Effects of different coagulants on flocculation performance and floc properties in northwest China raw water treatment
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ABSTRACT
The water of northwest China, characterized by low turbidity, low temperature, and micro-pollution, has posed difficult problems for water treatment plants. This study deployed a pilot-scale grid flocculation system to treat melt water from the Qinghai-Tibet Plateau in northwest China. A range of traditional coagulants were used on the low temperature, low turbidity, and micro-polluted melt water, to investigate the effect of coagulant types on flocculation performance and floc properties. Flocculation performance varied, depending upon the coagulant used. Turbidity and organic matter were removed with the greatest efficiency by polyaluminum chloride (PAC), followed by polyaluminum ferric chloride, followed by aluminum sulfate (alum). At a PAC dosage of 25 mg/L, the settled water’s residual turbidity was lower than 1 NTU, meeting the Chinese national water-quality standard. Floc fractal dimensions of the three coagulants initially decreased, and then increased as the flocculation process yielded larger particles. This suggested that low turbidity could significantly affect the floc fractal dimension. Studying floc size distribution indicated that floc size in the grid flocculation tank was relatively uniform; the floc size distribution of PAC was the narrowest. The results could be used to inform operations of the Xining water treatment plant.

Key words | floc size distribution, fractal dimension, grid flocculation system, low temperature, low turbidity, melt water

INTRODUCTION
Coagulation and flocculation are well-established processes for removing colloids (or suspended particles) and natural organic matter in conventional water treatment plants (WTPs) (Simate et al. 2012). Coagulation and flocculation effectiveness, however, is greatly affected by many factors, including temperature, coagulant type and dosage, and raw water quality (Lee & Choo 2014).

Surface water temperature can be lower than 5 °C for about 2–3 months in winter at places situated at the same latitude as northwest China. The water quality of these areas is usually low in turbidity and high in organic matter and has caused some unpleasant issues in northern Chinese WTPs (Deng et al. 2011; Lou et al. 2012). At low temperature, the metal hydrolysis reaction rate, coagulation rate, and particle settling rate are slow, and the mixing velocity gradient is poor (Deng et al. 2011). At low turbidity, insufficient particles can decrease collision potential during coagulation, leading to the inability to form large and compact flocs (Lou et al. 2012). Moreover, the micro-polluted water can lead to the formation of disinfection by-products, which are thought to be carcinogens, during the disinfection process (Valencia et al. 2014).

China’s 2007 Standards for Drinking Water Quality (GB5749-2006) have created challenges for the water quality of Xining WTP, which uses polyaluminum chloride (PAC). The raw water of Xining WTP is the melt water of Qinghai-Tibet Plateau in northwest China, which is characterized by low temperature, low turbidity, and
olfication. The PAC dose has had to be set higher than 50 mg/L to meet the national water-quality standard, as well as the internal guideline of 1.0 NTU for settled water. However, the high PAC dosage may result in elevated concentrations of residual Al in treated water. This high residual Al can cause several treatment problems, including increased turbidity and reduced disinfection efficiency. In addition, ingesting high concentrations of Al may lead to adverse human health effects (Kimura et al. 2015).

To increase coagulation performance in treating water with low turbidity, low temperature, and micro-pollution, a variety of new coagulants have been tested (Jarvis et al. 2012; Lou et al. 2012; Ng et al. 2013; Hussain et al. 2014; Nateghi et al. 2014). At a public utility, however, water quality security must be the top priority, whereas testing new coagulants presents certain challenges and risks. Therefore, using traditional coagulants such as PAC, aluminum sulfate (alum), and polyaluminum ferric chloride (PAFC) are good options for the Xining WTP. Conversely, new flocculation systems may increase coagulation efficiency for low turbidity, low temperature, and micro-polluted raw water. Grid flocculation systems, based on micro-eddy flocculation theory, are increasingly attracting attention for water treatment in China (Liem et al. 1999). The advantages of these systems over more traditional types include their uniform energy distribution, better flocculation efficiency, and lower flocculation time (Xie et al. 2008).

Floc properties (i.e. floc size, fractal dimension, and floc size distribution) significantly influence removal efficiency and cost, and are affected by coagulant type and dosage. Larger flocs with compact structures settle faster than smaller flocs with loose structures. A narrower floc-size distribution is preferable (Ehlers et al. 2012).

In previous research, coagulation using metal salts in conjunction with organic polymers was conducted at high particle concentrations and normal temperature using jar test apparatus, mechanical flocculation tanks, and folded plate flocculators (Jarvis et al. 2012; Yu et al. 2013; Hussain et al. 2014). However, few studies have investigated how pilot-scale grid flocculation systems would perform when treating source water with low temperatures, low turbidity, and micro-pollution. Consequently, the purpose of this study was to investigate the influence of various traditional coagulants on flocculation performance and floc properties when treating raw water from northwest China using a pilot-scale grid flocculation system. Flocculation performance was described in terms of turbidity, chemical oxygen demand (CODMn), and total organic carbon (TOC) removal efficiency. Floc characterizations considered floc size, fractal dimension, and size distribution. Coagulation mechanisms were also considered.

**MATERIALS AND METHODS**

**Materials**

To conduct the pilot-scale tests, we collected source water from the Heiquan reservoir, a typical northwest reservoir filled with melt water from the Qinghai-Tibet Plateau. The raw water was sampled between February and April 2012, and had the following characteristics: temperature was 2.1–8.7 °C, turbidity was 2.78–5.16 NTU, pH was 8.01–8.23, CODMn was 2.85–3.58, TOC was 3.96–5.42 mg/L, and zeta potential was −19.86 to −17.54 mV. This raw water was characterized as being of low temperature, low turbidity, and micro-polluted.

The coagulants used in the study, alum (with Al2O3 content of 17%), PAC (with Al2O3 content of 50%), and PAFC (with Al2O3 content of 26%–30% and Fe2O3 content of 1%–5%) were produced by Zhengzhou Future Environmental Protection Technology Co. LTD, in Henan, China. All the tested solutions (each 50 g/L) were prepared using tap water. All study reagents were of analytical grade, except where specified.

**Pilot-scale tests**

The study was conducted using a continuous pilot-scale treatment system in Xining WTP; the pilot system had mixing, flocculation, and sedimentation functions. Raw water was pumped through the plant at 10 m³/h. After peristaltic pumps pumped coagulants into the front-end of a static mixer, the raw water was mixed for 30 s. The mixed water was then flocculated for 12 min in a grid flocculation system containing 12 small shafts. The flocculation process was divided into two stages. Seven group grids were installed in each of the first four shafts; five group grids were installed in each of the remaining eight shafts. The
sedimentation tank’s surface load was 8.64 m$^3$/h. For each pilot-scale test, the plant was run in continuous operation for 4 h.

**Analytical methods**

Turbidity and zeta potential were measured using a turbidimeter (2100P, Hach Co., USA) and a zetasizer (Zetasizer2000, Malvern, UK), respectively. COD$_{Mn}$ was measured using an acidic potassium permanganate method (Lou et al. 2012). TOC was measured using a TOC analyzer (multi N/C 2100S, Analytic Jena, Germany). The floc size and fractal dimension were directly monitored during the flocculation process using a particle size distribution analyzer (Mastersizer 2000, Malvern Instruments, UK). Floc size distribution was also detected using a particle size distribution analyzer that had been used for a previous study (Wang et al. 2009).

**RESULTS AND DISCUSSION**

**Effects of various coagulants on flocculation performance**

**Zeta potential and residual turbidity**

Alum, PAC, and PAFC dosages ranging from 0 to 50 mg/L were added to flocculate the raw water. As Figure 1 shows, coagulant type and dosage significantly impacted zeta potential and residual turbidity.

Zeta potential gradually increased with an increase in coagulant dose, reversing from negative to positive charge when the dosage increased further (Figure 1(a)). The PAC system generated more positive zeta potentials than PAFC or alum, demonstrating that PAC neutralized more charge than other coagulants. The zeta potentials of PAC, PAFC, and alum switched from positive to negative charge as dosages were increased to 25, 30, and 40 mg/L, respectively.

Figure 1(b) shows that PAC was superior to PAFC and alum in turbidity removal across the dosage range. PAC and PAFC achieved an optimum turbidity removal efficiency at a dosage of 35 mg/L; the optimum dosage of alum was 45 mg/L. At the optimum dosage, the residual turbidity of PAC in settled water was much lower than with other coagulants. Furthermore, at a PAC dosage of 25 mg/L, the residual turbidity in settled water was lower than 1 NTU, meeting the national water-quality standard.

Past research has demonstrated that the speciation of Al-based coagulants, such as monomeric species (Al$_{m}$), medium polymer species (Al$_{p}$), and colloidal or solid species (Al$_{c}$), plays an important role in determining flocculation performance (Yang et al. 2010). The Al$_{p}$ was highly charged; correlating well with turbidity removal. PAC contained much more Al$_{p}$ compared to PAFC at the same dose, leading to higher turbidity removal. According to Yu et al. (2013), alum solubility was very low at low temperatures. Because PAC and PAFC were pre-hydrolyzed products, the effect of
temperature on the hydrolysis rate was negligible. As such, turbidity removal with alum was the lowest. At an even higher dosage, colloids and particles re-stabilized due to the formation of positively charged particles, thereby increasing residual turbidity.

The PAC dosage needed to meet the national water-quality standard at the Xining WTP (50 mg/L) was much higher than the dosage used in this study (25 mg/L). This suggested that the grid flocculation tank improved turbidity removal more than the current mechanical flocculation tanks used to treat raw water from this part of China. Energy distribution in the grid flocculation tank was more uniform than in the mechanical flocculation tank, leading to higher flocculation efficiency. In addition, the grown flocs were easily broken in the mechanical flocculation tank, so the grid flocculation tank needed less coagulant to achieve the same turbidity removal.

**Organic matter removal**

In addition to turbidity, organic matter removal efficiency, expressed as COD$_{\text{Mn}}$ and TOC, was also used to evaluate flocculation performance. Figure 2 shows the variation of residual COD$_{\text{Mn}}$ and TOC in settled water.

The residual COD$_{\text{Mn}}$ of each coagulant visibly decreased at first and then increased slightly with the coagulant dose increase (Figure 2(a)). Removal efficiencies of PAC and PAFC were much higher than those of Alum. The residual COD$_{\text{Mn}}$ at optimal dosages of PAC, PAFC, and Alum was 2.12, 2.16, and 2.43 mg/L, with corresponding removal rates of 35.37%, 31.86%, and 24.30%, respectively. This result was possible because of the high charge-neutralization ability of PAC and PAFC. Generally, COD$_{\text{Mn}}$ was adsorbed by grown flocs and then removed with the turbidity in subsequent solid–liquid separation processes (Yu et al. 2010). In the case of PAC and PAFC, turbidity removal was more efficient than with alum; thus, the residual COD$_{\text{Mn}}$ of alum was higher than with the other two coagulants.

TOC removal experienced an initial downward trend, followed by a slightly upward trend as coagulant dosage increased (Figure 2(b)). The major decrease in the residual TOC of all three coagulants after precipitation was at the dosage of 40 mg/L. At a lower dosage, PAC and PAFC had a better decontamination effect than alum, due to its higher positive charge. Polymer coagulants contain more intermediate polymers, and alum mainly exists in hydroxide form in neutral media after being added to raw water (Yang et al. 2010; Ng et al. 2015). When alum dosage increased to 40 mg/L and above, the residual TOC of alum was close to PAC and PAFC. The high TOC removal of alum was rooted in the sweep flocculation process, because the concentration was close to saturation level (Yang et al. 2010). The residual TOC of PAFC was lower than PAC when the dosage increased above 40 mg/L. This can be explained by PAFC ingredients, which include pre-hydrolyzed aluminum and ferric chloride, which possess advantages over PAC and iron coagulants.

**Figure 2** | Effect of coagulant dose on organic matter removal: (a) residual COD$_{\text{Mn}}$ and (b) residual TOC measured in settled water, respectively.
Effects of various coagulants on floc properties

Floc formation processes of different coagulants

Figure 3 compares floc size and fractal dimension variation in the floc formation process. Alum, PAC, and PAFC dosages were 45, 35, and 35 mg/L, respectively, which were the optimum dosages of each coagulant for turbidity and organic matter removal.

We found three phases in the floc formation process, consistent with previous studies (Wang et al. 2009; Yu et al. 2013), with all three coagulants: lag phase, swift growth phase, and steady-state phase (Figure 3(a)). In the lag region, coagulant fully mixed with raw water, and then began to contact particles. Floc did not grow much and floc size varied little. In the swift growth region, floc size increased to form large flocs. Flocculation curves show that floc size no longer increased in the steady-state region. The lag time of alum was the longest, because low temperatures slowed down the alum endothermic hydrolysis rate. In contrast, because PAC and PAFC were pre-hydrolyzed products, the effect of temperature on the hydrolysis rate was negligible. After the lag phase, floc sizes quickly increased with all three coagulants, but floc growth rates and final sizes were different. With PAFC, flocs grew to the largest size with the fastest grow rate; the size of the formed PAFC floc was about 480 μm. Compared to PAC and PAFC, the floc formed by alum was the smallest with the longest growth time. The alum flocs reached the steady-state region at 11 min, and the final floc size was about 340 μm.

Figure 3(b) shows that the floc fractal dimension with the three coagulants initially decreased and then increased with flocculation time. This result was inconsistent with previous studies (Wang et al. 2011; Yu et al. 2013), which showed the floc fractal dimension increasing with coagulation time. This inconsistency may be because of low turbidity. At low turbidity, fewer primary particles form large and compact flocs at the beginning of the flocculation process; without this floc formation, primary particles, which have a large fractal dimension, made up the main ingredient in the system. When flocculated for more than 2 min, particles rapidly aggregated and formed into large flocs as the result of the shear condition. This led to a marked decrease in fractal dimensions. As flocculation time continued, the fractal dimension increased, because the inner pores of large flocs were filled by small but compact particles or clusters. The PAC flocs had the largest fractal dimension, followed by PAFC and alum. This means that PAC formed the most compact flocs with the largest density. However, Wang et al. (2009) found that humic acid flocs formed by alum had the largest fractal dimension. This inconsistency may be due to the low temperature, which caused more irregular alum floc structures with smaller fractal dimension.

Influence of coagulant type on floc size distribution

Residual turbidity was mainly attributable to small flocs and particles. If there were many small particles in the sample,
then the resulting average floc size could be large. Consequently, floc size distribution in the flocculated water was studied at the optimum coagulant dosage. The results are shown in Figure 4.

The floc sizes created by the three coagulants ranged from approximately 80 to 1,000 μm (20–1,200 μm at Xining WTP), indicating that flocs created in the grid flocculation tank were relatively uniform. There were two possible reasons for this. Firstly, the grid flocculation tank was developed based on micro-eddy flocculation theory. Energy distribution was uniform, because many small eddies dissipated a large portion of the energy. Furthermore, the turbulence intensity of the flow was relatively high due to the multi-layer grid installed in the shaft (Liem et al. 1999). Unstable bonded particles were destroyed through particle collision and flow shear, limiting floc growth and increasing compactness.

The floc size distribution peaks with the three coagulants were visibly different. Alum, PAC, and PAFC peaks were approximately 350, 440, and 480 μm, respectively, consistent steady-state floc size in Figure 3(a). The volume percentage of alum flocs around 350 μm was 5.27%, while the volume percentages of PAC and PAFC flocs were 7.12% and 5.91%, respectively. This demonstrated that the volume percentage of the median-size flocs with PAC was higher than PAFC or alum. As a result, the floc size distribution of PAC was narrower. This could be explained by the flocculation mechanisms; in addition to charge neutralization, strong adsorption and bridging played an important role in PAC flocculation processes.

**CONCLUSIONS**

The grid flocculation system provided better flocculation performance and floc properties than a mechanical flocculation tank in treating the study’s raw water. The residual turbidity of the grid flocculation tank was much lower, and the flocs created in the grid flocculation tank were relatively uniform. The coagulant PAC showed greatest removal efficiency for turbidity and organic matter, followed by PAFC, followed by alum. When PAC dosage was 25 mg/L, the residual turbidity in settled water was lower than 1 NTU, meeting the national water-quality standard. The floc fractal dimensions of the three coagulants initially decreased and then increased as particle size increased during flocculation. PAC produced a narrower floc size distribution. The pilot-scale test results could be used to inform future designs and operations of the Xining WTP to improve the water quality.

**REFERENCES**


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