Chemical Engineering Journal 287 (2016) 225–232

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Effect of reused alum-humic-flocs on coagulation performance and floc characteristics formed by aluminum salt coagulants in humic-acid water

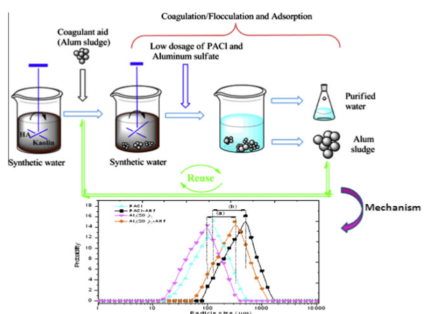
Yongpeng Xu *, Ting Chen, Fuyi Cui *, Wenxin Shi

State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China
School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

HIGHLIGHTS

- The recycling alum sludge as a new coagulant aid was used to enhance removal of HA.
- Charge neutralization, entrapment and adsorption are dominant in dual-coagulants.
- Addition of AHF improved flocs with large size and fractal dimension.
- The regrowth of breakage flocs facilitated the further removal of the organic matters.
- The regenerated flocs could be an adsorbent to further remove organic matter.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 September 2015
Received in revised form 6 November 2015
Accepted 8 November 2015
Available online 1 December 2015

Keywords:
Humic acid (HA)
Alum-humic-floc (AHF)
Dual coagulant
Floc characteristics
Coagulation mechanism

ABSTRACT

Recycled alum sludge was used as a coagulant aid with poly aluminum chloride (PACl) and aluminum sulfate ($Al_2(SO_4)_3$) in the evaluation of coagulation behavior and floc structure of humic acid (HA)-rich solutions. The alum sludge, alum-humic-floc (AHF), was produced under coagulation jar test conditions. The dual coagulants, PACl–AHF and $Al_2(SO_4)_3$–AHF, were obtained by dosing AHF 30 s after traditional coagulants were added. Due to the lack of apparent changes in zeta potential values, physical adsorption was likely the primary mechanism by which AHF removed organic matter. Charge neutralization was not the only dominant mechanism for the dual coagulants in the coagulation process; entrapment and adsorption also played significant roles. The addition of AHF played a significant role in improving floc structure and developing flocs with larger sizes and fractal dimensions, especially at the steady state stage. Floc breakage was also shown to induce the release of organic matter into solution, regardless of the coagulant type, and re-growth processes facilitated the additional removal of organic matter. The regenerated flocs with larger sizes and more compact structure could be used as adsorbents to further remove organic matter.

1. Introduction

Coagulation and flocculation processes followed by a treatment step for sedimentation, flotation, and sand and membrane filtration are mostly used for the removal of particles and organic matter in drinking water treatment processes. The removal of organic matter is very important to reduce coagulant and disinfectant

* Corresponding authors at: State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China. Tel.: +86 451 86283001.

E-mail addresses: xuyongpeng@hit.edu.cn (Y. Xu), hit_cuifuyi@hotmail.com (F. Cui).

http://dx.doi.org/10.1016/j.cej.2015.11.017
1385-8947/

demand and the potential for forming disinfection by-products and carcinogenic substances [1,2]. Furthermore, the existence of natural organic matter (NOM) in drinking water could inhibit catalytic or biological iron and manganese removal and result in color, taste and odor problems [3]. Humic acid (HA) is one of the most common types of NOM in the environment. HA is not typically removed from water due to its higher molecular weight and complicated oxygen-containing functional groups [2]. Therefore, the effective removal of NOM has become increasingly important in modern water treatment systems.

The type of coagulant used is believed to play a significant role in coagulation processes. Alumic-based coagulants have been more widely used than ferric-based coagulants, likely because alumic coagulants have superior NOM removal capacity, and ferric coagulants create color problems in water [4]. However, large dosages of alum salts has also been suspected to be harmful to humans and other living organisms [5]. Consequently, increasing attention has been placed on identifying novel coagulants to satisfy the increasing demands for organic matter removal and lower coagulant dosage. Organic polymeric coagulants, such as polyacrylamide (PAM), have been used to improve water purification for several decades [6]. Additionally, composite coagulants have been assessed for their ability to remove organic substance [7]. Anionic polymeric bioflocculants have been combined with titanium tetrachloride ($TiCl_4$) and aluminum sulfate ($Al_2(SO_4)_3$) to form dual coagulants to significantly improve the removal efficiency of dissolved organic matter (DOC) [8,9]. It is most likely that the dual coagulants have the characteristics of the two components and improve the coagulation process. However, the additional chemical reagents increase production costs and may also have negative health effects. Thus, a lower coagulant dose is as important as the promotion of coagulant efficiency.

Alum sludge contains a large portion of insoluble alum hydroxides. To minimize drinking water treatment plant (DWTP) sludge waste, the sludge can be recycled. In our previous studies, we recycled coagulation sludge for use as low-turbidity raw water as an alternative treatment to enhance conventional coagulation efficiencies [10]. Guan et al. showed that the removal efficiencies of suspended solids (SS) and chemical oxygen demand (COD) in sewage could be improved by the addition of alum sludge [11]. Highly amorphous sludge contains a high density of micropores and could be used as a sorbent to absorb multiple types of heavy metals [12] or to complement the primary treatment process in waste water treatment [13]. Few investigations have directly recycled DWTP sludge in DWTP processes, perhaps due to stringent drinking water quality standards; harmful substances may accumulate over multiple cycles of DWTP sludge reuse. However, we have shown that alum sludge from DWTP removes NOM by physical adsorption mechanisms without requiring additional treatment processes.

The impact of coagulation mechanisms on floc size and the regrowth capacity of broken flocs have been discussed in a number of investigations. However, little attention has been given to changes in water chemistry during liquid–solid separations [14,15]. Previous studies have reported that dissolved organic carbon may be released under certain conditions. Tseng and Edwards [16] speculated that organic matter removal is partly reversible with increases in pH. As pH levels increase, metal hydroxide precipitate surfaces release adsorbed organic matter. Other studies have also concluded that pH may influence the release of DOC [17]. However, the role of floc breakage in triggering the release of bonds responsible for the incorporation of organic matter in floc aggregates remains unclear.

In this study, synthetic wastewater was prepared by mixing HA and kaolin in deionized water. Alum-humic-floc (AHF) sludge was produced under coagulation jar test conditions. Dual coagulants, PACl–AHF and $Al_2(SO_4)_3$–AHF, were prepared from traditional coagulants (PACl and $Al_2(SO_4)_3$) and used in the treatment of the synthetic water. First, the traditional coagulants were added and rapidly mixed in the coagulation process. After 30 s, AHF was added as a coagulant aid. The coagulation performances of the dual coagulants in flocculation–sedimentation process were studied through a series of comparisons. Floc characteristics, such as size and fractal dimension, are generally considered the primary physical properties that influence the efficiency of unit processes in water treatment plants. Floc size, size distribution and fractal dimension as functions of coagulation time were measured by an on-site recognition system. The relative release of organic matter was determined by comparing changes in the amount of organic matter that was incorporated into the flocs before and after breakage and re-growth.

2. Materials and methods

2.1. Synthetic water

Kaolin clay (Tianjin, China) and humic acid (Shanghai, China) were used in preparing water samples. Kaolin clay was prepared by dissolving 50.0 g of kaolin clay in 1 L deionized water under continuous stirring for 24 h. After sedimentation for 1 h, an 800 mL aliquot of the supernatant was saved as a stock suspension of kaolin clay.

Ten grams of humic acid (Shanghai, Jufeng, China) were dispersed in 0.1 mol/L NaOH and mixed for 24 h by a magnetic stirrer. The suspension was filtered by a 0.45-μm fiber filter membrane. The pH of the filtered solution was adjusted to 7.5 using 0.01 mol/L NaOH or HCl, and the solution was diluted to 1000 mL in a measuring flask. The solution was stored in the dark. Tap water in Harbin, China has an alkalinity of 15 mg/L $CaCO_3$ and a pH of approximately 7.2. The HA–kaolin synthetic water was prepared by adding a specific amount of HA and kaolin stock solution into Harbin tap water. The properties of the synthetic water are shown in Table 1. During the experiments, the temperature of the synthetic water solution was 22 ± 2 °C.

2.2. Preparation of coagulants and AHF

Poly aluminum chloride (PACl; 28% Al_2O_3), with a basicity of 72.3%, was prepared at 1% concentration by dissolving 5 g reagent in 500 mL deionized water.

$Al_2(SO4)_3 \cdot 18H_2O$ was used in the experiment. Stock alum solutions were prepared at a concentration of 0.1 M in deionized water.

Synthetic water: The HA–kaolin synthetic water was prepared by adding a certain specific amount of HA and kaolin stock solution into Harbin tap water.

AHF: The HA–kaolin synthetic water was prepared by adding a specific amount of HA and kaolin stock solution into Harbin tap water. The turbidity and UV_{254} of synthetic water were 300 NTU and 0.125 cm^{-1}, respectively. The PACl was used as a coagulant at 15 mg/L. Jar tests were performed to simulate a conventional

Table 1
Characteristics of the synthetic water and AHF.

	Synthetic water	AHF
Turbidity (NTU)	10.0 ± 0.5	7420 ± 95
Zeta potential (mV)	−19.03 to −21.56	−22.3 to −33.73
TOC (mg/L)	4.5 ± 0.5	3.2–4.25
DOC (mg/L)	3.36 ± 0.5	3.0–4.17
UV_{254} (cm^{-1})	0.22 ± 0.05	0.2–0.31
pH	7.2 ± 0.10	7.10–7.82
Total Al (mg/L)	–	33.49–76.21
Solid content (w/w%)	–	1.5–2.33