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Comparison of epichlorohydrin–dimethylamine with other cationic organic polymers as coagulation aids of polyferric chloride in coagulation–ultrafiltration process

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HIGHLIGHTS

- DAM–ECH achieved highest turbidity and DOC removal.
- PAM achieved optimum membrane performance.
- R_{ef} was the dominant part of R_f that mainly determined by floc properties.

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ABSTRACT

Epichlorohydrin–dimethylamine (DAM–ECH) copolymer was acquired by polycondensation of hazardous reagents: epichlorohydrin (analytical reagent, A.R.) and dimethylamine (A.R.) with ethanediamine (A.R.) as cross-linker. Its coagulation and membrane performance as coagulation aid of polyferric chloride (PFC) was evaluated by comparing with other two cationic coagulation aids: poly dimethyl diallyl ammonium chloride (PDMDAAC) and polyacrylamide (PAM) in humic acid–kaolin (HA–Kaolin) simulated water treatment. Firstly, optimum dosages of PFC&DAM–ECH, PFC&PDMDAAC and PFC&PAM were identified according to their coagulation performance. Then their impacts (under optimum dosages) on membrane fouling of regenerated cellulose (RC) ultra-membrane disc in coagulation–ultrafiltration (C–UF) process were reviewed. Results revealed that small addition of DAM–ECH was the effective on turbidity and DOC removal polymer. Furthermore, in the following ultra-filtration process, external membrane fouling resistance was demonstrated to be the dominant portion of the total membrane fouling resistance under all circumstances. Meanwhile, the internal membrane fouling resistance was determined by residual of micro-particles[1] that cannot be intercepted by cake layer or ultrafiltration membrane.

1. Introduction

Humic substances (HSs) are widespread natural organic matters (NOM) in water bodies which derived from decomposition of organic substances [1,2]. Existing of HSs not only introduces brown color but also jeopardizes human health by forming hypertoxic disinfection byproducts such as trihalomethanes [3]. As one of HSs fractions, high concentrations of humic acid (HA) in drinking water resources have been proved to be the pathogeny of many diseases, such as blackfoot disease and apoptosis of fibroblasts [4–6]. Nowadays, treatment processes like coagulation, photocatalysis, and membrane filtration have been extensively applied in water treatment for HA removal in water bodies [7–13]. Thereinto, coagulation has been recognized as one of the traditional techniques for its cost saving and feasibility in water treatment [9,14]. As a dominated factor, efficiency of coagulant would be essential for coagulation process. Traditional inorganic coagulants such as ferric and aluminum salts are cheap but not as effective as organic polymers. Meanwhile, dosage of organic polymer must be limited in portable water treatment for its exorbitant price and

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[1] Micro-particles: Humic acid molecules, Kaolin and micro-floc formed in coagulation process that cannot be intercepted by cake layer or ultrafiltration membrane.

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possible toxicity to human body [15–18]. It has been proved by our previous studies that the combination of polyferric chloride and epichlorohydrin–dimethylamine (DAM–ECH) could ensure quality of reclaimed water by remarkably improve NOM removal efficiency and reduce the dosage of coagulants [16,19,20]. Nonetheless, its effect combining with PFC on HA–Kaolin water treatment has not been compared with other cationic organic polymers. Thus, two other cationic organic polymers, poly dimethyl diallyl ammonium chloride (PDMDAAC) and polyacrylamide (PAM) were selected as coagulation aids of PFC. Meanwhile, ultra-filtration has been widely used in water treatment processes to enhance water quality by reducing particle and NOM. But there are several inherent problems which limit the application of ultra-membrane filtration (UF) process, such as the relatively large pore size of ultra-membrane comparing with dissolved organic molecules, which means UF process cannot intercept most of dissolved organic matter (DOM) existing in water resources [7,21,22]; moreover, unavoidable flux decline caused by membrane fouling would enormously rise the operation cost by increasing energy consumption and reducing the service life of ultra-membrane [11,23].

Hence, coagulation process has been recognized as one of the most effective pretreatments of UF process, because it could significantly reduce the drop of filtration flux by forming large and strong flocs that could be intercepted by ultra-membrane [16,24,25]. So coagulation–ultrafiltration (C–UF) hybrid system was adopted in this study for further understanding the internal connection of coagulation and membrane fouling. Dosage of PFC and coagulation aids would be optimized by evaluation of the turbidity UV_{254} (ultraviolet absorbance at 254 nm) and DOC (dissolved organic carbon concentration) reduction rate. UV_{254} has been used as indicator of humic substances and aromatic organic matter (containing C=C and C=O). Previous studies revealed that according to SUVA[2] result, 70–80% of DOC removal was hydrophobic humic substances with high UV_{254} absorption value [9,23]. In other words, tendencies of UV_{254} and DOC removal should be consistent. SUVA from this research varied from 7 to 8 $L(mg\,m)^{-1}$ to around 1 $L(mg\,m)^{-1}$, which means coagulation process removed most of hydrophobic organics, and hydrophilic organics became dominated in coagulated water. Furthermore, floc properties were monitored during the coagulation process. Membrane fouling of different coagulated water was evaluated and analyzed in detail by comparing the total membrane fouling resistance and the distribution of external/internal membrane fouling resistance (Fig. 1). The coagulation and membrane performance of these polymers would be further studied under other NOM conditions in the following research before application in real water treatment, which would be valuable for application of organic polymers as coagulation aids in potable water treatment and further understanding of membrane fouling mechanism to reduce operation cost of C–UF process.

2. Methods and materials

2.1. Chemicals

$FeCl_3{\cdot}6H_2O$ and Na_2CO_3 were applied for preparation of PFC (10 g/L as Fe^{3+}) with basicity value 0.5 (mole ratio of $[OH^-]/[Fe^{3+}]$). The detailed procedure was as follows: firstly, 24.1330 g of $FeCl_3{\cdot}6H_2O$ and 2.3658 g of Na_2CO_3 were completely dissolved in deionized water respectively, and then Na_2CO_3 solution was slowly dripped into $FeCl_3{\cdot}6H_2O$ solution. After that 2.5583 g of $Na_2HPO_4{\cdot}12H_2O$ was dosed into the mixture as a stabilizer. Finally, the mixture was diluted to constant volume of 1 L and stirred until the solution was pellucid.

DAM–ECH copolymer was synthesized by polycondensation of epichlorohydrin (analytical reagent, A.R.) and dimethylamine (A.R.) with ethanediamine (A.R.) as cross-linker. Polycondensation reaction was conducted in a round bottom flask (250 mL) with four necks. In addition, a mechanical stirrer, a thermometer, a dropping funnel and corresponding glass spigots were employed for the synthesis process. Certain dose of epichlorohydrin was filled into the round bottom flask and temperature of the flask was kept at 10 °C in a thermostated water bath. Then dimethylamine was dripped into the flask using dropping funnel constantly, as the mixture was stirred throughout the process. At last, cross-linker ethanediamine was dosed into the flask under steady stirring [16]. The viscosity of synthesized DAM–ECH was 280 mPa s, and its solid content was 79.48%. The mole ratios of reagents were as follows:

n(epichlorohydrin):n(dimethylamine) = 1.5:1;
n(ethanediamine):n(epichlorohydrin&dimethylamine) = 3:100.

PDMDAAC with 40% solid content intrinsic viscosity of 1.02 dL/g was obtained from Binzhou Chemical Co., China. Cationic PAM with MW of 8000 kDa were purchased from KOLON Industry, Korea.

2.2. Test water

Humic acid stock solution was obtained by diluting 1.0 g of HA[3] (Aladdin, Shanghai, China) and 0.40 g of NaOH (Tianjin Damao Co., Tianjin, China) into deionized water; then the mixture was transferred into a 1000 mL volumetric flask and diluted to 1 L after 30 min stirring. Kaolin stock solution was prepared using kaolin purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. 5.0 g of kaolin was dissolved into 1.0 L deionized water and then followed by 30 min of sedimentation. Then upper 500 mL was drawn out as kaolin stock solution. HA–Kaolin simulated water was prepared as follows, 10 mL of the HA stock solution was diluted into 1.0 L of tap water, and appropriate kaolin stock solution was added to adjust the initial turbidity to 15.0 ± 0.5 NTU. Characteristics of raw water prepared as mentioned above were shown as follows: UV_{254} = 0.320 ± 0.010, DOC = 3.55 ± 0.03 mg/L, pH 8.32 ± 0.02.

2.3. Design of coagulation experiments and analytical methods

Jar test was designed to test the coagulation efficiencies of coagulants and optimize their dosages in this study. All jar tests were repeated for two all more times to ensure the repeatability of the experimental results. A program-controlled flocculator, with six cylindrical plexiglass beakers of 1.5-L and six flat paddle impellers for each breakers (ZR4-6, Zhongrun Water Industry Technology Development Co., Ltd., China) was applied to implement jar tests. Upper 200 mL of mixture was drawn from each breaker for turbidity, UV_{254}, and DOC tests. Turbidity of water sample was measured by a 2100P turbidimeter (Hach, USA) and zeta potential was measured by Zetasizer 3000Hsa (Malvern Instruments, UK) at room temperature (around 20 ± 1 °C). Water sample was filtered through a 0.45 μm fiber membrane before DOC analysis by Shimadzu TOC-VCPH analyzer and UV_{254} measurement by UV-754 UV/VIS spectrophotometer (Precision Scientific Instrument Co., Ltd., Shanghai, China)

[2] SUVA: (UV254/DOC) × 100, SUVA > 4 $L(mg\,m)^{-1}$ means high content of hydrophobic organics; SUVA < 2 $L(mg\,m)^{-1}$ indicates that approximate 80% of organics are hydrophilic.

[3] Molecule weights of HA: Approximate 87% of HA applied in this research was around 2000 Da; meanwhile some of these HA molecules were over 10,000 Da, but the mean value was rather low.