Study on the PAC Hydrolysis Speciation Analysis (HSA) in Membrane Fouling Control

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ABSTRACT

Among various membrane separation technologies, ultrafiltration membrane (UF) and micro-filtration membrane (MF) are considered to be perfect choices to take the place of traditional processes in the micro-polluted water treatment. The Al-Ferron method was used to research the Al speciation distribution and find out the control effects of polymeric metal salt coagulants on membrane fouling. Results showed that the effluent contained a small amount of Al₃ after filtration, which could be deduced that the membrane was effective to intercept Al₅. Moreover, it could be discovered that the membrane flux recovery rate of acidic washing was better than that of neural water or alkaline washing. The study has been proved to be a very proper technique for effectively evaluating the effects of membrane fouling control and providing a new way for determining the optimal cleaning method by monitoring the reaction rate between the different Al₇ forms and Ferron reagent.¹

INTRODUCTION

Membrane separation is an efficient technology, which has been widely used in the process of separation, purification and the condensation in the water and wastewater treatment in recent years. Among various membrane separation technologies, ultra-filtration membrane (UF) and micro-filtration membrane (MF) are considered to be perfect choices to take the place of traditional processes in the micro-polluted water treatment [1]. But the membrane fouling becomes more and

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more protruding after long-term operation, which has a clear negative impact on the removal efficiency of membrane separation. Therefore effective regeneration is the key to maintain a stable and efficient operation for membrane through a series of washing methods[2].

Based on years of research, it has been found that Al3+ can combine with Ferron, and the complex has a maximum absorption peak at 370nm. Accordingly, AlT can be divided into three parts [3] as follows:

1. Ala: it refers to the aluminum hydrolysate that reacts with Ferron within 1 min. It is generally believed that it includes mainly mononuclear complexes such as: Al+, Al(OH)2+, Al(OH)2+ etc.
2. Alb: the reaction time is 1 -120min and the complex is composed of AI2 (OH)42+, Al3 (OH)54+, Al13 (OH)327+ and Al13O4 (OH)247+ etc.
3. Alc: the reaction time exceeds 120min and the majority of the complex is macro-polymer (Al>13) and sol [n Al(OH)3].

Among the three forms of AlT, positive charge of Ala is comparatively little so that the ability of Ala to neutralize the negatively charged colloidal particles is relatively poor[4]. While multi-core aluminum complexes (Alb), especially the Al13 (OH)327+ and Al13O4 (OH)247+, have high positive charge and long molecular chains, leading to the strong ability of charge neutralization, high adsorption capacity and good coagulation effect. In addition, Alc plays an important role in coagulation by absorption and bridging at higher pH level[5].

The impacts of PAC residues on the membrane flux, the distribution of the three forms of speciation and the transformation rules among them, were firstly investigated by Ferron Hourly Complexometry in this paper, which has been proved to be a very important index for effectively evaluating the effects of membrane fouling control and providing a new way for determining the optimal cleaning method by monitoring the reaction rate between the different AlT forms and Ferron reagent.

EXPERIMENTAL PROCEDURE

Laboratory Instruments and Materials

1. Experiment drugs: PAC (15%Al2O3): coagulant; clay; 0.25mol/LNaOH; 100mg/LNaClO and 0.02%HCl;
2. Raw water quality: SS: 18- 20mg/L; Turbidity: 6.50-7.00NTU;
3. Experiment device was shown as follows:
Firstly, the raw water was treated by coagulation in the tank. And then, the supernatant was ascended into membrane module by centrifugal pump. Filtration rate was adjusted from 0.17-0.67 cm/h and the whole cycle was 60 min. In this experiment, the absorbance of the effluent was detected at different time during membrane filtration.

Experiment preparation: the jar tests were carried out before this experiment to obtain the optimal experiment parameters which were listed as follows: the dosage, pH, retention time and filtration rate were 40 mg/L, 6.5, 30 min and 0.25 cm/h respectively.

**Experimental Procedures**

The experiment was conducted at the optimum dosage and pH including 5 steps described below:

1) 30 mg PAC was dissolved in 500 mL deionized water;
2) 10 mL colorimetric buffer solution was moved into 50 mL volumetric flask;
3) 5 mL of the measured solution was moved into the volumetric flask;
4) The absorbance of the solution was measured at 1, 15, 30, 120, 150, 180 min respectively. (the absorbance of the reagent excluding the aluminum was tested at the wavelength of 370 nm as blank)
RESULTS AND DISCUSSION

Analysis of Aluminum Components Before/After The Membrane Filtration

![Absorbance Curves](image)

Figure 2. The absorbance curves before / after the membrane filtration.

In this study, the difference between the maximum and minimum value was defined as the denominator d (the blank test absorbance was 0.146). Meanwhile, a refers to the value in instantaneous reaction, b to the value within 120 min, c after 120 min. If a (b/c) < 0.146, then a (b/c) = 0. From figure 2 (1), the speciation of AlT after coagulation can be calculated: Ala/(a-0.146)/d=0%, Alb=(b-a)/d=85.7%, Alc=(c-b)/d=14.3%. As was shown in figure 2 (2), Ala and Alb could be hardly found in the effluent (b<0.146, a=0, b=0) while a small amount of Alc could be detected.

Actually, the reactions of transforming one form into another among different species of aluminum occurred simultaneously after the PAC was added[6]. In the reaction between PAC and colloidal particles in the water, the oligomer (Ala as an example) was transformed to super-polymer (Alb) consistently. Only a small amount of Alc could be found in the effluent, which indicated an obvious effect of interception after membrane filtration[7].

Membrane Washing

ALKALINE WASHING

The washing and backwashing of alkaline solution were conducted at different time of Ferron complexation experiments[8]. The following figures showed that the washing absorbance curve varied with the effluent of different time.
According to figure 3 and table 1, it could be observed that, with the growth of the washing time, the proportion of Alₐ and Alₙ in the treated water showed a consecutive decline. Besides, the Alₐ had been in a dominant position and the Alₜ level increased gradually.

The results revealed that much of Alₐ had been converted to the larger molecules Alₖ. Moreover, the decrease of Alₙ would be attributed to the de-polymerization to Alₖ or Alₐ. The growth of Alₜ revealed that the trapped pollutants disintegrated into some kinds of dissolved materials containing various forms of Al that could pass through the membrane by a series of processes such as hydrolysis, peptizing, saponification. In addition, a small number of inorganic particles on the membrane surface dispersed into the alkaline liquid after a certain time of soaking[9].

| Time (min) | Alₐ | Alₖ | Alₙ | d | Maximum | Blank |
|-----------|-----|-----|-----|---|---------|-------|
| 1min      | 14.3% | 71.4% | 14.3% | 0.007 | 0.153 | 0.146 |
| 5min      | 13.8% | 75.1% | 11.1% | 0.009 | 0.155 | 0.146 |
| 10min     | 13.3% | 80.0% | 6.7% | 0.015 | 0.161 | 0.146 |
It was obvious that the longer backwashing was, the less proportion of Alₐ became, and eventually down to zero with the ratio of Alₐ growing and keeping a dominant position all the time. It could be explained that the cleaning liquid and pollutants had a full-contact at the early stage of backwashing, which would lead to the initial larger proportion of Alₐ. The Alₜ and Alₐ became fewer and fewer with the increase of backwashing time[10]. The reaction mechanism of the decline of Alₐ was similar to alkaline washing and the reason of the drop of Alₜ was that the residuals passing through the membrane had been discharged from the effluent[12]. After that, parts of Alₐ were transferred into larger molecules or macromolecules Alₖ due to the internal structure rearrangement, resulting in a graduate rise of Alₖ. As the backwashing continued, the majority of large multi-nucleus molecules and complexes were intercepted on the surface of membrane, which made the portion of Alₖ stable in the effluent[14].

| Time (min) | Alₐ  | Alₗ  | Alₖ  | d    | Maximum | Blank |
|-----------|------|------|------|------|---------|-------|
| 1min      | 29.1%| 66.7%| 4.2% | 0.024| 0.170   | 0.146 |
| 5min      | 7.7% | 84.6%| 7.7% | 0.013| 0.159   | 0.146 |
| 10min     | 0%   | 88.9%| 11.1%| 0.009| 0.155   | 0.146 |

Figure 4. The absorbance of alkaline backwashing at different time.
ACIDIC WASHING

From table 3, it was obvious that the initial content of Alₐ was zero, while the Alₖ occupied the vast majority. Then with the washing time going on, the percentage of Alₐ gradually increased and Alₖ slowly decreased until they got the equal amount after 10min. In addition, the content of Alₜ reduced with the growth of time but Alₜ increased contrarily. The reason lay in that most compacted contaminants were difficult to decompose in a short period of time, which would inevitably cause the ascension of Alₜ with the extension of time. Additionally, the substantial rise of Alₐ was due to the existence of hydroxyl neutralization reaction. As a consequence, the poly-aluminum was bound to decompose into Al³⁺ or low poly state of small molecules[17].

**TABLE III. THE HYDROLYSIS MORPHOLOGY OF ALUMINUM CHANGED AT DIFFERENT TIME AFTER THE ACIDIC WASHING.**

| Time (min) | Alₐ  | Alₖ  | Alₜ  | d      | Maximum | Blank |
|------------|------|------|------|--------|---------|-------|
| 1min       | 0%   | 87.5%| 12.5%| 0.008  | 0.154   | 0.146 |
| 5min       | 42.9%| 50%  | 7.1% | 0.014  | 0.160   | 0.146 |
| 10min      | 47.8%| 47.8%| 4.4% | 0.023  | 0.169   | 0.146 |
From the experimental results above, it was evident that AIT enhanced with the increase of time, while Ala was the largest species in AIT in the original phase and kept a gradual increase, which indicated that the majority of Al could infiltrate membrane easily. The results revealed that the contact happened between the cleaning liquid and pollutants, which arose AIT in the water at the first 5min. Consequently, the high concentration of AIT made it easier to engage and react roughly[20].

To sum up, the high content of AIT indicated that the backwashing was more favorable than the washing. Besides, it could be inferred from the results that the performance of acidic washing was better compared with alkaline.

**TABLE III. THE HYDROLYSIS MORPHOLOGY OF ALUMINUM CHANGED AT DIFFERENT TIME AFTER THE ACIDIC BACKWASHING.**

| Time (min) | Alₐ | Alₙ | Alₜ | d   | Maximum | Blank |
|------------|-----|-----|-----|-----|---------|-------|
| 1min       | 80.7% | 17.5% | 1.8% | 0.057 | 0.203   | 0.146 |
| 5min       | 81.7% | 15.5% | 2.8% | 0.071 | 0.217   | 0.146 |
| 10min      | 83.8% | 14.9% | 1.3% | 0.074 | 0.220   | 0.146 |
The Comparison Test of Membrane Flux

The membrane flux is a significant operation parameter in the process of membrane separation, which refers to an amount of liquid through the membrane per unit area per unit time.

It could be easily observed from figure 7 that the acidic washing achieved the best effect with the membrane flux recovery of 98%, while the alkaline and water washing reached 96% and 90% respectively, indicating that the effect of chemical cleaning was better. The results were consistent with the speciation analysis of aluminum mentioned above. What could be illustrated was that this kind of analysis method to evaluate the efficacy of the membrane fouling process control and regeneration was appropriate and plausible.

It could also be found out that acidic washing effect was better than alkaline by monitoring the changes of Ala content. It could be explained that the polymerization of aluminum coagulants hydrolysis was rich in the hydroxyl Alx(OH)y(3x-y)\(^+\). In the experiment, the low concentration of strong acid solution was adopted. The H\(^+\) neutralized with the -OH group in various sorts of aluminum hydroxyl complex that existed in the form of Alx(OH)y(3x-y)\(^+\). As a result, the small molecular reactants produced during the neutralization were more easily to go through the membrane, causing a sharp reduction of the residual aluminum and perfect membrane flux recovery rate. As for alkaline washing, - O - chain could be generated by combination between OH\(^-\) and Alx(OH)y(3x-y)\(^+\). Therefore the macro-molecular compounds, which were difficult to pass the membrane, would take up the majority in the Al speciation through the bridging and binding by means of - O - chain. In a word, the alkaline washing effect was slightly inferior to the acid washing fluid.

CONCLUSIONS

1. The result of the membrane flux recovery rate tests on the water, alkaline and acidic washing were consistent with the speciation analysis of aluminum mentioned above. This kind of analysis method to evaluate the efficacy of the membrane fouling process control and regeneration was appropriate.
2. Ala and Alb could be hardly found in the effluent while a small amount of Alc could be detected after the filtration.
3. The contrast experiment showed that the effect of acidic was slightly better than alkaline washing under the same conditions. The reason was that the H\(^+\) neutralized with the -OH group in various sorts of aluminum hydroxyl complex that existed in the form of Alx(OH)y(3x-y)\(^+\).
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