Natural organic matter (NOM) removal in a typical North-China water plant by enhanced coagulation: Targets and techniques

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ABSTRACT

Seasonal coagulation objectives for a typical North-China water treatment plant with micro-polluted and high alkalinity source waters are proposed in this paper. These are based on a yearlong data collection period where raw water characteristics, trihalomethanes formation potential (THMFP) and coagulation features were investigated using a jar test procedure, resin absorption and ultrafiltration fractionations. Three approaches beyond simply increasing the coagulant dose were used to achieve optimized coagulation. One is coagulation by adjusting the pH of the raw water when metal salt coagulants (FeCl_3 and AlCl_3) are used. At pH levels of about 5.0 for FeCl_3 and about 5.8 for AlCl_3 , the highest removal of natural organic matter (NOM) was obtained, which is twice that without pH control. The second is enhanced coagulation through coagulant optimization based on raw water characteristics. A high efficient composite polyaluminum chloride (HPAC) coagulant was developed for the water taking the advantages of polyaluminum chloride (PACl) and other additives. HPAC exhibited 30% more efficiency than AlCl_3 , FeCl_3 and polyaluminum chloride (PACl) in dissolved organic carbon (DOC) removal and was also very effective in turbidity removal. The third is enhanced softening with coagulant addition. Higher removal of NOM is achieved by enhanced softening with coagulant addition conditions as compared with conventional coagulation at natural pH. Especially with PACl addition, it can enhance the formation of $\text{Mg}(\text{OH})_2$ precipitate and remove NOM efficiently at a relatively lower pH range ($\text{pH} < 10$). By this approach, the pH for enhanced softening can be decreased significantly into a practical operation pH range for high-hardness water at a treatment plant.

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1. Introduction

Coagulation and flocculation are important steps in the treatment of water for drinking purposes, allowing the removal of particles and natural organic matter (NOM). Historically, most coagulation processes were primarily designed for particle and turbidity removal. Only some plants, especially those having to treat highly colored water, were primarily designed to remove NOM. NOM can cause many problems such as odor, taste, color, transportation of hydrophobic contaminants and bacterial regrowth in the distribution systems. It is now well recognized that NOM in drinking water can react with oxidative chemicals during treatment processes, resulting in the formation of trihalomethanes (THMs), haloacetic acids (HAAs), and a lot of other halogenated disinfection by-products (DBPs) [1].

The US Environmental Protection Agency (USEPA) has established maximum contaminant levels for the sum of four THMs and five HAAs at 80 and 60 $\mu\text{g L}^{-1}$, respectively in US drinking waters and has mandated that water utilities remove NOM as a means to reduce DBP precursors [2]. Enhanced coagulation and enhanced softening were selected by USEPA as the stage 1 treatments of choice because it is effective for the removal of total organic carbon (TOC) and can be implemented at most water utilities using existing treatment processes [2]. The approach includes two steps. Step 1 defines the percentage TOC removal by the plant based on the raw water TOC and alkalinity levels. If it is technically unfeasible to meet the TOC removal requirements in stage 1, the plant operators can follow the second step of the D/DPB rule for alternative performance criteria. In step 2, jar testing is required to assess TOC removal. For enhanced coagulation, alum (or an equivalent dose of ferric coagulant) is added in 10 mg L^{-1} increment until the pH is lowered to a target pH value (based on the alkalinity of the raw water). The TOC removal is then plotted versus coagulant dose and the 'point of diminishing return' is defined as the dose wherein the last 10 mg L^{-1}

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addition of alum, or equivalent dose of other coagulant, results in less than 0.3 mg L^{-1} removal of TOC is then used as an alternative minimum TOC removal criteria. For enhanced softening, plants that remove more than 10 mg L^{-1} Mg hardness as CaCO_3 are proposed to be exempted from the enhanced softening requirements in the step 1 by the USEPA [2].

Applying increased dosages of coagulants and the control the raw water pH by addition of acid or base are two common options to enhance NOM removal. However, both of these methods have some disadvantages, such as increasing the corrosive tendency of the water and treatment costs [2–4].

With rapid industrial development and economic expansion, drinking water sources in China have become ubiquitously polluted by organic contaminants. Chinese governments and communities recognize the importance of safe drinking water and are making great efforts to ensure its safety. This study is part of these efforts, which aims to improve current water treatment performance by coagulation optimization. Typical water sources in North-China were used to conduct this study. The main objectives were as follows: (1) determine the water quality characteristics of drinking water sources in North-China; (2) determine the coagulation characteristics of the waters and the optimized coagulation criteria for the water; and (3) demonstrate efficient measures to improve NOM removal by coagulation.

2. Materials and methods

2.1. Materials

All the reagents used were of analytical grade, except those otherwise specified. The two coagulants, aluminum chloride (AlCl_3) and ferric chloride (FeCl_3) used in bench scale tests were reagent grade (Chemical Reagent Co., Tianjin, China). The FeCl_3 (with Fe_2O_3 content of 40%), AlCl_3 , NaSiO_3 , and polydiallyldimethyl ammonium chloride (PDADMAC) used in pilot-plant trials were made by a local company (Tianjin Tianshui Water Cleaning Agent Co., China). Polyaluminum chloride (PACl) and a novel composite polyaluminum chloride (HPAC) (both with 10% Al_2O_3 content) were produced by a company (Beijing Wanshui Water Cleaning Agent Co., China) using a technique developed in our laboratory. PACl was produced by forced aluminum hydrolysis with alkali addition; the basicity (OH/Al molar ratio) is about 1.6. HPAC was prepared from PACl and other organic and inorganic additives such as active silicates and PDADMAC [5,6].

2.2. Jar and pilot-scale tests

Jar tests were performed with 1 L of raw water in 1.4-L beakers with a sampling port located 3 cm below the water surface. A programmable jar testing apparatus (Daiyuan Jar Test instruments, China) was used with the following procedure: addition of coagulant followed by 30 s rapid mixing at 300 rpm ($G = 172.1 \text{ s}^{-1}$), 2 min rapid mixing at 250 rpm ($G = 134.4 \text{ s}^{-1}$), 10 min flocculation at 40 rpm ($G = 11.3 \text{ s}^{-1}$) and 20 min settling. Treated water samples were taken after settling for later analyses. The pH was adjusted (if needed) by predetermined amount of HCl or NaOH, which was dosed 30 s before adding coagulant, during rapid mixing period. Coagulant dosages were measured using a calibrated pipette.

Pilot-scale tests were performed with two parallel systems, including coagulation, flocculation, dissolved air flotation, and sand filtration. The flow rate of each system was controlled at $5 \text{ m}^3 \text{ h}^{-1}$. The coagulation process was carried out using the following conditions, rapid mixing ($t = 1 \text{ min}$ and $G = 756 \text{ s}^{-1}$) and two-stage flocculation (in each stage, $t = 9 \text{ min}$ and $G = 91.5 \text{ s}^{-1}$). The surface loading rate of flotation was $11 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$, the recycle ratio was

10% and the saturator pressure was 400 kPa, residence time was 126 s. The depth of the sand filtration bed was 2.7 m and the filtration rate was 7.86 m h^{-1} . The sand filter medium was sand of 400 nm average diameter. The details of the pilot-plant have been previously reported [5,6].

2.3. Analytical methods

Total organic carbon (TOC) was analyzed using a Phoenix 8000 system (Tekmar-Dohrman Co., USA). Dissolved organic carbon (DOC) was analyzed after filtration through a $0.45 \mu\text{m}$ membrane. UV_{254} was measured by a spectrophotometer (UV-VIS 8500, China) after filtration through a $0.45 \mu\text{m}$ membrane. Turbidity was measured using a 2100N Turbidimeter (Hach, USA). pH was measured by a PHS-3C (Shanghai, China) pH meter, which was calibrated daily. Alkalinity, THMPF and chemical oxygen demand (COD_{Mn}) were measured by standard methods [7]. DOC was characterized using resin absorption and ultrafiltration (UF) fractionation methods, as described elsewhere [8].

3. Results and discussion

3.1. Water characteristics

3.1.1. Water quality

The source water for a typical northern China water treatment plant, Jieyuan Water Treatment Plant (WTP) was selected for this study. The source water for Jieyuan WTP changes seasonally. In the rainy seasons, summer and autumn, the source water is from the Luanhe River (LW). The Luanhe River is a local river running through industrial and residential areas. In the dry seasons, spring and winter, the Luanhe River is short of water and the plant takes in downstream water from the Yellow River (YW). The Yellow River is one of the two largest rivers in China. It runs through several geological areas from west to east of China.

The quality of the source water of Jieyuan WTP has changed regularly with season in the past three years, as exemplified by the daily water quality reports in one year shown in Fig. 1 (provided by the water company). The alkalinity was generally about 110 mg L^{-1} as CaCO_3 , and for YW, it was as high as 200 mg L^{-1} as CaCO_3 . The pH was up to 8.1. Turbidity and algae were found to be strongly dependent on temperature. The increase of turbidity in summer and early autumn was mainly due to algal blooms during those periods.

Based on the source water quality trends, one year could be divided into six different periods, i.e. (1) low temperature and turbidity: Yellow River water (LTTY, December and January); (2) spring Yellow River water (SprY, from February to April); (3) early summer Yellow River water (ESumY, latter April and early May); (4) early summer Luanhe River water (ESumL, from May to July); (5) high temperature and algae: Luanhe River water (HTAL, from July to October); and (6) autumn Yellow River water (AutY, October and November).

3.1.2. NOM characteristics

NOM in LW and YW were characterized using resin adsorption and UF fractionation methods. Partial results are shown in Fig. 2.

The fraction with a molecular weight of less than 10 kDa is more than 80% of the DOC in LW and YW. Particularly in LW, the DOC with molecular weight less than 1 kDa is the greatest fraction, which accounts for about 60% in Jun LW. While in YW, the DOC with molecular weight in the range of 1–10 kDa is the greatest fraction. Although the percentage of hydrophobic DOC is highest in Nov YW, as high as 60%, which is less than the ordinary value of more than 70% [8–10]. The data suggests that the water in North-China is polluted by hydrophilic and low molecular weight DOC.

Fig. 1. Characteristics of raw water for North-China water plant (divided into six water periods): (1) low temperature and turbidity: Yellow River water (LTTY, December and January); (2) spring Yellow River water (SprY, from February to April); (3) early summer Yellow River water (ESumY, latter April and early May); (4) early summer Luanhe River water (ESumL, from May to July); (5) high temperature and algae: Luanhe River water (HTAL, from July to October); and (6) autumn Yellow River water (AutY, October and November).

3.1.3. THMFP of NOM

The THMFP of YW in April is shown in Fig. 3. The DOC with low molecular weight has higher THMFP (Fig. 3a). Fig. 3b shows that not only the hydrophobic acid but also the hydrophilic have higher THMFP. The result shows that if the organic is hydrophilic and low molecular weight organic pollution is very likely to have higher THMFP, thus it could pose health issue

of the formation of DBPs in disinfection process with Cl₂ [11,12].

3.2. Seasonal variation of coagulation feature

Coagulation of the North-China water was studied during a year period and the results using the coagulant FeCl₃ in the six

Fig. 2. Comparison of NOM by (a) ultrafiltration and (b) resin absorbent in the Yellow River water (YW), hydrophobic basic and neutral (HoB&N), hydrophobic acid (HoA), weakly hydrophobic acid (WHoA), and hydrophilic (Hi).

water periods are shown in Fig. 4. The coagulation performance exhibited seasonal influences. LW was easier to treat than YW in terms of both UV_{254} and turbidity removal. For YW, the coagulation performance changed with season also. Higher temperatures resulted in higher coagulation efficiencies in UV_{254} removal. Higher UV_{254} removal from raw waters in different periods occurred in the following sequence: AutY, ESumY > SprY > LTTY. Although the optimal dosages for turbidity removal are the same (about 0.04 mM) for all raw waters, the residual turbidity changes seasonally. For LW, although the raw turbidities differ greatly, residual turbidities could reach almost the same low. While for YW, residual turbidities changed greatly in different seasons, and more efficient removal occurred for SprY and AutY.

From Fig. 4, we can see that the dosage for turbidity removal is less than that for UV_{254} removal. In natural water, the dosage of coagulant for organic matter removal is determined by the anionic charge of dissolved organics, which must be neutralized or partly neutralized. The historical measure to determine coagulant dosage based on turbidity is not satisfactory, and at which the removal of NOM may not be adequate.

UV_{254} removal is affected by many factors, particularly alkalinity, temperature and NOM characteristics.

Many researchers have found that for high pH water with lower alkalinity, the NOM is removed more efficiently [13,14]. LW is of lower alkalinity than YW and the NOM in it was removed more efficiently. The reason that alkalinity is an important factor influencing the performance of coagulation could be explained by the alkalinity in controlling the pH of coagulation after coagulant addition, and

further in controlling the hydrolyzed species of metal coagulants. The higher the alkalinity, the further the extent of the hydrolysis process, formation of larger polymers and more precipitation that occurs. These are not necessarily beneficial for maximizing NOM removal [6].

The temperatures affect the concentration of OH^- present for metal salt hydrolysis and the hydrolysis kinetics of metal salts [15]. The performances of three traditional coagulants were compared at different seasons and it was found that pre-hydrolyzed aluminum chloride could improve the efficiency of coagulation, especially for NOM removal at various temperatures. At low temperature, the removal of UV_{254} by PACl was not affected significantly, in contrast to $AlCl_3$ and $FeCl_3$ (data not shown in this paper).

Although the COD_{Mn} did not change obviously in the year (about 3–5 $mg\ L^{-1}$), the change in NOM character shows great different in coagulation performance [8].

3.3. Coagulation targets

Enhanced coagulation of North-China water was studied, based on the USEPA jar test protocol [2] using the coagulant aluminum chloride ($AlCl_3$). The results for the water periods, ESumL and AutY, are shown in Fig. 5. The dosage of $AlCl_3 \cdot 6H_2O$ is shown in Fig. 5 was transformed to $Al_2(SO_4)_3 \cdot 14H_2O$, based on Al ion.

A TOC removal efficiency of 20.8% at a dosage of 30 $mg\ L^{-1}$ for ESumL (arrow B), and 9.5% at a dosage of 18 $mg\ L^{-1}$ (arrow A) for AutY should be attained if the second step of the USEPA Enhanced

Fig. 3. Trihalomethanes formation potential of NOM fraction in the Yellow River water (YW): (a) ultrafiltration and (b) resin absorbent. Hydrophobic basic (HoB), hydrophobic neutral (HoN), hydrophobic acid (HoA), weakly hydrophobic acid (WHoA), and hydrophilic (Hi).

Fig. 4. The comparison of UV₂₅₄ and turbidity removal seasonally by coagulant FeCl₃ in Jar test: (a) residual turbidity and (b) UV₂₅₄ removal.

Coagulation standard was adopted, i.e. continue dosing to achieve a TOC removal of 0.3 mg L⁻¹ per increasing 10 mg L⁻¹ coagulant (as shown as the line USEPA in Fig. 5). These percentages are very low, and USEPA Enhanced coagulation standard is not suitable for these kinds of high alkalinity and seriously polluted waters.

Fig. 5. The comparison of TOC removal by AlCl₃ for AutY and ESumL referring the USEPA protocol jar test.

Fig. 6. The effect of pH on DOC removal by coagulants, FeCl₃, AlCl₃, PACl and HPAC at dosage 0.08 mM for the Yellow River water in autumn.

For ESumL, when the dosage was increased up to 50 mg L⁻¹ Al₂(SO₄)₃ · 14H₂O (arrow D), the TOC removal reached 31.0%. With further increases in the dosage, the TOC removal increased only slightly. For AutY, when the dosage was 23 mg L⁻¹ (arrow C), the residual TOC was still decreasing slowly, but the residual turbidity began to increase, indicating that re-stabilization had occurred (data not shown). As the dose increased up to more than 35 mg L⁻¹, the removal rate of TOC slowed and the residual turbidity increased significantly.

There are two ways to optimize coagulant dosing. One is to select the lowest dose to achieve aims in residual TOC, turbidity, color and so on; the other is the dose that gives the highest removal efficiencies for the lowest coagulant dosage. According to the latter, the optimum for TOC removal should be 31.0% at the dosage of 50 mg L⁻¹ for ESumL, and 16.8% at the dosage of 35 mg L⁻¹ for AutY. It should be noted that the above does not mean that these doses should be used in water plant, and the removal efficiency of TOC refers to the portion of NOM that could be removed by coagulation economically.

Many researchers have found that the UV₂₅₄ absorbance correlates to the concentration of NOM in water, especially the aromatic carbon content [11,16]. This fraction of NOM can more easily react with oxidants to produce DBPs. Edzwald et al. [11] and Weishaar et al. [17] found UV₂₅₄ is a good surrogate parameter for monitoring organic matter and disinfection by-products formation potential. The measurement of UV₂₅₄ is quick and easy for operation and is suitable for routine monitoring at a WTP.

Based on the results shown in Fig. 2, the seasonal coagulation targets for NOM removal for the North-China water plant are set with parameter UV₂₅₄. The corresponding parameter of turbidity is also given for reference, in Table 1.

3.4. Strategies for NOM removal

The concentration of OH⁻ in water should determine the degree of hydrolysis and hydrolysis products of metal salt coagulants, AlCl₃ and FeCl₃ that affect performance of these coagulants in coagulation process [15,18]. The effect of pH on DOC removal by four typical coagulants FeCl₃, AlCl₃, PACl and HPAC in the pH range of 3–12 was investigated. The results at doses of 0.08 mM Al/Fe are shown in Fig. 6.

As shown in Fig. 6, the optimum pH for AlCl₃, PACl and HPAC is about 5.8, and the optimum pH for FeCl₃ is about 5.0. Especially for AlCl₃ and FeCl₃, these are very efficient for NOM removal at their optimum pH, but their performances can be affected significantly by pH. Those deteriorate obviously at neutral and basic pH range. However for some high alkalinity and pH waters, the pH is at about 7.5, even higher than 8.0, at which the efficiency of DOC removal would be very low.

Table 1

The seasonal coagulation aims for North-China water.

	Raw water					Traditional aims			Optimized aims		
	<i>T</i> (°C)	pH	Alkali. (mg L ⁻¹)	Turb. (NTU)	UV ₂₅₄	Dose (mM)	Turb. (NTU)	UV ₂₅₄ removal (%)	Dose (mM)	Turb. (NTU)	UV ₂₅₄ removal (%)
SprY	17.0	8.6	200	4.90	0.126	0.04	1.54	7.0	0.10	1.2	16.5
ESumY	22.5	8.49	194	5.46	0.139	0.04	2.23	5.0	0.14	1.7	20.0
ESumL	22.5	8.10	115	4.61	0.065	0.04	1.14	17.0	0.10	0.75	27.5
HTAL	25.6	8.18	115	8.76	0.069	0.04	1.60	20.0	0.12	0.8	27.0
AutY	13.0	7.72	185	7.87	0.108	0.06	1.96	17.5	0.12	1.0	22.5
LTTY	3.5	7.67	166	5.25	0.079	0.04	2.44	<5.0	0.10	2.4	15.0

As shown in Fig. 6, the effect of pH on DOC removal by HPAC and PACI as coagulant is less than metal salts because polymeric aluminum species pre-formed in HPAC and PACI are less affected by pH [14,19], especially for HPAC. The HPAC results are likely due to the nature of the polymerized Al species but also the presence of the synthetic cationic polymer which would not be affected by pH so should improve NOM removal relative to the standard PACI. Although they are less efficient than FeCl₃ and AlCl₃ in acid condition, they are more efficient in basic condition. Thus they are more efficient for waters with high pH/alkalinity such as North-China water.

With pH further increased to 11, NOM removal efficiency increased again. At which the process becomes enhanced softening

and the NOM is removed by co-precipitate of Mg(OH)₂ and coagulants.

As discussed above, for high alkalinity water, there are three strategies that can go beyond increasing coagulant dose to enhance NOM removal. These are coagulation using metal salts with pH control, coagulant optimization, and enhanced softening with coagulant.

3.4.1. pH control

pH control is a common technique applied to enhance NOM removal [2]. The effect of pH on DOC removal by coagulants FeCl₃, AlCl₃ for North-China source waters was investigated. The effect of pH and coagulant dose on DOC removal by FeCl₃ and AlCl₃ was

Fig. 7. The effect of pH and dose on NOM removal for the Yellow River water in autumn: (a) for coagulant FeCl₃ and (b) for coagulant AlCl₃.

Fig. 8. The comparison of TOC and turbidity removal by four coagulants AlCl₃, PACI and HPAC compared with traditional coagulants strategy in pilot-scale test for the Luan River water in summer.

Fig. 9. The effect of PACI on softening by NaOH for the Luan River water in winter.

shown in Fig. 7. It shows that adjusting pH before coagulation with coagulants $FeCl_3$ and $AlCl_3$ is a good measure to enhanced NOM removal, particularly with $FeCl_3$.

Unfortunately, pH control has some disadvantages [4]. The first is that it could increase the corrosive tendency of treated water. Secondly, the addition of acid and base for pH control would increase the operational costs. The third is that it would increase the complexity of water treatment operation and facility.

3.4.2. Coagulant optimization

The technique to treat high alkalinity and micro-polluted waters through coagulant optimization has been reported in a previous paper [6]. DOC and turbidity removal correlated well with the hydrolyzing behavior of the coagulants with the minimum solubility of $FeCl_3$ and $AlCl_3$ at pH 5.8 and pH 6.3, respectively. DOC removal was most efficient at a pH slightly lower than the pH of their minimum solubility because at this pH, the hydrolysis products of $FeCl_3$ and $AlCl_3$ are mainly medium polymers or monomers, which have a high ability to remove DOC by complexation and charge neutralization. PACI, one form of inorganic polymer flocculant, contains high level of charged polymeric Al hydrolysis products through pre-hydrolysis. The pre-formed medium polymer species (Al_b) are highly stable, even after being dosed into a high alkalinity and pH water [14,19]. The performance of PACIs in the treatment of high alkalinity water was investigated. DOC removal was correlated with Al_b content in PACI. However, it was observed that the flocs formed by Al_b are small, with low settling efficiency. When overdose levels are used particles may re-stabilize due to the formation of positively charged small flocs, and particularly when high content Al_b PACIs are used [18].

In the context of attempting to address the disadvantages of PACI, a new composite coagulant, HPAC (a modification of PACI that focuses on the efficient species of Al_{13} , etc., and in combination of large composite polymer coagulation aids such as active silicates and cationic organic polymer) was developed. These additives are

able to enhance both the charge neutralization and bridging properties of PACI [5].

Coagulation using HPAC for northern China waters was compared with three commonly used coagulants $FeCl_3$, $AlCl_3$ and PACI, during different seasons [6,8]. The results of pilot-scale tests with $AlCl_3$, PACI and HPAC were compared with the traditional coagulation strategy (a composite coagulant prepared using $FeCl_3$, $NaSiO_3$ [prepared before dosing in 1:1] and coagulant aid PDADMAC [$0.15\ mg\ L^{-1}$]) at natural pH about 8.0 are shown in Fig. 8. The coagulant dose was 0.04 mM Al/Fe. HPAC was the most efficient in both NOM and turbidity (by flotation) removal. Residual turbidity by HPAC was reduced to as low as 0.27 NTU after flotation and 0.15 NTU after filtration, being much lower than other coagulants.

Tests at pilot-scale and at full-scale have shown that particles and NOM are removed synergistically with HPAC as coagulant by sequential treatment processes including pre-ozonation, coagulation, flotation and sand filtration [6,8,20]. The residual Al is relatively low [21]. Coagulant optimization such as by HPAC application can be considered as an alternative option to enhance NOM removal from high alkalinity and micro-polluted waters.

3.4.3. Enhanced softening with coagulant

Softening is employed in drinking water treatment primarily for the removal of polyvalent metallic ions, principally calcium and magnesium. Previous research indicates that only limited NOM removal can be achieved during the conventional softening process [13]. Even the use of high doses of lime ($200\ mg\ L^{-1}$) may not be effective to remove DBP precursors due to electrostatic repulsion arising from the high negative charge density of humic substances and the negatively charged calcium carbonate dense crystalline surface [22]. Unlike calcium carbonate, magnesium hydroxide precipitates as positively charged particles with an amorphous structure and larger surface area [13]. It has been found that a small increase in the magnesium precipitation results in a significant NOM removal [23]. Systems that remove at least $10\ mg\ L^{-1}$ Mg hardness as $CaCO_3$ are proposed to be exempt from

the enhanced softening requirements of the USEPA [2]. However, for typical concentrations of magnesium in raw water supplies, the precipitation of magnesium hydroxide requires a high pH (above 11), a condition uncommon in water treatment practice. It is not an attractive choice for softening plants. Addition of coagulant (e.g. activated silica, ferric chloride and organic polymers) during softening has been proposed as an alternative to enhanced NOM and particle removal [24].

The treatment of organic-polluted high-hardness surface water by enhanced softening via precipitation using PACl, FeCl_3 and AlCl_3 has been investigated and reported in our previous paper [25]. It is found that higher removal of natural organic matter (NOM) (UV_{254} removal reaches about 50%) is achieved by enhanced softening with PACl addition as compared with conventional coagulation at natural pH or by softening alone without coagulation. PACl could enhance NOM removal more efficiently than FeCl_3 and AlCl_3 at relatively lower pH range ($\text{pH} < 10$).

The performance of DOC, turbidity, Ca^{2+} and Mg^{2+} removal with or without PACl under softening conditions by pH adjustment using NaOH was investigated with source water LW in winter. The results are shown in Fig. 9.

With just the softening process alone (without PACl), only minor DOC removal is observed at pH below 10. With the use of PACl under the softening conditions, higher DOC removal is observed as compared with softening alone. At pH above 10, DOC removal is increased for both cases. The residual turbidities are significantly lower for softening with than without PACl, in the pH range used.

PACl plays a complicated role in the process of NaOH softening. The PACl can increase the precipitation of magnesium through formation positively charged amorphous structure $\text{Al}_x\text{Mg}_y(\text{OH})_z$ [26], and the residual Mg is lower than that of the NaOH softening without PACl (Fig. 9c). At the same time, the pre-formed positive charged polymer in PACl is relative stable at high pH [19]. On one hand, the PACl can act as coagulant to remove particle and NOM at high pH in softening process. On the other hand, it can act as cationic organic polymer to reform the surface charge property of the product of CaCO_3 precipitate [27]. Under this circumstance, the pH for enhanced softening can be decreased significantly into the practical pH range for treatment plant operation.

The performance of enhanced softening is affected significantly by magnesium content in raw water [25]. For water with higher content of Mg^{2+} , the inflexion pH for favorable NOM removal is lower. It is of practical value for organic-polluted water with high content of magnesium to be treated by enhanced softening with PACl.

4. Conclusion

During this study, water qualities and coagulation features of typical North-China water were investigated, and some main conclusions can be drawn as follows.

(1) Source waters in North-China are seriously polluted by hydrophilic and low molecular weight organic matter, which is of high THMFP. It would pose serious health issue in disinfection process with Cl_2 , however it could not be removed favorably by traditional coagulation. Seasonal optimized coagulation targets for turbidity and NOM removals for North-China waters are proposed from Jar tests based on water characteristics.

(2) Three techniques that are beyond simple increasing of coagulant dose were demonstrated to achieve optimized coagulation. One is coagulation of the high alkalinity northern China water by adjusting the pH of raw water when metal salt coagulants (FeCl_3 and AlCl_3) are used. The second is enhanced coagulation through coagulant optimization based on raw water characteristics. The third is enhanced softening with coagulant addition, especially with coagulant PACl. This can enhance the formation of $\text{Mg}(\text{OH})_2$ precipitate at a relatively lower pH range ($\text{pH} < 10$).

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