

# The impact of anionic polyacrylamide (APAM) on ultrafiltration efficiency in flocculation-ultrafiltration process

Ruijun Zhang, Shengnan Yuan, Wenxin Shi, Cong Ma, Zhiqiang Zhang, Xian Bao, Bing Zhang and Yan Luo

## ABSTRACT

With the purpose of improving the ultrafiltration (UF) efficiency, anionic polyacrylamide (APAM) has been used as a coagulant aid in the flocculation-UF process. In this study, the impact of APAM on UF efficiency has been investigated with regard to membrane fouling, membrane cleaning and effluent quality. The results indicated that the optimal dosage of APAM had positive impacts on membrane fouling control, membrane cleaning and effluent quality. According to the flux decline curve, scanning electron microscopy and contact angle characterization, the optimal dosage of APAM was determined to be 0.1 mg/L coupled with 2 mg/L (as Al<sup>3+</sup>) poly-aluminium chloride. Under this optimal condition, membrane fouling can be mitigated because of the formation of a porous and hydrophilic fouling layer. APAM in the fouling layer can improve the chemical cleaning efficiency of 0.5% NaOH due to the disintegration of the fouling layer when APAM is dissolved under strong alkaline conditions. Furthermore, with the addition of APAM in the flocculation-UF process, more active adsorption sites can be formed in the flocs as well as the membrane fouling layer, thus more antipyrine molecules in the raw water can be adsorbed and removed in the flocculation-UF process.

**Key words** | anionic polyacrylamide, flocculation, membrane cleaning, membrane fouling, pharmaceuticals, UF

**Ruijun Zhang**  
**Wenxin Shi** (corresponding author)  
**Zhiqiang Zhang**  
**Xian Bao**  
**Bing Zhang**  
**Yan Luo**  
 State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China  
 E-mail: [swx@hit.edu.cn](mailto:swx@hit.edu.cn)

**Shengnan Yuan**  
 North China Municipal Engineering Design & Research Institute Co., Ltd, Tianjin 300000, China

**Cong Ma**  
 Department of Chemical and Biomolecular Engineering, University of Connecticut, 191 Auditorium Rd. Unit 3222, Storrs, CT 06269-3222, USA

## INTRODUCTION

With the cost reduction and technique maturation of the ultrafiltration (UF) membrane, UF technology has been increasingly applied in the renovation and new construction of water supply plants. In order to intensify the contaminant removal ability and relieve membrane fouling, various pre-treatment methods, such as coagulation, adsorption and pre-oxidation, have been coupled with the UF process (Huang *et al.* 2009). Depending on its effectiveness, low cost and easy operation, coagulation with inorganic coagulants has become the most widely used membrane pre-treatment method (Huang *et al.* 2009; Lai *et al.* 2015), for which the technological process mainly includes flocculation-UF, and coagulation-sedimentation-UF, coagulation-sedimentation-sand filtration-UF. Compared with other technological processes, the flocculation-UF process has been proved to have some advantages, such as a shorter flow process, smaller floor area, and lower investment (Vickers *et al.* 1995; Liang *et al.* 2008; Yu *et al.* 2014).

In traditional drinking water treatment processes, polyacrylamide (PAM), as a kind of organic polymer coagulant-aid, is always used in the treatment of low-temperature and low-turbidity water, as well as high-turbidity water. According to its charged situation, PAM can be divided into three kinds: cationic polyacrylamide (CPAM), non-ionic polyacrylamide (NPAM) and anionic polyacrylamide (APAM). The coagulation efficiency of PAM is much better than inorganic coagulants. A small dosage can effectively increase the floc size and density, thus improving the subsidence effect (Jarvis *et al.* 2008).

Based on the above fact, we naturally considered what impact would be generated if PAM was used in the flocculation-UF process. A small number of research results involving this question can be found in the literature. The research of Huang *et al.* suggests that trace amounts of CPAM in addition to PACl coagulation can effectively increase

the permeate flux when microfiltration is coupled with pre-treatment by coagulation (Huang *et al.* 2004). Conversely, Wang *et al.* found that CPAM would aggravate membrane fouling because of the electrostatic attraction between the positively charged polymer and the negatively charged membrane surface, but the fouling layer on membrane surface could improve dissolved organic matter rejection (Wang *et al.* 2011, 2013). In order to avoid the electrostatic attraction between CPAM and the membrane, Yu *et al.* took NPAM as a coagulant aid for alum before a UF membrane and examined its potential benefit and impact on membrane fouling. They found that the addition of NPAM cannot improve the removal of natural organic matter, but the membrane fouling can be obviously mitigated at a NPAM dosage of 0.2 mg/L (Yu *et al.* 2013). However, a higher NPAM dosage of 1 mg/L would aggravate membrane fouling. Yao *et al.* studied the influence on UF membrane fouling when adding NPAM in the floc breakage process. According to their research, broken flocs re-formed with additional NPAM have a larger size and lower effective density, which is available to form a loose and porous cake layer on the membrane surface (Yao *et al.* 2015). In this way, reversible fouling and irreversible fouling can be simultaneously decreased. However, their NPAM dosage is higher, reaching 5 mg/L.

In general, the addition of PAM in the flocculation-UF process will firstly lead to a change in the floc structure and floc physicochemical properties. Then, the changed flocs will form a fouling layer with a specific structure and function on the UF membrane surface. This formed fouling layer will not only affect the membrane fouling, but also influence the membrane cleaning and contaminant removal. Up to now, the impact of CPAM and NPAM on membrane fouling in the flocculation-UF process has been relatively systematically studied. However, APAM has not been studied. As a kind of hydrophilic linear polymer, there are many carboxyl groups in the APAM molecule. In aqueous solution, the carboxyl groups make APAM negatively charged and it is easy to form a hydrogen bond with other polar groups. Therefore, compared with CPAM and NPAM, APAM is expected to mitigate membrane fouling due to the electrostatic repulsion between the negatively charged polymer and the negatively charged membrane surface. Moreover, other hydrophilic contaminants in water are expected to integrate with APAM based on hydrogen interaction, and this action is beneficial to improving the hydrophilic contaminants removal.

In this study, the impact of APAM on UF efficiency in the flocculation-UF process was systematically summarized. APAM was used as a coagulant-aid with PACl coagulation. The optimal dosage of APAM was obtained according to the

flux decline curve. Scanning electron microscopy (SEM) and a contact angle goniometer were employed to support the conclusions. Membrane cleaning with ultrapure water or 0.5% NaOH was conducted to verify whether APAM would affect the membrane cleaning feasibility. The occurrence of pharmaceutical and personal care products (PPCPs) in natural water is an emerging environmental problem. Antipyrine (ANT), a commonly used analgesic, is one of the mostly commonly identified PPCPs. The ecotoxicity of ANT is still largely unknown, but it has high environmental persistence (Tan *et al.* 2013). Here, the hydrophilic ANT was further used to study the impact of APAM on UF effluent quality. The present work can be a theoretical guidance for the application of APAM as a coagulant-aid in the flocculation-UF process.

## MATERIALS AND METHODS

### Synthetic raw water and coagulants

In order to ensure sample reproducibility and consistency, synthetic raw water was used in our study. Kaolin clay (Tianjin Kemiou, China) and humic acid (Shanghai Aladdin, China) were firstly used to prepare stock solution (Yu *et al.* 2011; Yao *et al.* 2015). Tap water (Harbin, China), which had been left overnight, was used to dilute the Kaolin clay and humic acid stock solution to obtain the target synthetic raw water with a turbidity of  $20 \pm 1$  NTU and 4 mg/L humic acid. The solution pH was adjusted to  $7.5 \pm 0.1$  with 0.1 mM/L NaOH or HCl. The temperature of the solution was kept at  $20 \pm 2$  °C during the experimental period. A certain amount of ANT (Purity > 99%, Shanghai, Aladdin, China) was added into the synthetic raw water or ultrapure water according to experimental requirements. The concentration of ANT in the synthetic raw water or ultrapure water was fixed at 250 µg/L. The chemical structure of the ANT molecule is illustrated in Figure 1.

Poly-aluminium chloride (PACl, 28% quality calculated as  $Al_2O_3$ ) was used as the coagulant in this study. The dosage of PACl (2.0 mg/L as  $Al^{3+}$ ) was fixed in all conditions. APAM (Henan Jucheng Chemical Reagent Co. Ltd, China) with a molecular weight of 10 million g/mol

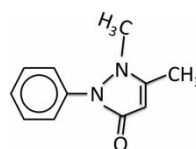


Figure 1 | The chemical structural of the ANT molecule.

was used as a coagulant-aid in this study. Before use, the APAM powder was firstly prepared to 100 mg/L stock solution and left overnight.

### Experimental set-up

The schematic diagram of the experimental set-up is illustrated in Figure 2. It mainly consists of six parts: flocculator (ZR4-2, Zhongrun, China), UF beaker (XFUF07601, Millipore, USA), high-pressure nitrogen gas bottle, pressure controller, electronic balance (BSM-420.3, Yousheng, China) and computer. The electronic balance can record the instantaneous mass of cumulative permeate and send data to the computer equipped with a data acquisition system. The effective membrane surface area in the UF cup is 0.04 m<sup>2</sup>. High-pressure nitrogen gas bottle and pressure controller can provide a constant pressure of 0.1 MPa. The membrane used in the UF beaker is a polyvinylidene fluoride (PVDF) membrane with a cut-off molecular weight of 100 kDa (Sepro, USA).

### Operational procedure

In the coagulation procedure, PACl (2.0 mg/L as Al<sup>3+</sup>) coupled with a certain amount of APAM coagulant-aid were added into the prepared synthetic raw water. Simultaneously, the water sample was mixed rapidly at 200 rpm ( $G \approx 184 \text{ s}^{-1}$ ) for 2 min, and then reduced to 50 rpm ( $G \approx 23 \text{ s}^{-1}$ ) for 20 min.

The UF procedure includes five steps: (1) the new membranes were soaked in ultrapure water for 48 h prior to use; (2) a piece of fresh membrane was pre-pressured with ultrapure water at 0.1 MPa until the water flux became constant; (3) 300 ml suspension liquid after flocculation was gently decanted

from the flocculator to the UF beaker without sedimentation; (4) the filtration process was started (0.1 MPa,  $20 \pm 2 \text{ }^\circ\text{C}$ ) until 50 ml suspension liquid remained in the UF beaker; (5) step 3 and step 4 were repeated until the accumulated filtration time meet the experimental requirements.

In the membrane cleaning procedure, the fouled UF membrane was taken out from the UF beaker and put into the flask containing 500 ml ultrapure water or 0.5% NaOH solution with a temperature of 30 °C. The flask was located in the air bath thermostat oscillator (30 °C, 120 r/min) for 0.5 h. Then the membrane was taken out and flushed with ultrapure water to remove the cleaning agent. Again, the cleaned UF membrane was installed into the UF beaker and the flux was measured after cleaning ( $J_c$ ). The flux before fouling was regarded as  $J_0$ , while the flux after fouling was regarded as  $J_f$ . The cleaning efficiency was evaluated by calculating and comparing the flux recovery (FR). The FR was calculated according to Equation (1).

$$\text{FR} = \frac{J_c - J_f}{J_0 - J_f} \times 100\%, \quad (1)$$

### Other analytical methods

The concentration of ANT was determined by ultra-high performance liquid chromatography (Acquity, Waters, USA). The chromatographic column was Poroshell 120EC-C18 (50 mm\*4.6 mm, 2.7 nm, Agilent). Column temperature: 30 °C. Sample volume: 10 μL. Mobile phase: V (methanol): V (ultrapure water) = 45:55. Flow rate: 0.1 ml/min. Detection wavelength: 242 nm. Retention time: 5 min. The external standard method was adopted to determine the ANT concentration based on the peak area. Water turbidity

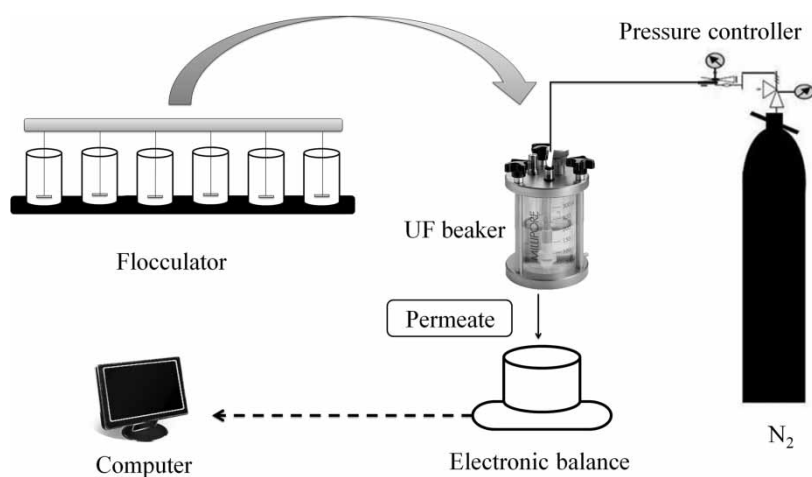


Figure 2 | The schematic diagram of the experimental set-up.

was determined by a turbidimeter (2100AN, HACH, USA). The zeta potentials of 10 mg/L APAM solution at different pH were measured with a zeta potential analyser (Nano-Z, Malvern, UK). The floc size was measured with a laser diffraction instrument (Mastersizer 2000, Malvern, UK). A SurPASS streaming potential analyzer (EKA, Anton Paar GmbH, Austria) was adopted to measure the membrane surface Zeta potential using 1 mM KCl aqueous solution, with the pH value being adjusted using 0.1 M of HCl or NaOH. The new and fouled membrane samples were characterized by SEM (QUANTA 200, FEI, The Netherlands) and a contact angle goniometer (SL200B3, Solon, China). All the membranes used for characterization should be dried in a vacuum drying oven at 25 °C for 48 h prior to analysis.

## RESULTS AND DISCUSSION

### Impact of APAM on membrane fouling

The flux decline and change of membrane surface property are respectively the macro-behaviour and micro-behaviour of membrane fouling. In this section, filtration experiments, SEM and the contact angle goniometer are adopted to understand the impact of APAM on membrane fouling.

### Impact of APAM on flux decline

Filtration experiments were conducted by taking different coagulated suspensions as the feed solution of the UF beaker. Direct filtration of synthetic raw water was also conducted for comparison. All the experiments were conducted three times, and each experiment result showed a similar tendency. The average changing characteristic is illustrated in Figure 3. The accumulated filtration time was all set as 480 min. As shown in Figure 3, direct filtration of raw water without flocculation could result in rapid and serious membrane fouling, and the normalized flux obviously decreased from 1 to 0.49 at the end. However, when 0.2 mg/L PACl (as  $\text{Al}^{3+}$ ) was added to the flocculation-UF process, membrane fouling was distinctly mitigated, and the normalized flux just decreased to 0.7 in the end. With the co-addition of PACl and APAM, the impact on membrane fouling relied on the APAM dosage. At a low APAM dosage of 0.1 mg/L and 0.2 mg/L, the fouling rate was much lower compared to that with PACl only, with the normalized flux only decreasing to 0.83 and 0.78, respectively. As the APAM dosage continuously increased to 0.4 mg/L and 0.8 mg/L, membrane fouling was aggravated, with the normalized flux decreasing to 0.71 and 0.65, respectively.

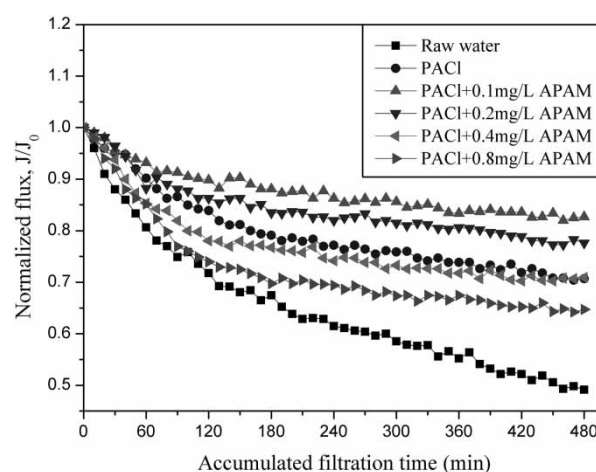


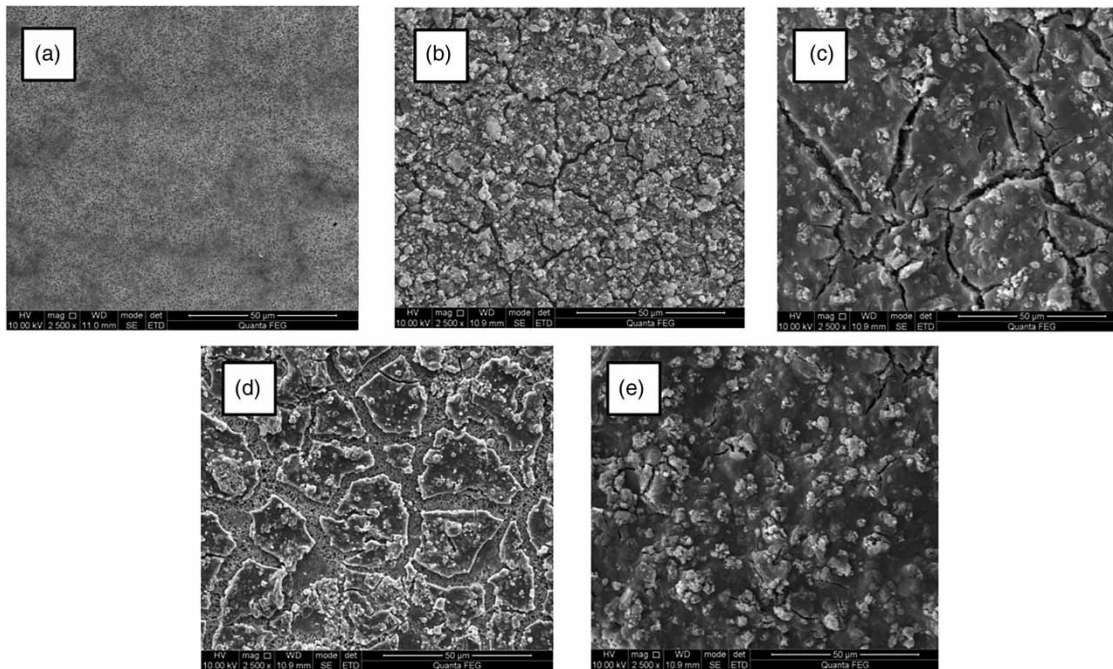
Figure 3 | Variation of UF membrane flux with time for different pre-treatment conditions.

The foulants in the raw water evenly dispersed in the form of colloids, with a particle size smaller than the UF membrane pore size. They can easily enter the membrane pores and result in membrane pore blockage. This action could lead to serious and continuous flux decline. Flocculation pre-treatment can cause the collision and aggregation of colloids, thus forming flocs with a particle size larger than the UF membrane pore size. The flocs will be transported to the membrane surface by drag force and form a cake layer with a pore structure, thus hindering membrane pore blockage. Therefore, membrane fouling was mitigated when PACl was added to the flocculation-UF process. According to the research of Li and Yao, adding NPAM in the flocculation process can form larger floc clusters and a cake layer with more porosity/permeability on the membrane surface (Yu *et al.* 2013; Yao *et al.* 2015). As a coagulant-aid, APAM can play a similar role at a low APAM dosage of 0.1 mg/L and 0.2 mg/L. Besides, the negative APAM in the fouling layer can repel the negative humic acid because of electrostatic repulsion. This repulsion action can protect the membrane from being fouled by humic acid. However, when the dosage increased to 0.4 mg/L and 0.8 mg/L, excess APAM formed a residue in solution or resulted in re-stabilization of flocs. All changes caused higher residual APAM on the surface of the cake layer and membrane, which was adverse to membrane fouling control.

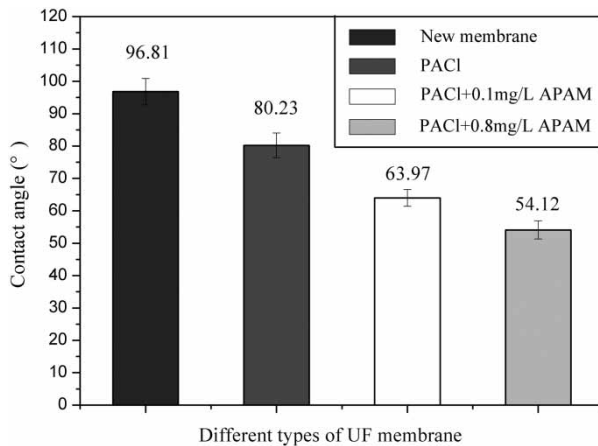
### Characterization of fouled membranes

In order to understand the impact of APAM on membrane fouling from the viewpoint of the fouling layer, SEM and a contact angle goniometer were employed to characterise various UF membranes. The results are presented in Figures 4 and 5, respectively.





**Figure 4** | SEM images of various UF membranes: (a) new membrane after pre-pressure, (b) membrane fouled by raw water, (c) membrane fouled by a coagulated suspension with PACl, (d) membrane fouled by a coagulated suspension with PACl and 0.1 mg/L APAM, (e) membrane fouled by a coagulated suspension with PACl and 0.8 mg/L APAM.



**Figure 5** | Contact angles of various UF membranes.

As shown in [Figure 4](#), there are clearly visible pores distributed on the new membrane surface. Different flocculation conditions led to cake layers with different structures being deposited on the membrane surface. The fouling layer formed by the raw water without coagulation consisted of denser and smaller particles, and this structure would have higher hydraulic resistance. By comparing [Figure 4\(c\)](#) and [4\(d\)](#), we can find that addition of 0.1 mg/L APAM formed a flake-like fouling layer with more porosity. This distinction explains why a low dosage of APAM can mitigate membrane fouling and slow down flux decline. However, when the dosage of APAM increased to 0.8 mg/L, excess APAM acted as a cross linking

agent and led to a much denser fouling layer in [Figure 4\(d\)](#). As a result, membrane flux decreased at a higher rate.

[Figure 5](#) indicates that new membrane was relatively hydrophobic, with a contact angle of  $96.81^\circ$ . The contact angle of the membrane fouled by the coagulated suspension with PACl decreased to  $80.23^\circ$ . This change is attributed to the formation of hydrolyzed precipitate layers, rich in hydroxyl, formed by the PACl. The addition of APAM, a kind of hydrophilic polymer, further decreased the contact angle to  $63.97^\circ$ . Although the hydrophilic fouling layer itself is a resistance for mass transfer, it is generally accepted that improving hydrophilicity is beneficial to flux increase and fouling control ([Gohari \*et al.\* 2014](#); [Rajabzadeh \*et al.\* 2015](#)). In the research of [Chu \*et al.\*](#), PAM was used to alter and control the interfacial properties of the membrane surface, so that improved the membrane anti-fouling ability ([Chu & Sidorenko 2013](#)). Thereby, a low dosage of APAM can mitigate membrane fouling and slow down flux decline. However, as the dosage of APAM increased to 0.8 mg/L, the negative impact occupied the main position in spite of a lower contact angle ( $63.97^\circ$ ).

In general, a low dosage of APAM as coagulant-aid is beneficial to fouling control. Particularly, when the dosage of APAM is 0.1 mg/L, coupled with PACl as the coagulant, the flux decline rate is at its lowest, the membrane fouling layer is porous, and the membrane contact angle is low. Therefore, 0.1 mg/L APAM can be regarded as the optimal coagulant-aid dosage.

### Impact of APAM on membrane cleaning

Although pre-treatment with flocculation can mitigate membrane fouling, fouling cannot be completely avoided. Membrane cleaning is required when there is a serious drop in permeate flux. Therefore, it is important to clarify whether the addition of the optimal dosage of APAM (0.1 mg/L) would increase the difficulty of membrane cleaning.

Two kinds of coagulated suspension were respectively taken as the feed solution for the UF procedure. The first one was a coagulated suspension with only PACl, and the second one was a coagulated suspension with PACl and 0.1 mg/L APAM. The filtration process was conducted until the normalized flux decreased to 0.8. Then the two kinds of fouled membrane were respectively used to experience the membrane cleaning procedure with ultrapure water or a 0.5% NaOH solution. Each cleaning experiment was repeated three times. The average FR of each cleaning experiment is shown in Figure 6.

As shown in Figure 6, cleaning with ultrapure water was ineffective for both kinds of fouled membranes, as the flux recoveries were only 19.17% and 19.69%. This is because the water molecule itself cannot break up the adsorption interaction between the fouling layer and the membrane surface. Nevertheless, the similar flux recoveries indicate that the addition of 0.1 mg/L APAM did not increase the difficulty of physical membrane cleaning. As for the chemical cleaning with 0.5% NaOH, the different flux recoveries of the two fouled membranes suggested that the addition of 0.1 mg/L APAM improved the chemical cleaning efficiency, with the FR up to 60.72%, which was much higher than 40.55%.

As a kind of hydrophilic linear polymer, there are many amide bonds and carboxyl groups in the APAM molecule. These two kinds of polar groups make APAM negatively charged and it easily forms a hydrogen bond with other

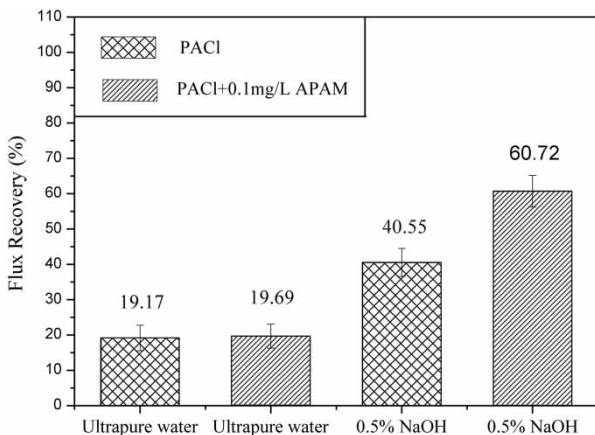


Figure 6 | Flux recoveries under different fouling and cleaning conditions.

polar groups. The influence of solution pH on the zeta potential of APAM and the PVDF membrane is shown in Figure 7. As indicated, both APAM and the PVDF membrane were negatively charged at pH = 7. What's more, their negative charges were enhanced with the increase in the solution pH. Therefore, if there was a low dosage of APAM in the fouling layer, when the fouled membrane was cleaned with 0.5% NaOH, the strong alkalinity could break the hydrogen bonds and increase the electrostatic repulsion between the negatively charged APAM and the negatively charged membrane surface. In this way, the APAM would be dissolved and the fouling layer on the membrane surface would be disintegrated, thus effectively restoring the membrane flux.

### Impact of APAM on effluent quality

Decreasing the membrane fouling rate and membrane cleaning difficulty, and increasing the effluent quality, are three different aspects of an ideal membrane process. An effective membrane process should be able to reject a pollutant as much as possible. A low dosage of APAM (0.1 mg/L) in the flocculation process has been demonstrated to be beneficial for fouling control and membrane cleaning in the above sections. As a kind of PPCPs, the molecular weight of ANT is 188.23 g/mol, much lower than the UF membrane cut-off molecular weight (100 kDa). ANT is hydrophilic and easy to dissolve in water. According to the size exclusion model, ANT cannot be rejected by the UF membrane. Therefore, if the addition of APAM (0.1 mg/L) in the flocculation process can improve the rejection of ANT, it can be inferred that the impact of APAM on effluent quality is favourable.

In the flocculation-UF process, ANT in the raw water may be removed in two ways: (1) the ANT, together with the floc,

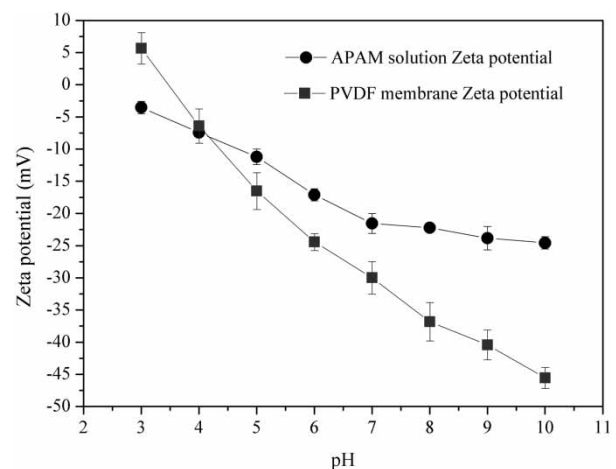


Figure 7 | Influence of solution pH on zeta potential of APAM and PVDF membrane.

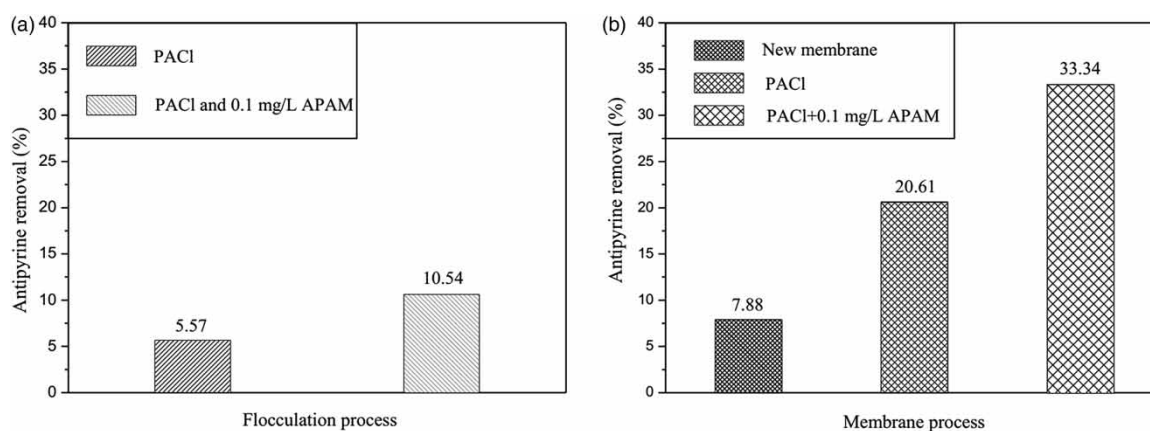
forms a 'coalition' in the flocculation process. Then the 'coalition' is rejected by the membrane process. Thereby the ANT can be simultaneously removed by the UF membrane; (2) the ANT dissolved in the coagulated suspension is adsorbed by the membrane fouling layer. In order to understand the impact of APAM on effluent quality from the two aspects, the flocculation process and membrane process were separated and studied respectively. In the flocculation process, PACl or PACl with 0.1 mg/L APAM was added in synthetic raw water to conduct the flocculation process. The coagulated suspension was then settled for 20 min. The turbidity removal and average floc size of two flocculation processes are presented in Table 1. The concentrations of ANT in the raw water and supernatant were used to calculate the ANT removal in the flocculation process. The results are shown in Figure 8(a). In the membrane process, a new membrane after pre-pressure, a membrane fouled by a coagulated suspension with PACl and a membrane fouled by a coagulated suspension with PACl and 0.1 mg/L APAM, were respectively used to filter ultrapure water containing ANT. The concentrations of ANT in the feed water and permeate were used to calculate the ANT removal in the membrane process. The results are presented in Figure 8(b).

As shown in Table 1, the turbidity removal rate of flocculation with PACl was 86.3%, while that of flocculation with PACl + APAM increased to 91.5%. Meanwhile, the floc sizes for flocculation with PACl and PACl + 0.1 mg/L APAM were 136  $\mu\text{m}$  and 248  $\mu\text{m}$ , respectively. Flocs with a larger size usually have better settleability. Therefore, flocculation with

PACl + 0.1 mg/L APAM has higher turbidity removal efficiency. As shown in Figure 8(a), the ANT removal of the single flocculation process with PACl was only 5.57%. The addition of 0.1 mg/L APAM increased the removal to 10.54%, which indicates the positive impact of APAM on ANT removal in the flocculation process. This is because APAM can increase the floc size and activity. The larger flocs containing APAM had more active adsorption sites, which can adsorb more ANT and form a 'coalition', as mentioned above. This 'coalition' can be removed from the system by sedimentation. Figure 8(b) indicates that new UF membrane without fouling had a weak removal ability for ANT (7.88%) as well, although the molecular weight of ANT was much lower than the UF membrane cut-off molecular weight. This phenomenon can be attributed to the adsorption interaction between the membrane material and ANT. When the fouling layer formed by the coagulated suspension with PACl appeared on the membrane surface, ANT removal increased to 20.61%. In the research of Ma *et al.*, they found the precipitate layer of aluminum sulfate hydrate on the UF membrane surface could adsorb humic acid of low molecular weight, thus improving the removal rate (Ma *et al.* 2013). Similarly, the fouling layer formed by the coagulated suspension with PACl can absorb the ANT and increase the ANT removal rate. When the fouling layer formed by the coagulated suspension with PACl and 0.1 mg/L APAM appeared on the membrane surface, ANT removal further increased to 33.34%. As mentioned earlier, the addition of 0.1 mg/L APAM makes the fouling layer more porous and hydrophilic. Figure 7 has indicated that the zeta potential of the APAM solution at pH = 7.5 was between -21.53 mV to -22.23 mV. Therefore, this fouling layer would have more active adsorption sites due to the negative charge and rich polar groups of APAM. As illustrated in the chemical structural of the ANT molecule in Figure 1, there are two nitrogen atoms in one ANT molecule.

**Table 1** | Turbidity removal and average floc size of different flocculation processes

Items	PACl	PACl + 0.1 mg/L APAM
Turbidity removal rate	88.3%	93.5%
Average floc size	156 $\mu\text{m}$	248 $\mu\text{m}$



**Figure 8** | ANT removal of different processes: (a) ANT removal of flocculation process, (b) ANT removal of membrane process.



According to the molecular conformational analysis, the lone pair of electrons of the nitrogen atoms would attract the H<sup>+</sup> intensely. Meanwhile, the asymmetric structure of the ANT molecule endows it with strong polarity. Thus more ANT molecules can be adsorbed in the fouling layer because of electrostatic attraction and hydrogen interaction.

## CONCLUSION

In this study, APAM was used as a coagulant-aid with PACl coagulation. The impact of APAM on UF efficiency in the flocculation-UF process has been investigated with regard to membrane fouling, membrane cleaning and effluent quality. The obtained results are concluded as follows. (1) The optimal dosage of APAM was 0.1 mg/L coupled with 2 mg/L PACl (as Al<sup>3+</sup>). Under this optimal condition, the membrane fouling can be mitigated, the membrane fouling layer is porous, and the membrane contact angle is low. Higher dosage of APAM will aggravate membrane fouling. (2) APAM did not increase the difficulty of physical membrane cleaning. Specifically, the addition of APAM can improve the cleaning efficiency of chemical cleaning with 0.5% NaOH due to the disintegration of the fouling layer when APAM was dissolved under strong alkaline conditions. (3) When 0.1 mg/L APAM was used as the coagulant-aid with PACl, more active adsorption sites were formed both in the flocs and membrane fouling layer, thus more ANT molecules in the raw water were able to be adsorbed and removed in the flocculation-UF process.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by the State Key Laboratory of Urban Water Resource and Environment (HIT, Grant no. 2016DX11), and National Natural Science Foundation (51508383).

## REFERENCES

- Chu, E. & Sidorenko, A. 2013 Surface reconstruction by a “grafting through” approach: polyacrylamide grafted onto chitosan film. *Langmuir the ACS Journal of Surfaces & Colloids* **29** (40), 12585–12592.
- Gohari, R. J., Halakoo, E., Nazri, N. A. M., Lau, W. J., Matsuura, T. & Ismail, A. F. 2014 Improving performance and antifouling capability of PES UF membranes via blending with highly hydrophilic hydrous manganese dioxide nanoparticles. *Desalination* **335** (1), 87–95.
- Huang, C., Jiang, W. & Chen, C. 2004 Nano silica removal from IC wastewater by pre-coagulation and microfiltration. *Water Science & Technology* **50** (12), 133–138.
- Huang, H., Schwab, K. & Jacangelo, J. G. 2009 Pretreatment for low pressure membranes in water treatment: a review. *Environmental Science & Technology* **43** (9), 3011–3019.
- Jarvis, P., Parsons, S. A., Henderson, R., Nixon, N. & Jefferson, B. 2008 The practical application of fractal dimension in water treatment practice—the impact of polymer dosing. *Separation Science & Technology* **43** (7), 1785–1797.
- Lai, C. H., Chou, Y. C. & Yeh, H. H. 2015 Assessing the interaction effects of coagulation pretreatment and membrane material on UF fouling control using HPSEC combined with peak-fitting. *Journal of Membrane Science* **474** (474), 207–214.
- Liang, H., Gong, W. & Li, G. 2008 Performance evaluation of water treatment ultrafiltration pilot plants treating algae-rich reservoir water. *Desalination* **221** (1–3), 345–350.
- Ma, B., Yu, W., Liu, H., Yao, J. & Qu, J. H. 2013 Effect of iron/aluminum hydrolyzed precipitate layer on ultrafiltration membrane. *Desalination* **330** (12), 16–21.
- Rajabzadeh, S., Sano, R., Ishigami, T., Kakihana, Y., Ohmukai, Y. & Matsuyama, H. 2015 Preparation of hydrophilic vinyl chloride copolymer hollow fiber membranes with antifouling properties. *Applied Surface Science* **324** (324), 718–724.
- Tan, C., Gao, N., Deng, Y., Li, L., Deng, J. & Zhou, S. 2013 Kinetic oxidation of antipyrine in heat-activated persulfate. *Desalination & Water Treatment* **53** (1), 263–271.
- Vickers, J. C., Thompson, M. A. & Kelkar, U. G. 1995 The use of membrane filtration in conjunction with coagulation processes for improved NOM removal. *Desalination* **102** (1), 57–61.
- Wang, S., Liu, C. & Li, Q. 2011 Fouling of microfiltration membranes by organic polymer coagulants and flocculants: controlling factors and mechanisms. *Water Research* **45** (45), 357–365.
- Wang, S., Liu, C. & Li, Q. 2013 Impact of polymer flocculants on coagulation-microfiltration of surface water. *Water Research* **47** (13), 4538–4546.
- Yao, M., Nan, J., Chen, T., Zhan, D., Li, Q., Wang, Z. & Li, H. 2015 Influence of flocs breakage process on membrane fouling in coagulation/ultrafiltration process – effect of additional coagulant of poly-aluminum chloride and polyacrylamide. *Journal of Membrane Science* **491** (1), 63–72.
- Yu, W., Liu, T., Gregory, J., Campos, L., Li, G. & Qu, J. 2011 Influence of flocs breakage process on submerged ultrafiltration membrane fouling. *Fuel & Energy Abstracts* **385–386** (385), 194–9.
- Yu, W. Z., Liu, H. J., Xu, L., Qu, J. H. & Graham, N. 2013 The pre-treatment of submerged ultrafiltration membrane by coagulation – effect of polyacrylamide as a coagulant aid. *Journal of Membrane Science* **446** (11), 50–58.
- Yu, W., Xu, L., Qu, J. & Graham, N. 2014 Investigation of pre-coagulation and powder activate carbon adsorption on ultrafiltration membrane fouling. *Journal of Membrane Science* **459** (459), 157–168.