), reflects the degree of humification of organic matter in solution and the degree of polymerization of organic matter. The larger the value of E<sub>300</sub>/E<sub>400</sub>, the lower the degree of humification of the organic matter in the solution and the lower the degree of polymerization of the organic matter. Statistical analyses were carried out with Origin 8.0 (Origin Lab).

## RESULTS AND DISCUSSION

### Optimization of Al<sub>13</sub> in electrolysis process

The increase in absorbance was measured at a wavelength  $\lambda$  of 370 nm for 120 min. According to the principle of the Al-Ferron method, it is possible to determine the relative availability of monomer, polymer and polymer or Al(OH)<sub>3</sub> colloid of Al<sub>a</sub>, Al<sub>b</sub> and Al<sub>c</sub>. The best Al<sub>13</sub> polymer obtained during electrocoagulation is shown in Figure 3.

This experiment investigated the effects of different initial pH (2, 4, 7, and 9) on the distribution of Al in the electrocoagulation/oxidation process. The pH value was positively correlated with the ability of Al<sup>3+</sup> to hydrolyze. At pH<sub>0</sub> = 4, the relative content of Al<sub>a</sub> was the largest and the relative content of Al<sub>c</sub> was the least. At 2 min of electrolysis, the relative content of Al<sub>a</sub> was about 55–57%, and the relative content of Al<sub>c</sub> was about 20–21%. At pH<sub>0</sub> = 6, the relative content of Al<sub>b</sub> was the highest. The content of Al<sub>b</sub> in electrolysis for 2 min reached 49–52%, then the content of Al<sub>b</sub> decreased gradually. The relative content of Al<sub>b</sub> in electrolysis for 30 min accounted for 15–17% of total Al, which was consistent with the distribution of aluminum in chemical coagulation. At high pH, more hydroxyl groups were involved in the hydrolysis-complexation-polymerization-peptization-precipitation in this process. Therefore, at low pH, Al<sup>3+</sup> is mainly present in the form of oligomers after hydrolysis, while at high pH, the polymer and Al(OH)<sub>3</sub> become the dominant aluminum forms. Compared to chemical coagulation, electro-flocculation requires a relatively low pH in the electro-flocculation reactor. As the aluminum hydroxide floc acts as a metal ion to adsorb or trap DOM, the DOM was eliminated from the solution. At the same time, when an aluminum electrode is used, the hydroxide ions generated at the cathode increase the overall pH of the solution, thereby reducing the use of the alkaline solution of the conditioning solution.



**Figure 3** | Characterization of Al species in EC/O process by Ferron.

The current density in the electro-flocculation oxidation process determines the elution amount of Al ions on the Al electrode. The selection of the optimal current density is of great significance when using electrocoagulation and oxidation to purify drinking water. According to the reports by Emamjomeha & Sivakumar (2011), we chose conventional current densities of 2, 10, 20, and 30  $A/m^2$  in the experiment. Figure 3(b) examined the effect of different initial current densities on the distribution of Al in the electrocoagulation/oxidation process. At a  $pH_0$  of 6, a current density of 10  $A/m^2$  could produce a maximum of 58–61% of  $Al_b$ ; however, at the same initial pH, a current density of 30  $A/m^2$  produced a maximum  $Al_b$  content of 50%. The yield of  $Al_b$  in the electro-flocculation process decreased as the current density increased. The operation of the electrolytic cell was most advantageous when the current density was high, since the volume of the electrolytic cell and the working surface of the electrode were fully utilized. However, as the current density increased, the polarization

phenomenon of the electrode and the passivation increased, which led to an increase in the required voltage and a loss of the secondary process power, and the current efficiency dropped sharply. Previous studies (Bi *et al.* 2001) have also shown that the amount of  $Al_{13}$  formed decreased with increasing alkali injection rate, which may be more conducive to the formation of colloidal polymers. In addition, previous studies on the electrochemical preparation of poly-aluminum chloride (Feng *et al.* 2012) presented that high concentrations of aluminum produced relatively little  $Al_{13}$  because high concentrations of aluminum produced more  $Al(OH)^{4-}$ , which was favorable for the direct formation of  $Al(OH)_3$  solids. The flocculation of the floc has a larger particle size, which will not only cause contamination inside the membrane, but will also form a loose filter cake layer on the surface of the membrane to prevent some flocs with smaller particle size from entering the membrane pore to cause membrane fouling. Reducing membrane fouling maintains good membrane flux. From this perspective,

electro-flocculation has advantages over chemical coagulation in mitigating membrane fouling.

The cell voltage had a major influence on the distribution of aluminum in the process of electro-flocculation. The results in Figure 3(c) show that although the content of  $Al_a$  and  $Al_b$  decreased with the increase in the plate voltage, the content of  $Al_c$  increased with the increase of the plate voltage. When the cell voltage was 1 V, the relative content of  $Al_b$  accounted for the highest total aluminum content. When the electrolysis was 2 min, the relative content of  $Al_b$  accounted for 44–46% of the total aluminum content. When the electrolysis was 15 min, the relative content of  $Al_b$  accounted for 52–54% of the total aluminum content. After 15 minutes of electrolysis, the  $Al_b$  content gradually decreased with the electrolysis. The relative content of  $Al_b$  in electrolysis for 30 min accounted for 28–31% of the total Al. At the cell voltages 1, 3, 6, and 9 V, the time at which  $Al_b$  reached its maximum was 15 min. The cell voltage was an important factor in controlling the rate of electrochemical reaction, and it also determined the amount of flocculation in the electro-flocculation process. Similar to the current density, the rate of electrolyzed water was positively correlated with the cell voltage. When a larger voltage was selected, the pH of the solution was also larger. As the pH of the solution increased, the amount of charge of the formed colloidal particles decreased, and the repulsive force between the  $Al^{3+}$  units was weakened, so that the colloidal particles were more likely to lose stability and aggregate into a large polymer or  $Al(OH)_3$  precipitate.

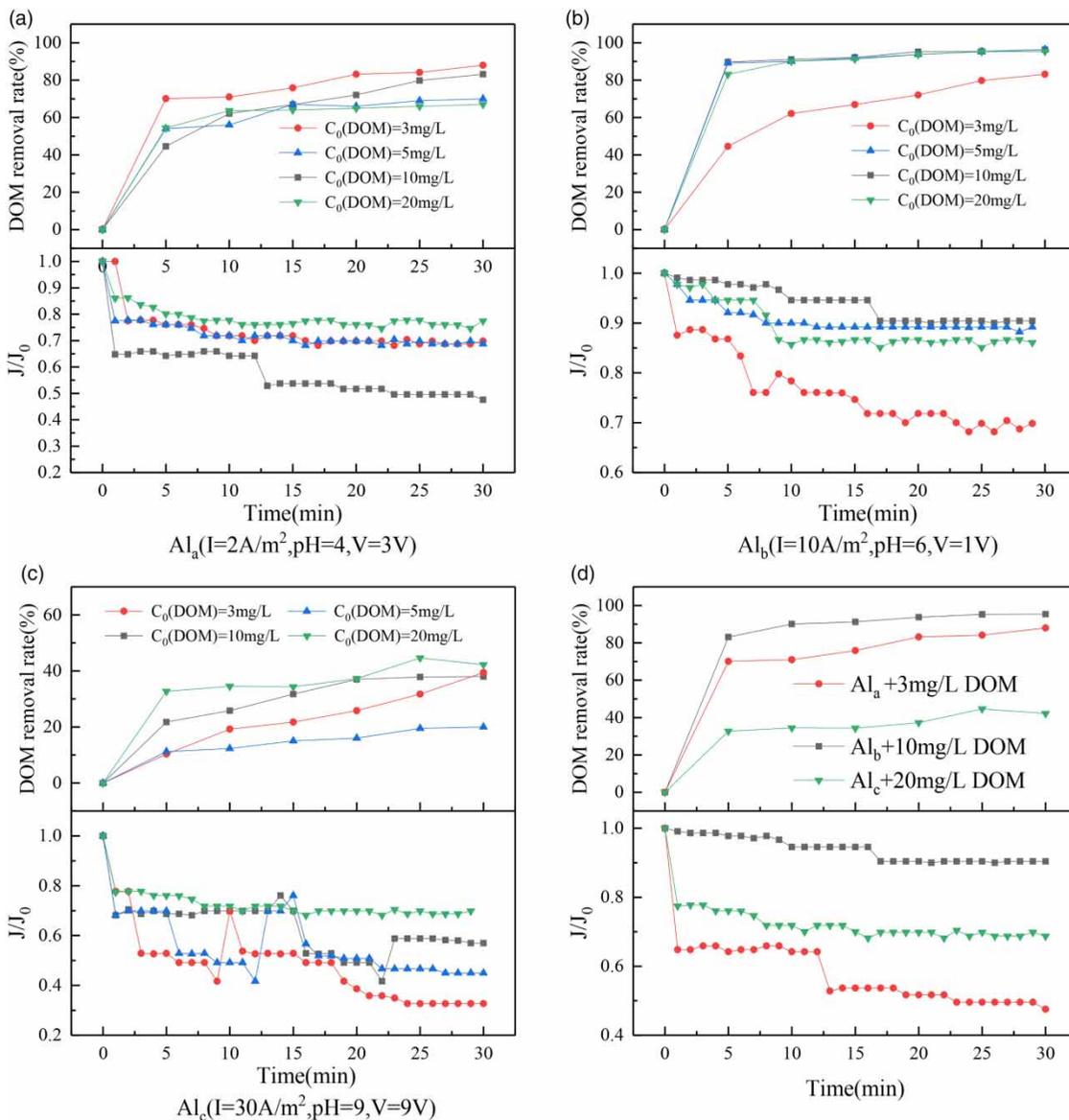
The optimum conditions for generating  $Al_a$  are: current density 2 A/m<sup>2</sup>, hydraulic retention time 10 min, initial pH 4, and tank voltage 3 V; the optimal conditions for generating  $Al_b$  are: current density 10 A/m<sup>2</sup>, hydraulic retention time 10 min, initial pH 6, and tank voltage 1 V. Instead, the optimum conditions for generating  $Al_c$  are: current density 30 A/m<sup>2</sup>, hydraulic retention time 10 min, initial pH 9, and tank voltage 9 V. It was obvious from Figure 3(d) that under the optimal conditions of generating  $Al_b$ , with the progress of electrolysis,  $Al_a$  (monomeric dominant form) was gradually transformed into  $Al_b$  (neutral dominant form) and then converted into  $Al_c$ .  $Al_a$  was rapidly formed and became dominant in the period from the start of electrolysis to 2 min. The relative content of  $Al_a$  decreased dramatically, and the content of  $Al_b$  gradually increased after 2 min. The relative content of  $Al_b$  reached a maximum of about 58–61% after electrolysis for about 10 minutes. The relative content of  $Al_b$  gradually decreased after 10 min. The relative changes in the relative contents of  $Al_a$  and  $Al_b$  were

consistent throughout the process. The relative content of  $Al_c$  increased as the electrolysis continued. Both  $Al_a$  and  $Al_b$  are intermediates in the  $Al^{3+}$  hydrolysis process (Hu *et al.* 2016), which are ultimately converted to high polymers and  $Al(OH)(s)$  undergoes further hydrolysis polymerization, and this was similar to the results acquired by Feng *et al.* (2015). The effect of different Al forms on DOM removal in the two processes was compared and analyzed. It is generally considered that  $Al_b$  is the most cohesive part in chemical coagulation, which is the same as the electro-flocculation in this study. Therefore, it can be concluded that chemical coagulation and electro-flocculation have no significant difference in DOM removal effects in different Al species, and both show that  $Al_b$  is the optimal form for DOM removal.

### The matching of flocculant $Al_b$ and DOM

Under the optimal conditions of  $Al_a$ ,  $Al_b$  and  $Al_c$ , different Al forms ( $Al_a$ ,  $Al_b$ ,  $Al_c$ ) and different DOM concentrations (3, 5, 10, 20 mg/L) were used to investigate the DOM removal rate and membrane flux  $J/J_0$ . The results are shown in Figure 4.

As can be seen from the figure, the optimal matching concentrations of  $Al_a$ ,  $Al_b$ ,  $Al_c$  and DOM are 3, 10, 20 mg/L, respectively. When  $Al_a$  was matched with the 3 mg/L DOM, the removal rate of DOM could reach 88% after electrolysis for 20 min, and  $J/J_0$  could be stabilized at about 0.66–0.68; when  $Al_b$  was matched with 10 mg/L DOM, the removal rate of DOM could reach 94–97% after 20 min electrolysis. Furthermore, under this condition, the membrane was less polluted with  $J/J_0$  stabilized at 0.91–0.94 after 20 minutes of electrolysis. When  $Al_c$  was matched with 20 mg/L DOM, the removal rate of DOM after electrolysis for 20 min was 40–42%, and  $J/J_0$  can be stabilized at about 0.66–0.68. Since the particle size of the contaminant was relatively small, not only was it easily adsorbed in the pores of the membrane, but also a relatively dense filter cake layer was easily deposited on the surface of the membrane, so the membrane flux was attenuated over time. At lower or higher DOM concentrations, the removal rate and membrane fouling reduction were difficult to achieve the desired effect, because the flocculant was difficult to match with DOM at lower or higher concentrations. It can be seen from Figure 4(d) that in the matching of three different aluminum forms with 10 mg/L DOM,  $Al_b$  had the optimum DOM removal effect. Moreover  $J/J_0$  was highest, indicating that the water flux was large. The more aluminum ions were electrolyzed as the electrolysis progressed, the larger the floc size formed by the aluminum hydrolysate, and the contaminant formed a loose filter cake layer on



**Figure 4** | Effect of different Al morphology and DOM concentration ratio on DOM removal rate and  $J/J_0$ .

the surface of the membrane, slowing down the membrane fouling and maintaining a stable water flux (Zhao *et al.* 2017). Chemical coagulation could reduce DOM to an acceptable level, but most were quite expensive and very few were in common practice. Electrochemical technology alone or in combination with other methods offers an ideal tool for addressing the pulp and paper mill effluent problem because the main compound used is electron, which was clean and usually required no additional reagent (Orori *et al.* 2010).

As can be seen from Figure 5, comparing the membrane surface composition of the original membrane (a),  $Al_a + 3 \text{ mg/L}$  (b),  $Al_b + 10 \text{ mg/L}$  (c) and  $Al_c + 20 \text{ mg/L}$  (d), it can be seen that the surface morphology of  $Al_b + 10 \text{ mg/L}$  (c)

treatment and the filter cake content (carbon, oxygen, fluorine, aluminum and silicon) were not much different from those of the original film (a). Figure 5(b) and (c) show that the cake layer of the membrane contained a large amount of aluminum, indicating that it was formed by a mixture of aluminum, HA, FA, and Kaolin, further confirming the above conclusion. And this was similar to the results acquired by Zhao *et al.* (2016). The surface morphology of the ultrafiltration membrane under four conditions was observed by scanning electron microscopy. Compared with  $Al_b$ , when  $Al_a$  and  $Al_b$  were matched with DOM, the surface of the cake layer became more coarsely packed and thicker, and membrane contamination deteriorated. Aluminum ions combined with DOM to

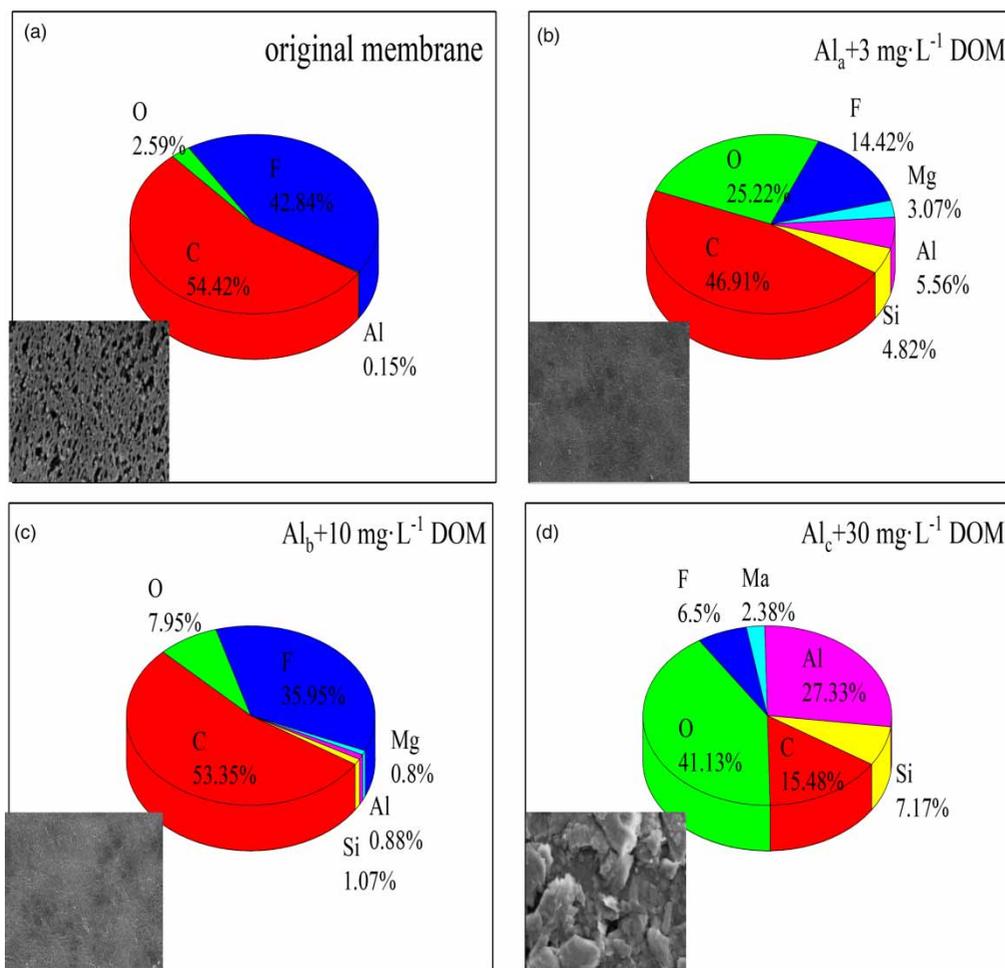


Figure 5 | Different Al morphology and surface DOM composition.

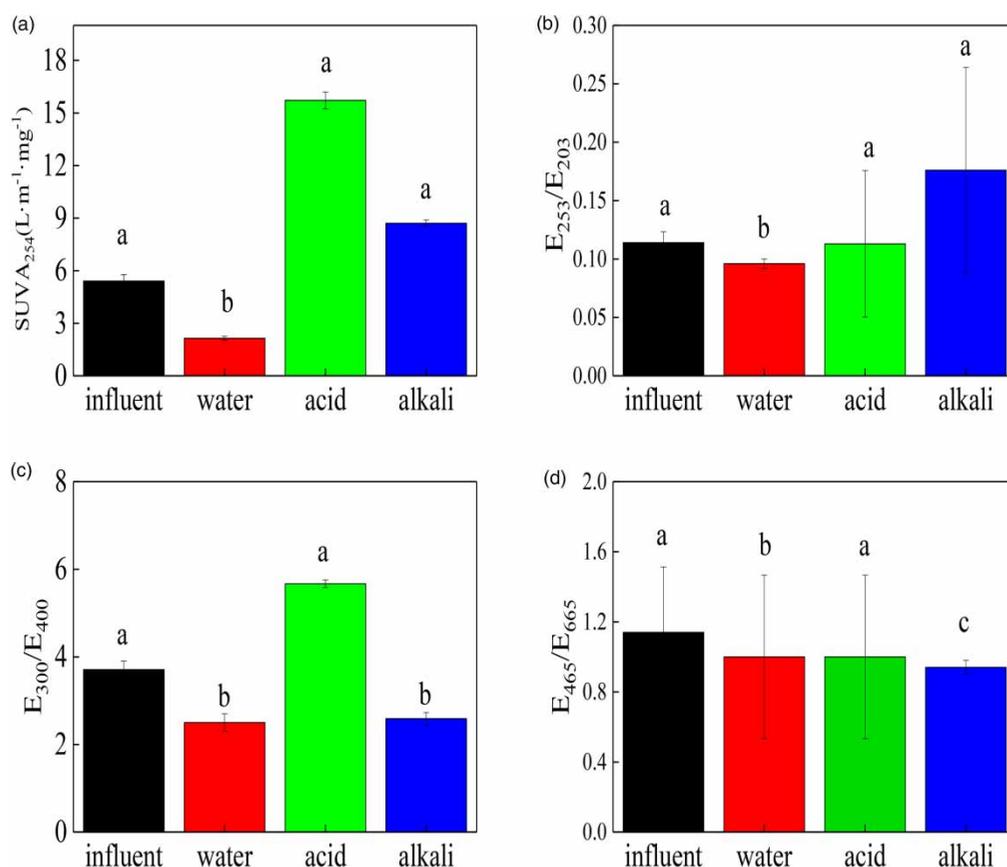
form a gel precipitate, which may be adsorbed in the pores of the membrane, clogging or depositing on the membrane surface. Considering the effect of DOM removal and the degree of membrane fouling,  $Al_b$  flocculant matched with 10 mg/L DOM was suggested as the optimal matching condition. Compared with chemical coagulation technology, electrochemical technology as an efficient water treatment technology could not only reduce membrane fouling, but also increase membrane flux, with high removal efficiency, simple operation, low sludge production, avoidance of chemicals, easily achievable automation and equipment control and other advantages.

### Characterization of dissolved organic matter

The UF film after washing with water, acid and alkali solution was characterized by UV-visible absorbance. The water samples were filtered through a 0.45  $\mu\text{m}$  filter before measurement. The variation of the four UV-visible

absorbance values of DOM in each cleaning solution of the UF membrane is presented in Figure 6.

Correlation analysis for Figure 6(a) and 6(b) suggested that the  $SUVA_{254}$  and  $E_{253}/E_{203}$  values in the influent, acid and alkali washing had significant correlation, but water washing had no significant difference. After cleaning, the  $SUVA_{254}$  values in the water, acid and alkali washing solutions were  $(2.14 \pm 0.11 \text{ L/m}\cdot\text{mg})$ ,  $(15.72 \pm 0.48 \text{ L/m}\cdot\text{mg})$ ,  $(8.71 \pm 0.19 \text{ L/m}\cdot\text{mg})$ , respectively (Figure 6(a)). The  $SUVA_{254}$  value was  $(5.41 \pm 0.36 \text{ L/m}\cdot\text{mg})$  in the UF influent. It can be concluded that the DOM containing the unsaturated double bond was lower in water, indicating that this part of DOM was not easily removed by water washing. Instead, the DOM of the cleaning solution was much higher than that in the influent, revealing that the DOM with unsaturated double bonds and aromaticity will accumulate on the membrane surface.  $E_{253}/E_{203}$  values in the influent, effluent after water washing, acid washing



**Figure 6** | Changes in UV-Vis absorbance in cleaning solutions. (Significant differences ( $P = 0.05$ ) between means are indicated by letters above the histogram bars. Where the letters are the same, there is no significant difference between different treatments.)

and alkali washing were  $(0.114 \pm 0.009)$ ,  $(0.096 \pm 0.004)$ ,  $(0.113 \pm 0.63)$ ,  $(0.176 \pm 0.088)$ , respectively. Alkali washing removed most DOM produced. Correlation analysis for Figure 6(c) and 6(d) demonstrated that the  $E_{300}/E_{400}$  and  $E_{465}/E_{665}$  values in the influent and acid washing had significant correlation.  $E_{300}/E_{400}$  in the influent, water cleaning solution, acid cleaning solution and alkali cleaning solution were  $(3.71 \pm 0.1)$ ,  $(2.5 \pm 0.2)$ ,  $(5.67 \pm 0.09)$ ,  $(2.59 \pm 0.14)$ , respectively. The degree of humification after washing with water and alkali was higher than that of the influent, while that of washing with acid was lower. The possible reasons may be that the UF membranes had a low retention of humus and less deposition of humus on the membrane surface. The essence of electro-flocculation and chemical coagulation was the removal of colloids or suspensions in water by the coagulation of metal ionized aluminum or extremely hydrolyzed iron polymers. Electro-flocculation could effectively remove the color and odor produced by dissolved organic matter in water. When chemical coagulation was used, it required a large amount of chemicals, and the treatment effect was poor. Generally speaking, the DOM

on the UF membrane surface contained some humus. The values of  $E_{465}/E_{665}$  after washing with water, acid and alkali were  $(1 \pm 0.47)$ ,  $(1 \pm 0.47)$ , and  $(0.94 \pm 0.04)$ , respectively, which were lower than that in the influent  $(1.14 \pm 0.37)$ . The DOM content of large molecular weight in the solution after washing was higher than that of the influent. The cleaning solution showed a higher  $SUVA_{254}$  value, indicating that the unsaturated double bond and the aromatic DOM were the main substances causing UF film contamination, and this part of the DOM was easily soluble in acid.

## CONCLUSIONS

DOMs are the main sources of membrane fouling in the integration process of EC/O-UF. The EC/O-UF operating parameters, including current density, hydraulic retention time and initial pH were optimized based on the production of flocculant  $Al_b$  and its matching with DOMs. Under the optimum conditions, the ionized  $Al_b$  could reach 58–61% and 94–97% of the DOM was removed. The DOMs with

unsaturated double bond and aromatic were the main substances causing UF film contamination, and this part of DOMs can be easily removed by acid. Because the UF membrane materials used in this study were polyvinylidene fluoride (PVDF), it was recommended that further study be carried out on the membrane fouling behavior of different membrane materials. It was also recommended that a study be carried out on the changes of pollutants in the membrane pool during long-term operation to make this method more effective and feasible.

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