Desalination 357 (2015) 163–170

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Coagulation performance and membrane fouling of polyferric chloride/epichlorohydrin–dimethylamine in coagulation/ultrafiltration combined process

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HIGHLIGHTS

- Coagulation performance of PFC/DAM–ECH was better than PFC at proper dosage.
- Adding sequence of coagulants was critical for HA removal and floc properties.
- Better removal efficiencies of HA by PFC/DAM–ECH achieved at acidic condition.
- DAM–ECH improved the floc properties by enhancing charge neutralization mechanism.
- Effects of DAM–ECH on floc properties reduced membrane fouling.

ARTICLE INFO

Article history:
Received 18 July 2014
Received in revised form 26 November 2014
Accepted 28 November 2014
Available online 2 December 2014

Keywords:
PFC/DAM–ECH
Coagulation
Floc properties
Membrane fouling

ABSTRACT

Polyferric chloride (PFC) and epichlorohydrin–dimethylamine (DAM–ECH) with different PFC (as Fe^{3+})/DAM–ECH mass ratios (MR) and dose methods were used in the treatment of humic acid–kaolin (HA–kaolin) simulated water under different pH conditions. Coagulation performance, floc characteristics and membrane fouling of PFC/DAM–ECH in coagulation–ultrafiltration (C–UF) process were investigated in this study. Results showed that the optimum coagulation performance was achieved when PFC dose was 15 mg/L with PFC/DAM–ECH MR of 2:1 under pH 6.0. Opposite adding sequence (DAM–ECH/PFC) would reduce UV_{254} (ultraviolet adsorption at 254 nm) and DOC (dissolved organic carbon) removal efficiency. Addition of DAM–ECH on the basis of PFC produced larger and stronger flocs with better regrowth ability. Proper dosage of DAM–ECH under certain coagulation condition could achieve the best coagulation performance and keep the UF membrane operating under a preferable status. Results of this study would be beneficial for application of composite coagulant PFC–DAM–ECH and DAM–ECH as coagulant aid in water treatment processes.

1. Introduction

Existence of natural organic matter (NOM) in potable water resources is hazardous to human health [1,2], of which humic substances dominate in most of potable water resources [3]. In recent decades, removal of NOM has drawn more and more attention in modern water treatment. As a commonly used coagulant, polyferric chloride (PFC) has been widely applied in water treatment. Moreover, many researchers found that better coagulation performance can be achieved by combining a metal coagulant with an organic polymer. Addition of cationic DAM–ECH polymer on the basis of PFC provided high charge density to improve the charge neutralization performance of PFC, which could remarkably improve its coagulation efficiency [4]. Thus, combination of metal coagulant and organic polymer in water treatment has drawn more and more attentions in recent years. Meanwhile, ultrafiltration (UF) has been applied worldwide for further reduction of particle concentration and NOM in drinking water [5]. Thus, combining of coagulation with ultrafiltration, also known as C–UF hybrid process, is becoming more popular for high removal of NOM in water bodies [6]. But as an inherent problem in all membrane systems, membrane fouling caused by NOM would severely impact membrane performance in ultrafiltration [7]. Previous studies show that even a rather low concentration of residual common organic macromolecules after pretreatment will cause significant membrane fouling which would tremendously increase operating pressure requirement and finally lead to much higher cost in practical treatment [8]. So to achieve the best treatment

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http://dx.doi.org/10.1016/j.desal.2014.11.031
0011-9164/

efficiency, not only the optimum dosage of coagulants, but also membrane fouling must be considered.

In this research, epichlorohydrin–dimethylamine (DAM–ECH) was chosen to be coagulant aid of polyferric chloride (PFC), which as cationic polyelectrolyte had both hydrophobic groups (methyl groups and backbone chain) and hydrophilic groups (positively charged quaternary amines). Both of these groups can be used to coagulate suspended solids and colloid particles in wastewater through charge neutralization and adsorption/bridging [9]. PFC and DAM–ECH had been applied in treatment of dye waste water by some researchers. But as DAM–ECH residual was still a risk for drinking water, they haven't tried application of DAM–ECH in drinking water treatment. In this study, treatment effect of PFC and DAM–ECH on HA–Kaolin water was observed in terms of coagulation performance and membrane fouling in coagulation–ultrafiltration hybrid process of humic acid (HA)–kaolin water under different coagulation conditions such as different PFC (as Fe^{3+})/DAM–ECH mass ratios, dosage sequences (PFC/DAM–ECH, PFC added before DAM–ECH; DAM–ECH/PFC, DAM–ECH dosed first) and various pHs. Furthermore, floc properties formed under different coagulation conditions, such as floc size, growth/regrowth ability, and strength, were also monitored and analyzed. Membrane fouling of pre-coagulated water by PFC and DAM–ECH with different dosage methods was also assessed during ultrafiltration. In addition, zeta potential of different coagulated water samples was monitored to recognize the coagulation mechanisms.

2. Materials and methods

2.1. Preparation of coagulants

PFC (Fe^{3+} = 10 g/L) with basicity value 0.5 (mole ratio of $[OH^-]/[Fe^{3+}]$) was prepared using two analytical reagents: $FeCl_3 \cdot 6H_2O$ (CAS no: 10025-77-1) and Na_2CO_3 (CAS no: 497-19-8). First, 24.1330 g of $FeCl_3 \cdot 6H_2O$ and 2.3658 g of Na_2CO_3 were dissolved in deionized water, separately. Then Na_2CO_3 solution was slowly dripped into $FeCl_3 \cdot 6H_2O$ solution before 2.5583 g of $Na_2HPO_4 \cdot 12H_2O$ (CAS no: 10039-32-4) as stabilizer was dosed into the mixture. Finally, the mixture was made volume to 1 L and stirred until the solution was clear.

DAM–ECH copolymer was acquired by polycondensation of epichlorohydrin (A.R.) and dimethylamine (A.R.) with ethanediamine (A.R.) as cross-linker. Polycondensation reaction producing DAM–ECH copolymer 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 used during the synthesis process. Certain dose of epichlorohydrin was filled into the round bottom flask and the temperature of flask was kept at 10 °C by 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 [9].

2.2. Raw water

Humic acid stock solution of this study was prepared as follows: 1.0 g of HA (Aladdin, Shanghai, China) and 0.40 g of NaOH (Tianjin Damao Co.,Tianjin, China) were diluted into deionized water under continuously stirring for at least 30 min; Then the mixture was transferred into a 1000 mL volumetric flask and diluted to volume (1 L).

Kaolin stock solution for adjusting turbidity of simulated water was prepared as follows: 5.0 g of kaolin (Tianjin Kermel Chemical Reagent Co., Ltd., China) was dissolved into 1.0 L deionized water, and then upper 500 mL was drawn out for later use after 30 min of sedimentation.

HA–kaolin simulated water of this study was prepared by diluting 10 mL of the HA stock solution into 1.0 L of tap water. Initial turbidity of the raw water was adjusted to 15.0 ± 0.5 NTU using a kaolin stock solution. Characteristics of raw water are presented in Table 1.

Table 1
Raw water characteristics.

Characteristics	Turbidity (NTU)	pH	UV_{254}	DOC (mg/L)	zeta potential (mV)
Value	14.5–15.5	8.30–8.32	0.12–0.30	4.0–5.5	−15.0–16.0

2.3. Jar tests

Jar tests were conducted to determine the coagulant dose, the effect of pH and dose sequences on coagulation behaviors. They were carried out on a flocculator with cylindrical plexiglass beakers (1.2 L) (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China). The running program was set as follows: first, raw water (1.0 L) was stirred at 200 revolutions per minute (rpm) for 0.5 min; then, certain dose of PFC or DAM–ECH was added, followed by another stirring period of 200 rpm for 0.5 min; following the third period, rapid stirring at 200 rpm for 1.5 min for coagulant/flocculant dispersion; after that in the fourth period, the stirring speed was reduced to 40 rpm for floc growth, which lasted for 15 min; finally in the fifth stage, the stirring speed was set to zero for flocs to settle in the jar for 20 min. At the end of jar test, about 200 mL of supernatant water was withdrawn from each jar as test water sample for further measurements (e.g. turbidity, UV_{254}, DOC, zeta potential). Turbidity and zeta potential of water sample were respectively measured using a 2100P turbidimeter (Hach, USA) and a Zetasizer 3000Hsa (Malvern Instruments, UK) at room temperature (around 25 °C). The test water samples were filtered through 0.45 μm fiber membrane before DOC analysis using a Shimadzu TOC-VCPH analyzer and UV_{254} (absorbance at 254 nm) measurement using a UV-754 UV/VIS spectrophotometer.

2.4. Floc properties

The evolution of flocs during coagulation was monitored by a laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK). The samples were monitored through the optical unit of the Mastersizer where a loop was formed by drawing water from and back into the jar using a peristaltic pump on the 5 mm internal diameter return tube at a flow rate of 2.0 L/h. Mastersizer 2000 was connected to a computer to collect data every 30 s during the process. Mean floc size ($d_{0.5}$) was chosen as the indicator of average floc size. In order to investigate floc strength and recoverability, rapid stirring (150 rpm, 200 rpm, 250 rpm and 300 rpm) for 5 min was applied for floc breakage after floc growth, followed by slow stir (40 rpm) for 15 min for floc regrowth.

2.4.1. Floc breakage and recovery factor

Floc breakage and recovery factors are normally used to reveal the breakage and re-growth of flocs, in which breakage factor indicates the ability of flocs to resist the shear power and recovery factor shows the capacity of flocs after breakage period. The breakage and recovery factor of flocs can be calculated by the following equations which have been used in other studies [10–13]:

$$\text{Breakage factor}\ (\%) = \frac{d_2}{d_1} \times 100$$

$$\text{Recovery factor}\ (\%) = \frac{d_3 - d_2}{d_1 - d_2} \times 100$$

d_1, d_2, and d_3 stand for floc sizes in the steady phase before breakage, after the breakage period and after the re-growth to another steady phase, respectively. Larger breakage factors means that the flocs are stronger and more difficult to be broken, meanwhile larger recovery factor expresses better regrowth ability of flocs.