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Impacts of epichlorohydrin–dimethylamine on coagulation performance and membrane fouling in coagulation/ultrafiltration combined process with different Al-based coagulants

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HIGHLIGHTS

- Coagulation performance could be enhanced by using DAM-ECH with Aluminum-based coagulant.
- DAM-ECH gave rise to larger, stronger floc with more loose structure.
- Membrane fouling could be mitigated by using DAM-ECH in C-UF progress.
- Cake layer resistance (R_c) played an important role in total resistance (R_t).
- DAM-ECH aid affected the value of R_c and R_p.

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ABSTRACT

Two kinds of aluminum-based coagulants and epichlorohydrin-dimethylamine (DAM-ECH) were used in the treatment of humic acid-kaolin simulated water by coagulation-ultrafiltration (C-UF) hybrid process. Coagulation performance, floc characteristics, including floc size, compact degree, and strength were investigated in this study. Ultrafiltration experiments were conducted by a dead-end batch unit to implement the resistance analyses to explore the membrane fouling mechanisms. Results showed that DAM-ECH aid significantly increased the UV_{254} and DOC removal efficiencies and contributed to the formation of larger and stronger flocs with a looser structure. Aluminum chloride (Al) gave rise to better coagulation performance with DAM-ECH compared with poly aluminum chloride (PACl). The consequences of ultrafiltration experiments showed that DAM-ECH aid could reduce the membrane fouling mainly by decreasing the cake layer resistance. The flux reductions for PACl, Al/DAM-ECH (dosing both Al and DAM-ECH) and PACl/DAM-ECH (dosing both PACl and DAM-ECH) were 62%, 56% and 44%, respectively. Results of this study would be beneficial for the application of PACl/DAM–ECH and Al/DAM–ECH composite coagulants in water treatment processes.

1. Introduction

Humic substance is a dominating portion of natural organic matter (NOM) in most of potable water resources, and it can lead to the formation of disinfection byproducts (DBPs) in the disinfection unit during the drinking water treatment (Zhang and Minear, 2002, 2006). DBPs have been regarded as a significant issue since they are closely related to certain types of cancers (Richardson, 2003; Richardson et al., 2007; Liu and Zhang, 2014). In recent decades, researchers have paid more and more attention to the removal of humic substances. Microfiltration (MF) and Ultrafiltration (UF) are the two most widely used technologies in feed water treatment (Jacangelo et al., 1997). UF can remove almost particles and colloids and exhibit significant advantages in controlling microorganisms and pathogens. However, the major obstacle to widespread application of UF is the membrane fouling which is considered to be caused by the accumulation of the retained matter on the membrane surface (Sutzkover-Gutman et al., 2010). Previous research has shown that using coagulation as the pretreatment to lower the NOM concentration can observably reduce membrane fouling and improve water quality of UF unit (Yu et al., 2014). Therefore, coagulation-ultrafiltration hybrid process has been extensively

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used to control membrane fouling.

In the coagulation progresses, aluminum-based coagulants such as aluminum chloride (Al) and poly aluminum chloride (PACl) were commonly used in drinking water treatment for its low cost and high efficiency. Moreover, previous studies indicated that some organic polymeric chemicals could be used as coagulant aids to improve the NOM removal, increase floc size and reduce membrane fouling of UF unit (Huang et al., 2015). Xu et al. (2015) reported that polydimethyldiallylammonium chloride (PDMDAAC) aid with high positive charge could essentially increase the humic acid (HA) removals. Yu et al. (2010) reported that using polyacrylamide as a coagulant aid also increased floc size.

In this research, epichlorohydrin-dimethylamine (DAM-ECH) was chosen to be the coagulant aid of aluminum chloride (Al) and poly aluminum chloride (PACl). DAM-ECH has both hydrophobic groups (methyl groups and the backbone chain) and hydrophilic groups (positively charged quaternary amines) which can coagulate colloid particles and suspended solids in feed water through neutralization and adsorption/bridging (Sun et al., 2015). The dosage of ferric-based coagulants may cause high residual turbidity and corrosion of the equipment because of the characters of ferric ion. Previous researchers have investigated the coagulation performance and membrane fouling of polyferric chloride/DAM-ECH. While the effect of the aluminum-based coagulants combined with DAM-ECH on the coagulation performance remains unclear (Sun et al., 2015). In this circumstance, this paper was focused on (1) the influences of DAM-ECH aid with different aluminum-based coagulants on HA-Kaolin water on coagulation processes; (2) floc properties and ultrafiltration performance under different coagulation conditions; (3) mechanism of membrane fouling caused by pre-coagulated water with and without DAM-ECH aids.

2. Material and methods

2.1. Raw water and coagulant preparation

The water sample was prepared by humic acid (Aladdin, Shanghai, China) and Kaolin (Kermel Chemical Reagent Co., Ltd., China) as previously described (Sun et al., 2015) (see Table 1). Two aluminum-based coagulants, Al and PACl with a basicity value (B, OH^-/Al molar ratio) of 2.0 were used in this study and the preparation details can be found in other papers (Rong et al., 2013).

The DAM-ECH copolymer was acquired by polycondensation of epichlorohydrin (A.R.) and dimethylamine (A.R.) with ethanediamine (A.R.) as cross-linkers. First, added suitable amount of dimethylamine into a round bottom flask (250 mL) with four necks. Second, epichlorohydrin was added dropwise under mechanical stirring at 10 °C. At last, cross-linker ethanediamine was dosed into the flask under 65 °C and reacted for 5–7 h which could supply larger amount of reaction sites and change the synthesized copolymer molecular from linear type to brunch chain type (Yang et al., 2012). The intrinsic viscosity of synthesized DAM-ECH was 850 mPa s and the cationic degree was 3.5 mmoL/g. The optimal mole ratios of raw materials were as follows:

n (epichlorohydrin):n (dimethylamine) = 3:2;

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

Table 1
Characteristic parameters of raw water.

Characteristic	Turbidity (NTU)	pH	UV_{254}	DOC (mg/L)	Zeta potential (mV)
Value	15.0 ± 0.5	8.3	0.29 ± 0.05	5.0 ± 0.2	−15.0 ± 0.5

Table 2
Characteristic parameters of RC membrane.

Characteristic parameters	Values
Nominal molecular weight limit (kDa)	100
Filter area (cm^2)	41.8
The filter diameter (mm)	76

2.2. Coagulation-ultrafiltration (C-UF) process

Jar tests were conducted in 1.0 L cylindrical plexiglass beakers using a programmable jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China). The running program was set as follows: first, raw water was stirred at 200 revolutions per minute (rpm) for 30 s to be uniform mixed. Then coagulants and coagulants aid were added, followed by another stirring period of 200 rpm for 1.5 min. After the rapid mixing stage, 15 min of slow stirring period at 40 rpm was introduced to allow floc growth. Finally, the water was let stand for 20 min to settle the flocs in the jar. Turbidity and zeta potentials (ZP) were measured using a 2100P turbidimeter (Hach, USA) and a Zetasizer Nano (Malvern Instruments, UK) respectively at room temperature. The sample was filtered through a 0.45 μm membrane to measure the UV absorbance at 254 nm (UV_{254}) and dissolved organic carbon (DOC) using UV-754 UV/VIS spectrophotometer and TOC-VCPH analyzer separately.

After coagulation process, the coagulated water was filtered through a hydrophilic disc ultrafiltration membranes which were purchased from EMD Millipore Corporation (CAT. NO. PLHK07610). A jar-scale dead-end UF setup with magnetically stirred cell (MSC050, Mosu, China) was used to perform the UF process with the constant pressure (0.8 MPa). The permeate flux were recorded by a computer that connected to the balancer. The characteristic parameters of the membrane were shown in Table 2 and the schematic of the setup could be found in a previous study (Xu and Gao, 2012).

2.3. Floc characterizations

2.3.1. On-line measurement of floc size

A laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK) was used to monitor the evolution of flocs during coagulation. The details have been reported in other papers (Li et al., 2014).

2.3.2. Floc strength, recovery ability and structure analyses

After the floc had reached their steady stage, 5 min of breakage period and 10 min of recovery period were conducted to investigate the floc strength and recovery abilities. Strength factor indicated the ability of flocs to resist the shear force and the recovery factor indicated the recovery ability of flocs after breakage. The breakage and recovery factors could be calculated by the following equations (Peter Jarvis and Parsons, 2005) (Wei et al., 2010):

$$\text{Strength factor } \left(S_f\right) = \frac{d_2}{d_1} \times 100 \quad (1)$$