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# Effect of coagulants on the fouling and performance of ultrafiltration (UF) membranes

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## ABSTRACT

The combined coagulation and ultrafiltration (UF) system (C-UF system) is an advanced technology to treat natural organic matter (NOM) present in water. Traditional coagulants—prehydrolyzed inorganic coagulants, organic coagulants and composite coagulants were chosen to treat synthetic water containing humic acid (HA) in order to find an efficient coagulant that could remove NOM from the water effectively. The fouling, removal efficiency of UF and the chlorine decay in the permeate were used to evaluate the effectiveness of the coagulants. The initial $UV_{254}$ absorption of the tested water samples were from 0.208 to 0.234, and the $UV_{254}$ after coagulation was from 0.05 to 0.184. The $UV_{254}$ did not increase after coagulation. Since the humic acid used was soluble, the initial turbidity of the tested water samples were very close to zero. The turbidity increased after coagulation, as the coagulants react with humic acid to form micro-flocs, which cannot be removed fully by sedimentation. The results showed that Polyferric chloride could not remove humic acid efficiently during coagulation process, but removed the humic acid well when used in the C-UF system. Moreover, for polyferric chloride and UF system, the concentration of organic compounds in permeates were minimal indicating very low levels of disinfection by-product formation, if chlorinated.

***Keywords:*** Coagulant; Membrane; Humic acid; Chlorine decay; Ultrafiltration

## 1. Introduction

Many water sources throughout the world contain natural organic matter (NOM), and it is best described as a complex mixture of organic compounds. NOM itself is considered harmless, however it is the conversion of NOM into disinfection by-products (DBPs) when chlorine is used that can cause major problems [1]. Moreover, NOM not only reacts with chlorine but also acts as a food source and leads to bacterial regrowth in the distribution networks [2]. NOM also reduces the effectiveness of membrane by causing irreversible fouling. Further, it will compete with target compounds for the active sites on activated carbon if adsorption is required as further treatment [3]. Therefore, it is important to remove NOM from water.

Traditionally, NOM is treated to some extent by coagulation [4]. However, stringent legislation to control the amount of disinfectant by-products (DBPs) allowed in drinking water has led to increased doses of coagulants and subsequent increase in sludge production so that sufficient NOM can be removed [5,6]. Thus, studies have started focusing on alternative methods for the removal of these DBP precursors.

Membranes have attracted considerable attention in the field of drinking water treatment because they can remove NOM effectively, especially by ultrafiltration (UF) membranes. UF—the low pressure membrane process, has been presented as very effective for the removal of particles, turbidity, bacteria and cysts from water. Many water

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utilities are now integrating UF with coagulation to provide treatment for small molecular weight contaminants and to prevent the fouling of UF [7]. Humbert et al. [8] found that the C-UF system significantly improves the permeability of UF, and reduces the dosage of coagulants. Moreover, after coagulation as pretreatment, the size fractions in the feed water to the UF would change significantly which in turn will change the fouling characteristics and the rate of fouling of UF membrane [9]. The C-UF process has been thought as an effective treatment technology for NOM, and can reduce the concentration of DBPs in the treated water. However, there are some aspects of the C-UF system that need further investigation.

One of the aspects is the effect of different coagulant types on the performance of C-UF system. In recent years, various types of coagulants have been developed including inorganic, organic and composite coagulants. The properties of these coagulants are different. For example, organic coagulants have larger molecules than inorganic coagulants, and there will be some interactions between inorganic and organic coagulants that are present in a composite coagulant which would affect the efficiency of the coagulant. Moreover, these coagulants will be effective for different optimal concentrations of constituents that were present in the raw (or source) water. Different coagulants would also produce feed water with different properties that will affect the performance of UF in different ways.

The purpose of this study was to examine the effect of different type of coagulants on the fouling and the performance of UF, and to determine which coagulant is effective for C-UF process by comparing the decay of chlorine in permeates.

## 2. Materials and methods

### 2.1. Coagulants

Coagulants such as aluminum chloride ($AlCl_3$), ferric chloride ($FeCl_3$), polyaluminum chloride (PAC), polyferric chloride (PFC), polydimethyldiallylammonium chloride (PDMDAAC), EPI-DMP, polyferric chloride-polydimethyldiallylammonium chloride composite coagulant (PFC-PDMDAAC), and polyaluminum chloride-polydimethyldiallylammonium chloride composite coagulant (PAC-PDMDAAC) were provided by Jia Yuan Environmental Co., Shandong, China. The stock solutions of coagulants (1%) were prepared by dissolving appropriate quantities of coagulants in de-ionized water.

### 2.2. Synthetic test water

The humic acid (HA) stock solution was prepared by dissolving 1 g of HA (Shanghai, China) in de-ionized that contained 4.2 g of $NaHCO_3$ and bringing the volume of the solution to 1 L. Under these conditions, the HA was soluble.

Apparent molecular weight (AMW) distribution, which is an important parameter for HA, was determined using ultra filtration membranes with an Amicon® cell device (Model 8200, Millipore, USA). For UF, the stock humic acid solution was diluted 200 times with de-ionized water. Pure nitrogen gas (at 0.35 MPa) was used as the driving force. The humic acid was divided into four molecular weight classes: >30, 10–30, 3–10 and <3 kDa. The total organic carbon (TOC) and $UV_{254}$ absorbance of each class were measured. The humic acid mainly consisted of high AMW constituents with fraction greater than 30 kDa accounted for 80.1% of TOC and 87.5% of $UV_{254}$ absorbance. Since TOC varies linearly with $UV_{254}$, the $UV_{254}$ values were chosen to evaluate the removal efficiency of HA.

The synthetic test solution was prepared by dissolving the HA stock solution (10 ml) in de-ionized water (500 ml). The $UV_{254}$ and the TOC of the synthetic test water were 0.208 ~ 0.234 and 7.7 respectively.

### 2.3. Coagulation-UF experiments

Coagulation tests were conducted prior to the UF experiments. Coagulant was added to raw water, and then agitated for 33 minutes (rapid mixing for 3 minutes at 120 rpm followed by slow mixing for 30 minutes at 40 rpm). The coagulated water was then settled for 30 minutes. The supernatant was then used as feed water for UF process.

The UF membrane was obtained from Langji Co. China. The membrane was made of binder-free glass fiber and 150-kDa molecular weight cutoff regenerated cellulose membranes. In the filtration phase, the feed and filter valves were opened to allow the feed water to be sent to the UF for 30 minutes of filtration. The feed and permeate flow rates were kept at 5 L $h^{-1}$ and 3 L $h^{-1}$, respectively. The trans-membrane pressure (TMP) was monitored regularly to evaluate the fouling of membrane.

### 2.4. Chlorine decay model

Water samples were collected before and after the filtration experiment. Two liters of samples were placed into dark colored testing bottles; each sample was dosed under controlled conditions with 2.5 or 3 mg $L^{-1}$ of chlorine. Free and total chlorine concentrations were taken immediately after dosing (1 minute) then at intervals of 5, 10, 20, 30 minutes, 1, 2, 4 and 6 hours and then twice a day until the chlorine was decayed below 0.1 mg $L^{-1}$. Chlorine concentrations were determined using the N,N-Diethyl-p-phenylenediamine (DPD) Colorimetric method, which consisted of a HACH pocket colorimeter model no. 46770-00 with DPD pillows dissolved in 10 ml of sample.

The chlorine decay data obtained were analyzed using AQUASIM [10] to estimate the initial concentrations of organic compounds along with their reaction rate constant values. The details of chlorine decay model have been described elsewhere [11]. The general chlorine decay model includes the following reactions between chlorine and other constituents in the water [10]:

$Cl_2$ + Fast reducing agents (organic compounds) (*FRA*)
$\rightarrow$ inert products (1)
$Cl_2$ + Fast reducing nitrogenous compounds (*FRN*)
$\rightarrow$ combined chlorine (2)
$Cl_2$ + Slow reacting agents (organic compounds) (*SRA*)
$\rightarrow$ inert products (3)
$Cl_2$ + Slow reacting nitrogenous compounds (*SRN*)
$\rightarrow$ combined chlorine (*CC*) (4)
Combined chlorine $\rightarrow$ inert products (5)

While $Cl_2$ indicates the available free chlorine present in the water and the sum of $Cl_2$ and combined chlorine (*CC*) indicates the total chlorine present in the water. The reaction rates for the above five equations are $k_1$, $k_2$, $k_3$, $k_4$ and $k_5$ respectively. Thus the equations governing the decay of free and combined chlorine can be written as:

$$\frac{d[Cl_2]}{dt} = -k_1[Cl_2][FRA] - k_2[Cl_2][FRN] - k_3[Cl_2][SRA] - k_4[Cl_2][SRN] \tag{6-a}$$

$$\frac{d[CC]}{dt} = -k_5[CC] + k_2[Cl_2][FRN] + k_4[Cl_2][SRN] \tag{6-b}$$

$$[Total\ Cl_2] = [Cl_2] + [CC] \tag{6-c}$$

In this study, since the water samples just contained HA, the experimental chlorine decay data were used to estimate the initial concentrations of fast and slow reducing organic compounds (*FRA* and *SRA*) along with their reaction rate constants $k_1$ and $k_3$.

## 3. Results and discussion

### 3.1. Effect of coagulants on the removal of HA

As presented in Table 1, the efficiency of HA removal in C-UF process was found to be strongly influenced by the type of coagulant. The initial $UV_{254}$ absorption of the tested water was 0.208–0.234, and the $UV_{254}$ after coagulation was 0.05–0.184. The $UV_{254}$ did not increase after coagulation. Since the HA used was soluble, the initial turbidity of the test water was very close to zero. The turbidity increased after coagulation, as the coagulants react with HA to form micro-flocs, which cannot be removed fully by sedimentation.

For the coagulation process alone, the residual turbidity was highest in PDMDAAC treatment, and it was lowest in PAC treatment. However, for the removal of organic substances in terms of $UV_{254}$, the lowest efficiency was obtained for the supernatant of PAC-PDMDAAC treatment and the highest efficiency was obtained for the supernatant of PAC treatment. In C-UF process, the effect of coagulant type was different to that of coagulation process alone. IN C-UF process, the lowest residual turbidity was obtained for (PFC-PDMDAAC + UF) treatment and the lowest $UV_{254}$ values were obtained for (PFC + UF) treatment. However, (PFC + UF) treatment did not remove the turbidity efficiently. By comparing the results obtained from coagulation and C-UF processes, it can be found that although PFC is not a good selection as coagulant for treating HA, its performance is better than other coagulants in the C-UF process.

### 3.2. Effect of coagulant types on membrane fouling

In order to investigate the effect of coagulant types on membrane fouling, the temporal variation of TMP was monitored at constant flux. The results are shown in

Table 1
The efficiency of coagulation and C-UF processes in terms of residual turbidity and organic substances (measured in terms of $UV_{254}$).

| | | $AlCl_3$ | $FeCl_3$ | PAC | PFC | EPI-DMP | PDMD AAC | PAC-PDMD AAC | PFC-PDMD AAC |
|---|---|---|---|---|---|---|---|---|---|
| Coagulation | Residual turbidity (NTU) | 2.26 | 2.66 | 1.52 | 9.04 | 2.47 | 9.31 | 7.62 | 2.47 |
| | $UV_{254}$ | 0.062 | 0.078 | 0.05 | 0.141 | 0.08 | 0.133 | 0.184 | 0.08 |
| C-UF | Residual turbidity (NTU) | 0.54 | 1.31 | 0.22 | 2.06 | 0.21 | 0.25 | 0.27 | 0.12 |
| | $UV_{254}$ | 0.041 | 0.043 | 0.02 | 0.009 | 0.077 | 0.032 | 0.044 | 0.017 |

Fig. 1. In the filtration of the raw water, TMP increased rapidly. For example, the TMP increased from 0.2 MPa to 1.0 MPa after 3 minutes of filtration. However, in C-UF process, the rate of increase of TMP was slow indicating the useful contribution of coagulation towards the reduction of membrane fouling.

From Fig. 1(A), it can be seen that the traditional coagulants such as $AlCl_3$ and $FeCl_3$ did not improve the performance of membrane in terms of fouling. The rate of increase of TMP was similar to the one observed for raw water. However, organic coagulants such as PDMDAAC and EPI-DMA improved the performance (Fig. 1(B)). In 15 minutes the TMP increased from 0.2 to 0.8 MPa. (in this study, the pressure was kept constant after 15 minutes). When PAC and PFC were chosen as coagulants (Fig. 1(D)), the final TMP reached 1.0 and 0.9 MPa, respectively. This indicates the performance of PFC is better than PAC in terms of fouling reduction. Composite coagulants are better than hydrolyzed inorganic coagulants (PAC and PFC) in preventing membrane fouling (Fig. 1(C)). These results indicate that the type of coagulants affects not only the efficiency of membrane efficiency but also the fouling of membrane.

### *3.3. Effect of coagulants on chlorine decay*

Tables 2 and 3 give the initial concentrations of fast and slow reducing organic compounds in the effluents from coagulation and C-UF process respectively, along with their reaction rate constants. It can be seen from these two tables that the performance of different coagulant in removing organic compounds is different. The organic compound removal efficiency of PFC is the highest in our study. In coagulation process, the initial total organic concentration in the treated supernatant is 0.903 mg/L of chlorine equivalent, and in C-UF process the initial total organic concentration in the permeate is 0.67 mg/L of chlorine equivalent. Since the organic compounds react with chlorine to form DBPs, the initial concentrations of total reducing organic compounds could be used to estimate the concentration of DBPs. From the above results, the concentration of DBPs in water treatment by PFC could be the lowest and therefore it can be concluded that PFC is the efficient coagulant for C-UF process. When EPI-DMP, PAC-PDMDAAC and PFC-PDMDAAC were chosen as coagulants, the initial concentration of total reducing organic compounds from

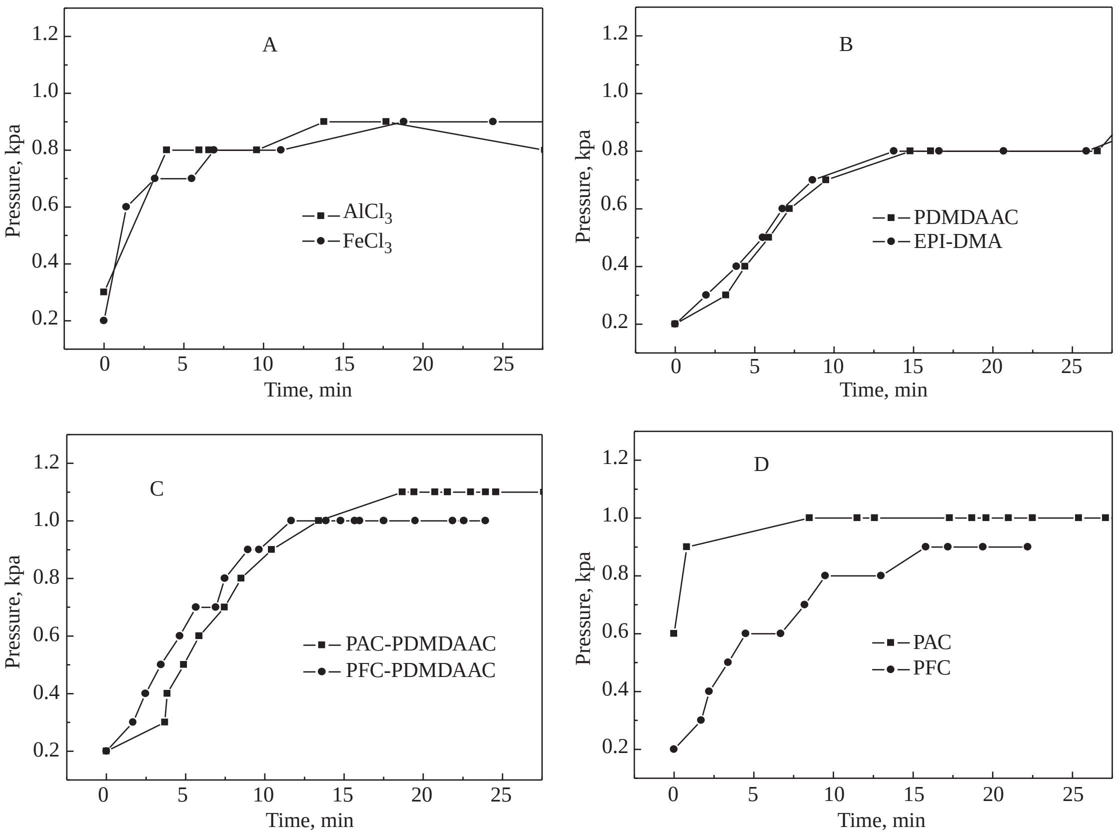

Fig. 1. The rate of change of TMP of UF process for the feeds from the supernatants of different coagulants. (A) Traditional (inorganic) coagulants, $AlCl_3$ and $FeCl_3$ (B) Organic coagulants, PDMDAAC and EPI-DMP (C) Composite coagulants PAC-PDMDAA and PFC-PDMDAAC (D) Inorganic coagulants PAC and PFC.

Table 2
The reaction rate constants and initial concentrations of fast and slow reducing organic compounds in the supernatant of coagulation process.

| | $AlCl_3$ | $FeCl_3$ | PAC | PFC | EPI-DMP | PDMDAAC | PAC-PDMDAAC | PFC-PDMDAAC |
|---|---|---|---|---|---|---|---|---|
| $k_1$ (L/mg.h) | 5.21 | 12.58 | 7.42 | 11.36 | 46.45 | 603 | 3.57 | 656 |
| $k_3$ (L/mg.h) | 0.0029 | 0.14 | 0.011 | 8.47 | 0.38 | 0.51 | 0.0029 | 0.02 |
| Initial conc. of FRA | 1.11 | 1.10 | 1.02 | 0.87 | 1.25 | 1.03 | 0.67 | 0.15 |
| Initial conc. of FRA | 8.59 | 1.39 | 7.01 | 0.033 | 3.01 | 1.55 | 25.24 | 10.65 |
| Initial conc. of total reducing organic compounds | 9.7 | 2.49 | 8.03 | 0.903 | 4.26 | 2.58 | 25.91 | 10.8 |

The units of initial concentrations are in (mg/L of chlorine equivalent).

Table 3
The reaction rate constants and initial concentrations of fast and slow reducing organic compounds in the permeate of C-UF process.

| | $AlCl_3$ | $FeCl_3$ | PAC | PFC | EPI-DMP | PDMDAAC | PAC-PDMDAAC | PFC-PDMDAAC |
|---|---|---|---|---|---|---|---|---|
| $k_1$ (L/mg.h) | 15.99 | 15.82 | 5.07 | 15.00 | 2.60 | 80.18 | 640 | 516 |
| $k_3$ (L/mg.h) | 0.047 | 0.025 | 0.0054 | 0.11 | 0.45 | 1.11 | 0.19 | 0.16 |
| Initial conc. of FRA | 0.65 | 0.68 | 1.27 | 0.41 | 1.46 | 0.92 | 0.55 | 0.23 |
| Initial conc. of FRA | 9.15 | 15.33 | 9.7 | 0.26 | 0.59 | 1.56 | 0.83 | 0.69 |
| Initial conc. of total reducing organic compounds | 9.8 | 16.01 | 10.97 | 0.67 | 2.05 | 2.48 | 1.38 | 0.92 |

The units of initial concentrations are in (mg/L of chlorine equivalent).

C-UF process is lower than that from coagulation alone. This indicates that these coagulants can react with HA to form micro-flocs which are filtered by UF, although they did not precipitate during the coagulation process. When $AlCl_3$ and PDMDAAC were chosen as coagulants, the initial total reducing organic compounds in the coagulated supernatant is similar to that in the permeate of C-UF process. When $FeCl_3$ and PAC were chosen as coagulants, the initial total reducing organic compounds in the permeate of C-UF process is higher than that in the coagulated supernatant. This indicates that C-UF process does not reduce DBPs effectively when $AlCl_3$, $FeCl_3$, PAC or PDMDAAC is used as coagulant.

## 4. Conclusion

(i) The filtration efficiency and fouling of C-UF process is strongly influenced by the type of coagulant. The traditional coagulants such as $AlCl_3$ and $FeCl_3$ did not improve the fouling of UF.

(ii) The removal efficiency of coagulants in coagulation process alone is entirely different to that in the C-UF process. Although PFC was not a good coagulant to remove HA in coagulation process, it was better than other coagulants to remove HA in C-UF process.

(iii) Minimal reducing organic compounds were present in permeate when PFC was used as coagulant in the C-UF process and would possibly produce minimal amount of DBPs when disinfected with chlorine. Therefore PFC can be considered as a better coagulant among the coagulants studied for C-UF process.

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