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Coagulation performance and membrane fouling of different aluminum species during coagulation/ultrafiltration combined process

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HIGHLIGHTS

- Coagulation performance of three high content Al species was first studied.
- Membrane fouling of ultrafiltration would be different because of flocs performance.
- The different floc properties and membrane fouling with Al species were discussed.
- Al_b has the best benefit to alleviate the membrane fouling.

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ABSTRACT

Three species of aluminum coagulants mainly consist of mononuclear Al species (Al_a), medium polymeric species (Al_b) and colloidal species (Al_c) were prepared, separated and purified by organic solvent precipitation method. The effect of different Al species on coagulation performance and membrane fouling were investigated through the coagulation–ultrafiltration hybrid process. The influence of flocs characteristics were also studied to build the relation model between Al species coagulation and membrane fouling mechanisms. The results showed different Al species combined with humic acid (HA) in diverse ways feature distinct floc properties and membrane fouling. Al_a coagulant had better UV_{254} and dissolved organic carbon (DOC) removal efficiency. Furthermore, Al_a and Al_c were beneficial to form larger flocs with lower strength and looser structure, whereas Al_b was prone to form small flocs with higher strength and compact structure. Ultrafiltration experiments indicated that Al_b is the most effective Al species to alleviate membrane fouling.

1. Introduction

Ultrafiltration (UF) technology has been recognized as an attractive process for water treatment due to its ability of entrapping particles, colloids and microorganisms [1]. However, the main barriers of this technology are low removal efficiency of natural organic matters (NOM) and serious membrane fouling. Thus researchers focus on pretreatment prior to UF combined technology to improve the removal of NOM and reduce membrane fouling [2]. Nowadays, coagulation is used frequently before UF process, namely, coagulation/ultra-filtration (C-UF) combined technology. In this system, flocs were formed by instable colloids after addition of coagulants, and then absorb NOM. Meanwhile, the flocs were apt to be entrapped by membrane which would form cake layer and improve the filtration performance [3]. Wang et al. conducted C-UF experiments for removing NOM in water and found the combined technology is able to enhance the removal of DOC and UV_{254}. Moreover, it could reduce the formation of trihalomethanes (THMs) [4]. Hence, flocs formed by coagulation were the key to enhance the performance of membrane.

Many researchers focus on the relationship between membrane fouling and floc characteristics, such as floc size, fractal dimension and floc strength etc. [4,5]. For example, it is reported that the floc size and fractal dimension formed by PACl had impact on the reduction of membrane fouling. Waite et al. reported the affinity between floc properties (size and structure) and the permeability of the cake that accumulated on the ultrafiltration membranes [6]. Guan et al. stated floc size and fractal dimension were related with specific cake resistance [7]. Cho et al. believed that flocs with

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lower fractal dimension have loose and porous structure which can enhance membrane permeability [8]. Latterly, research began to focus on the relation among the floc strength, the ability of regrowth and membrane fouling [9,10]. Results imply that floc with good characteristics could enhance coagulation efficiency and reduce membrane fouling. So improvement of floc characteristics is one of the most important affects in the combined technology.

At present, as one of the most popular traditional coagulants, polyaluminium chloride (PACl) has been widely used in C–UF processes. PACl that composed of partially hydrolyzed products of Al(III) is superior to traditional Al salt coagulants in performance of particulate and higher organic matter removal efficiency [11]. In PACl, Al species were divided into three categories according to the size of their hydrolysis compound: mononuclear Al species (Al_a), medium polymeric species (Al_b) and colloidal species (Al_c). Previous research showed the different Al species feature distinct characteristic, and distribution of Al species is the important factor of coagulation performance and mechanism. Furthermore, flocs formed by different Al species could be predicated and departed from water through different mechanisms of charge neutralization or bridge. So researchers paid attention to the structures of three Al species and their coagulation efficiency. Yan et al. concluded that Al_b was the most effective species in coagulation process [12]. Xu et al. found that pre-hydrolyzed Al_{13} polycation ($[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$) had been confirmed to be correlated well with Al_b species, generally resulting in smaller but more compact HA flocs than the commonly used PACl [13]. Luan et al. concluded that Keggin-type Al_{30} $[(AlO_4)_2Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ is the highest charged polycation in hydrolytic polymeric Al and belongs to a new optimum Al coagulation species [14]. However, study on floc performance formed by three species coagulates and membrane fouling was not clearly enough. Moreover, the most efficient specie of C-UF combined technology is remaining indistinct. Intrigued by these sealed effects, we undertook systematic studies in the effect of Al species on coagulation performance and membrane fouling of C-UF process.

In this study, three species of Al salts were used in coagulation process to demonstrate the relationship between removal of HA-Kaolin raw water and floc properties. Then we chose the optimum project and discuss the relation between floc performance and membrane fouling.

2. Materials and methods

2.1. Preparation and purification of Al_a, Al_b and Al_c

All the reagents used in this experiment were of analytical grade. Al_a was prepared by adding 1.7884 g $AlCl_3{\cdot}6H_2O$ in 200 mL deionized water directly.

Al_b: High Al_b content of PACl was prepared before purification. Then Al_b specie was purified with ethanol-acetone precipitation method. The method could be found in the paper [13,15].

Al_c was prepared as follow: PACl was heated at 85 °C and stirred continually for 24 h. Then 48 h for curing, the PACl was purified by mixed methanol/acetone solvent (1:9).

2.2. Characterization and concentration calculation of Al species

Total Al concentrations (Al_T) were determined by EDTA complexometric method according to the National Standard of China Standard method (GB15892-1995). Al_a and Al_b species were analyzed with an UV-754 spectrophotometer (Precision Scientific Instrument Co. Ltd., Shanghai, China) by Ferron colorimetric method [16,17]. The concentration of Al_c was calculated by the equation:

$$Al_c = Al_T - Al_a - Al_b \quad (1)$$

The results of purification Al_b were shown in Table 1, which showed that the sample of number 4 was optimal and used for the following experiments.

The sample of number 4 was characterized with NMR spectra method to ensure the experiment accuracy [15]. The concentration of Al_b was calculated according to the that of Al_{13} due to its high correlation to Al_b [18]. NMR spectra of sample 4 (Fig. 1b) indicate there only Al_{13} specie peak and internal standard peak. The concentration of Al_{13} was 96.4% from formula (2), which is according to the result based on Ferron method. The more details can be found in literature [13].

$$Al_{13} = [(a_2/a_r \cdot C_r \cdot k)/C_T] \times 13 \times 100\% \quad (2)$$

where a_2 and a_r are the peak areas at 62.5 ppm and 80.0 ppm of chemical shift, respectively, and C_r is the concentration of internal standard, and C_T represents the sample concentration and k is the ratio of sectional area between capillary and sample cell.

The results of purified Al_c were shown in Table 2, Number 2 were used for the highest content of Al_c.

2.3. Coagulation experiments

2.3.1. Synthetic test water

HA stock solution was prepared as follows: 1.0 g of HA (Aladdin, Shanghai, China) and 0.4 g of NaOH (Tianjin Damao Co., Tianjin, China) was dissolved in 1000 mL deionized water. Kaolin stock solution was prepared as follows: 5.0 g Kaolin was dissolved into 800 mL deionized water with 30 min magnetic stirring, diluted to 1 L, then transfer into a 1 L measuring cylinder. After 30 min for standing, the upper 500 mL was drawn out for using. The synthetic test water was prepared by diluting 10.0 mL of HA stock solution with deionized water to 1 L. Kaolin (Kermel Co., China) was added to adjust turbidity 15.0 ± 0.5 NTU. The property of this synthetic test water was as following: UV_{254} = 0.29 ± 0.03, TOC = 5.24 ± 0.50 mg/L, pH = 8.3 ± 0.1, Turbidity = 15.0 ± 0.5 NTU, Zeta = −16 ± 2 mV.

2.3.2. Coagulation procedure

Coagulation experiments were operated by jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China). Coagulation procedure contains 4 steps: 1. Rapid mix 200 rpm lasting for 30 s to form sample uniformly; 2. Coagulant of certain dose was added, keep 200 rpm for 90 s; 3. Slow mixing speed of 40 rpm for 15 min to make particles gathering each other; 4. The solution settling for 20 min.

After sedimentation, the supernatant was carefully withdrawn from about 2 cm below the surface for analysis. The turbidity was measured with turbidimeter (Hach 2100P Co., US). Zeta potential was tested by a Zetasizer (Malvern 3000Hsa, UK). Dissolved organic carbon (DOC) and UV_{254} absorbance were measured after the samples filtered through 0.45 μm fiber membrane. DOC values were measured by TOC analyzer (TOC-VCPH, Shimadzu, Japan) and

Table 1
Purification of the distribution of the Al_b species (Al_T 0.25 mol/L, B = 2.4, 85 °C).

Number	20% ethanol/acetone (mL)	Al_a%	Al_b%	Al_c%
1	0	9.76	90	0.24
2	160	6.04	78.96	15
3	60	5.85	72.88	21.27
4	100	0	100	0
5	160	1.3	81.82	16.88