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Coagulation optimization using ferric and aluminum salts for treating high algae and high alkalinity source water in a typical North-China plant

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ABSTRACT

Coagulation optimization using coagulants of ferric chloride ($FeCl_3$), polyaluminum chloride (PACl), and their combinations ($FeCl_3$/PACl) were evaluated through jar tests, by treating source water with high algal content (10–40 million cells/L) and high alkalinity (80–110 mg/L). The results indicated that when compared to single coagulants, the combined coagulants showed a superior coagulation performance in terms of turbidity, $UV_{254,}$ and algal removal. The optimal dosage was determined as 30–35 mg/L by using the combined PACl/$FeCl_3$ (1:2 by mass) and dosing PACl followed by $FeCl_3$. By adding the coagulant aids of polymerized diallyl dimethyl ammonium chloride (HCA) and polyacrylamide (FO4190), the floc sizes may enlarge up to 1.75–2.0 mm. Scanning electron micrographs showed that the coagulant combination can form a more compact reticular aluminum-ferric structure, and thus increased the settleability of the flocs. The combined coagulation was further evaluated in full-scale water treatment plants, confirming the improvement of the removal of algae, turbidity, and residual iron in the treated water.

Keywords: Combined coagulants; Coagulation optimization; High algae and high alkalinity source water; Luan River

1. Introduction

Eutrophication of surface water has emerged as a world-wide concern due to the increases in occurrence and severity. It is caused by the excessive nutrients, particularly phosphorus, discharged into bodies of water, resulting in the growth of algae. Algal bloom in source water can cause problems in drinking water treatment processes including producing undesirable tastes and odors, increasing coagulant demand, clogging filters, and forming disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). These DBPs have been found to be carcinogens. The US Environmental Protection Agency (USEPA) has established stringent regulations specifying the maximum contamination levels of 80 μg/L for THMs and 60 μg/L for HAAs [1]. Thus, the effective removal of algae and other natural organic matters (NOMs) is one of the major challenges for water utilities.

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Conventional coagulation is the most commonly used treatment processes for NOMs and particle removal. The coagulation effectiveness depends on various factors, including coagulant types and dosage, pH and particle properties. Metallic salt coagulants, such as aluminum and iron salts, are widely used in conventional coagulation [2]. The hydrolysis of mononuclear metallic salt in coagulation is rapid, and precipitates of metal hydroxide will soon be produced afterwards, making the coagulation hard to control [2,3]. The optimal pH level for alum coagulation and ferric-based coagulation were observed to be 5.0–6.5 and 4.5–6.0, respectively, leading to high turbidity, DOC (dissolved organic carbon), and UV_{254} removal [4–7]. Although coagulation using metallic salts can lower the pH level, the high alkalinity water still provides excessive OH^- for metal hydrolysis and the formation of hydroxide precipitates, therefore demanding a high metal salts dosage. Nevertheless, the hydrolysis of PACl can reduce the complex reaction, which makes the coagulation processes simpler and easier to precisely control [8,9] However, a disadvantage is that the preformed Al species are stable and cannot be further hydrolyzed during coagulation, and may not be efficient in removing highly hydrophobic NOMs [10,11].

For high algae and high alkalinity source water, enhanced coagulation is considered as the best available technology to date. As the combination of multiple coagulants has not been found in the literature, a series of well-designed tests were conducted in this study to evaluate the coagulation performance of the combination of $FeCl_3$ and PACl, and to optimize the conditions for treating high algae and high alkalinity water in Tanggu water treatment plants (WTPs).

2. Materials and methods

2.1. Source water

The source water investigated in this study was taken from the reservoir of Tanggu WTPs with an intake from the Luan River, a local river running through the Northern China. The turbidity of source water before entering the plant was around 8.0–15.0 NTU in summer and in early autumn. $FeCl_3$ was used as a coagulant in Tanggu WTPs. Algal bloom occurs each year from June to September, and the dosage of $FeCl_3$ needs to be increased to as high as 60 mg/L, to meet the national water quality standard [12] and the internal guideline of 0.5 NTU in settled water. However, even in such a situation, the residual turbidity is sometimes still high, ranging from 0.7 to 1.4 NTU with the pH of lower than 7.0, resulting in problems such as "yellow" water and the aging distribution pipelines. Thus, an effective enhanced coagulation process is urgently required for Tanggu WTPs and other plants that are facing the same situations.

During the jar tests to study the effectiveness of each individual operational condition on the coagulation performance, the source water was taken at the peak of algal growth, and the water quality is shown in Table 1. During the full-scale WTP studies in practice, the algal contents in the water were as high as 15 million cells/L and alkalinity was above 100 mg/L on average (Tables 2 and 3).

2.2. Reagents

All the reagents used were of chemically pure grade, unless mentioned otherwise. Liquid $FeCl_3$ (Qingyuan Water Purifying Reagent Company, Beijing) with the concentration of 38.27% and liquid PACl (MW of about 1000 kDa, Tianshu Purification Material Co. Ltd., Tianjin) with the Al_2O_3 content of 10–11% and 70–75% basicity, were used as coagulants. Liquid HCA (MW of 80–100 kDa, Fu Luo Ke Chemicals Co. Ltd., Jiangshu) with 39–41% concentration or powered FO4190 (MW of 5000–18,000 kDa, Fu Luo Ke Chemicals Co. Ltd., Jiangshu) were used as coagulant aids. Stock solutions of $FeCl_3$ and PACl of 10,000 mg/L each were prepared. The HCA working solution of 1000 mg/L and FO4190 of 100 mg/L, were used in the jar tests, with the dosing amounts of around 0.3 mg/L for each.

2.3. Jar tests

Coagulation jar tests were conducted in 1 L Plexiglass beakers using a programmable jar testing apparatus, DC-506 Laboratory Stirrer (Huashui New Technological Development Co. Ltd., Shanghai). The procedure of the batch coagulation tests was based on the practical operation and design in Tanggu WTPs. Source water was filled in six beakers with 1 L each. Coagulant(s) were added followed by a 3-min rapid stirring at 200 rpm ($G = 102.5\,s^{-1}$) to allow a complete coagulation/reaction and then followed with a 20-min slow stirring at 40 rpm ($G = 11.8\,s^{-1}$) to allow a good flocculation and a 10-min settling for floc–liquid separation. In combined coagulants tests, the second coagulant was dosed 1 min after the first coagulant, i.e., 1 min after the rapid mixing. Supernatant samples were withdrawn at 2 cm below the water surface. Coagulation dosage was measured by a calibrated pipette.

2.4. Full-scale WTP studies

In order to evaluate the effect of combined coagulants on the coagulation performance in full-scale

Table 1
Source water quality characteristics

Parameter	Unit	Min	Max	Mean ± standard deviation	Number of measurements
Temperature	℃	22	27	25 ± 1.5	30
pH	–	8.14	8.47	8.29 ± 0.09	30
Turbidity	NTU	8.25	14.20	10.69 ± 1.54	30
Alkalinity	mg $CaCO_3$/L	98	126	104 ± 5.7	30
NH_4^+	mg/L	0.12	0.39	0.21 ± 0.08	30
COD[a]	mg/L	3.10	4.85	3.79 ± 0.37	30
DOC	mg C/L	3.32	7.70	4.91 ± 1.07	45
UV_{254}	cm^{-1}	0.123	0.088	0.100 ± 0.007	30
SUVA[b]	1/m/(mg C/L)	1.34	2.81	2.13 ± 0.40	30
Algae	10^3 cells/L	7560	34,240	14,947 ± 5318	30

[a] COD – chemical oxygen demand.
[b] SUVA – specific UV absorbance.

WTPs using the conventional treatment process, two approaches were used: The first approach was comparing two Tanggu WTPs (WTP1 and WTP2) by treating the same source water taken at the peak of high algal growth and high alkalinity period (June–September), in which WTP1 used the combined coagulants of PACl/$FeCl_3$ combined with HAC, while WTP2 only used single $FeCl_3$. The second approach was comparing WTP3 coagulation performance in two consecutive years, in which only the single $FeCl_3$ was used in the first year, while the combined coagulants of PACl/$FeCl_3$ were used in the second year.

2.5. Analytical methods

Turbidity was measured using a turbidimeter (RATIO/XR, Hach, USA), while COD_{Mn} was determined using an acid potassium permanganate method (NEPB, 2002). Collected water samples were filtered through a 0.45 μm pore size filtration membrane to measure the UV_{254} absorbance. UV_{254} was measured at 254 nm with a UV-754 UV/Vis spectrophotometer (Jinghua Precision Scientific Instrument Co. Ltd., Shanghai, China). Then pH was measured using a pH meter (F-30, Shanghai, China), and iron residual was determined using the orthophenanthroline photometric method [13]. The algal samples were fixed using 5% formaldehyde and transported to laboratory for microscopic counting. Morphologies of the air-dry flocs were examined and measured spectroscopically using SEM (S-3500 N, HITACHI) under a 20 kV voltage. Floc sizes were measured using image analysis. It was performed by first calibrating distances, thresholding floc sizes, and then measuring floc size using the integrated morphometry program in Metamorph [24]. Floc size thresholding was performed manually.

3. Results and discussion

3.1. Effects of single $FeCl_3$, single PACl, and combined $FeCl_3$/PACl dosage on coagulation performance

Coagulation performance was examined with a dosage range of 10–80 mg/L for single $FeCl_3$, single PACl, and combined PACl/$FeCl_3$ (1:1 by mass) dosing PACl followed by $FeCl_3$. Fig. 1 showed that the coagulant dosage greatly affected the turbidity removal efficiency. The residual turbidity in settled water decreased with increasing coagulant dosage from 5 mg/L to 35 mg/L. The difference using three dosing methods was that as the dosage continued to increase after 35 mg/L, the residual turbidity continued to decrease when $FeCl_3$ was used, while it remained stable and even slightly increased when PACl or the combined coagulants of PACl/$FeCl_3$ was used. The combined PACl/$FeCl_3$ gave better turbidity removal efficiency than single PACl or single $FeCl_3$. The second highest turbidity removal efficiency was that of the single PACl under a high dosage of 60 mg/L. It was noted that by using the combined PACl/$FeCl_3$ at a dosage of 30–35 mg/L, the residual turbidity in settled water can reach below 0.5 NTU (Tanggu WTP's internal guideline).

It has been reported that the alkalinity/pH affects the chemistry of coagulants, particularly the speciation distribution of the coagulants after dosing, and further speciation transformation [14]. The source water in Tanggu WTP has high alkalinity and requires a high $FeCl_3$ dosage to adjust the pH level and make it favorable for coagulation. These results indicated that the combined PACl/$FeCl_3$ have a better coagulation performance than single $FeCl_3$ or single PACl in terms of turbidity removal with an optimal dosage of 30–35 mg/L.

Table 2
Comparison of coagulant dosing and treated water quality of WTP1 using combined coagulants PACl/$FeCl_3$ and WTP2 using single $FeCl_3$

Parameter	Unit	Max.	Min.	Avg.
Raw water quality				
Temperature	℃	23	15	21
Turbidity	NTU	14.9	6.5	11.7
pH		8.47	8.04	8.26
Color	Pt/Co	25	15	17
Alkalinity	mg/L	174	90	114
COD_{Mn}	mg/L	5.04	2.75	4.13
Ammonium	mg/L	0.28	0.02	0.13
DOC	mg C/L	7.68	3.30	4.83
UV_{254}	cm^{-1}	0.118	0.068	0.090
Total iron	mg/L	0.97	0.31	0.46
Algae	10^6 cells/L	20.58	9.72	14.16

Parameter	Unit	WTP1	WTP2
Coagulant dosing			
Production	km^3/d	95	57
PACl	mg/L	12	–
$FeCl_3$	mg/L	24	66
HCA	mg/L	0.3	–

Parameter		WTP1			WTP2		
		Max.	Min.	Avg.	Max.	Min.	Avg.
Treated water quality							
Turbidity	NTU	0.30	0.15	0.25	0.47	0.26	0.31
pH		7.64	7.45	7.52	7.47	6.83	7.13
COD_{Mn}	mg/L	2.32	1.82	2.01	2.46	1.72	1.93
DOC	mg C/L	5.42	2.51	3.43	5.50	2.65	3.62
UV_{254}	cm^{-1}	0.089	0.055	0.066	0.092	0.059	0.073
Iron	mg/L	0.11	0.05	0.07	0.17	0.05	0.10
Algae	10^6 cells/L	0.21	0.12	0.16	0.31	0.23	0.27

3.2. Effects of dosing order of the combined PACl/$FeCl_3$ on coagulation performance

Particle coagulation can be explained through charge neutralization, entrapment, adsorption, and complexation [7]. Under different conditions, different mechanisms or their combination may be dominant. The dominant turbidity removal mechanisms using PACl were suggested to be adsorption, entrapment, and sweep-flocculation. When using $FeCl_3$, the likely mechanism is that of charge neutralization, which is evident when pH is optimized [15–17]. Besides, precipitation and “sweep coagulation” can be very important at around neutral pH. Thus, the dosing order’s effect on turbidity removal mechanisms should be studied.

As the combined coagulant, PACl/$FeCl_3$ had a better coagulation performance, different dosing orders, $FeCl_3$ followed by PACl (1:1 by mass) and PACl followed by $FeCl_3$ (1:1 by mass), were investigated. The results showed that dosing PACl followed by $FeCl_3$ gave the better turbidity removal efficiency in comparison to the others (Fig. 2). At a low combined coagulant dosage of 25 mg/L, the residual turbidity in the settled water was 0.55 NTU when dosing PACl followed by $FeCl_3$, while it was 1.19 NTU when dosing $FeCl_3$ followed by PACl. As the dosage increased, the difference of residual turbidity between the two dosing methods decreased. This is because PACl is a less pH-dependent coagulant, compared to ferric salts that have the most effective range of pH suggested to be 4.5–6 [7]. When dosing $FeCl_3$ first into source water with the pH of 8.0, the charge neutralization effect would be very weak, and consequently greatly decreased the efficiency of $FeCl_3$ coagulation. How-

Table 3
Comparison of coagulant dosing and treated water quality of WTP3 in two consecutive years, with only single $FeCl_3$ used in the 1st year and the combined coagulants $PACl/FeCl_3$ used in the 2nd year.

Parameter	Unit	WTP3 in the 1st year			WTP3 in the 2nd year		
		Max.	Min.	Avg.	Max.	Min.	Avg.
Raw water quality							
Temperature	℃	29	14	26	28	15	25
Turbidity	NTU	13.4	3.42	6.26	18.3	3.83	7.48
pH	–	8.78	7.42	8.38	8.48	7.60	8.11
Color	Pt/Co	25	10	12	20	10	15
Alkalinity	mg/L	122	84	101	126	92	102
COD_{Mn}	mg/L	5.30	2.93	3.71	4.25	2.30	3.49
Ammonium	mg/L	0.27	0.02	0.12	0.45	0.03	0.16
DOC	mg C/L	7.68	3.30	4.83	7.25	3.31	4.78
UV_{254}	cm^{-1}	0.118	0.068	0.090	0.110	0.067	0.086
Total iron	mg/L	0.42	0.09	0.23	0.38	0.10	0.22
Algae	10^6 cells/L	14.04	3.58	7.34	15.58	2.44	5.84
Coagulant dosing							
Treatment capacity	km^3/d		80			80	
Production	km^3/d		62.2			81.2	
PAC	mg/L		–			10.1	
$FeCl_3$	mg/L		51.9			20.3	
HCA	mg/L		–			0.31	
Treated water quality							
Turbidity	NTU	0.67	0.12	0.28	0.36	0.19	0.26
pH	–	7.74	6.92	7.30	7.83	7.20	7.53
COD_{Mn}	mg/L	2.27	1.31	1.65	2.10	0.97	1.63
DOC	mg C/L	5.58	2.52	3.32	4.71	2.48	3.1
UV_{254}	cm^{-1}	0.088	0.058	0.07	0.078	0.055	0.062
Iron	mg/L	0.22	<0.05	0.11	0.17	<0.05	0.06
Algae	10^4 cells/L	30	2.4	25	57	2.4	15

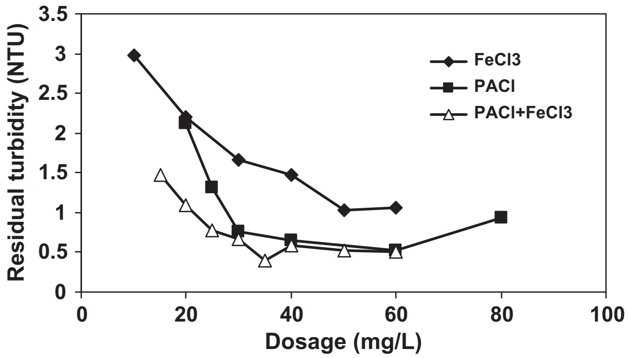

Fig. 1. Effects of dosage of single $FeCl_3$, single PACl, and combined $FeCl_3$/PACl on turbidity removal.

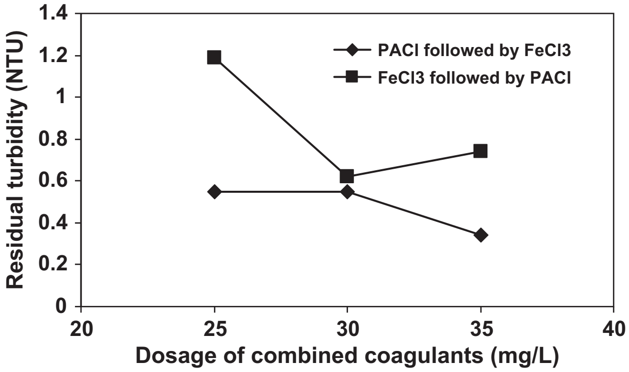

Fig. 2. Effect of dosing order of combined $FeCl_3$/PACl on turbidity removal.

ever, PACl is less sensitive to pH levels and when dosing PACl first, the mechanism of entrapment, adsorption, and complexation may be dominant. As the dosage of the combined coagulation increased to 30–35 mg/L, the pH in the solution decreased. Such decrease is beneficial for $FeCl_3$ coagulation and thus, results in the residual turbidity between the two types of dosing.

3.3. Effects of combined PACl/$FeCl_3$ dosing ratio on coagulation performance

Since the dosing order of the combined coagulant affects the turbidity removal, we further hypothesized that there would be an optimal ratio of PACl/$FeCl_3$ on the turbidity removal. Different PACl/$FeCl_3$ ratios (5:1–1:5 by mass) with total dosage of 10 mg/L were investigated. As addition of PACl with $FeCl_3$ can enhance the bridging ability of coagulants and flocs were relatively large, the corresponding floc size was also measured in this study. The results (Fig. 3) showed that using 1:2 mass ratio and dosing PACl followed by $FeCl_3$ can reach the maximum floc size with higher turbidity removal efficiency. When the ratio of PACl/$FeCl_3$ increased to more than 1:2, the floc size decreased. When the ratio decreased to from 1:2 to 1:5, i.e., decreasing PACl and increasing $FeCl_3$ contents, the floc size maintained the same size, while the residual turbidity increased.

3.4. Effect of coagulant aids of HCA and FO4190 on coagulation performance

Coagulant aids are commonly used to improve the performance of primary coagulant for algae and turbidity removal by particle bridging and charge neutralization, which is facilitated by high molecular weight polymers with a relatively low charge density [7].

Two cationic coagulant aids, HCA and FO4190, were selected for testing the coagulation efficiency using different PACl/$FeCl_3$ ratio (5:1–1:5 by mass) dosing PACl followed by $FeCl_3$ with a total dosage of 10 mg/L. The results (Fig. 4) showed that by adding HCA or FO4190 during coagulation, a more effective turbidity removal was achieved. The flocs formed were

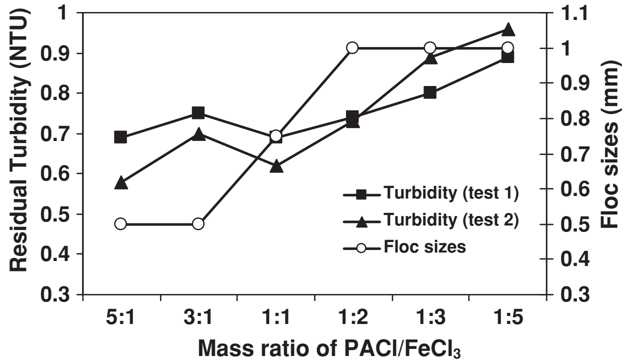

Fig. 3. Effect of dosing ratio of combined PACl/$FeCl_3$ on turbidity removal.

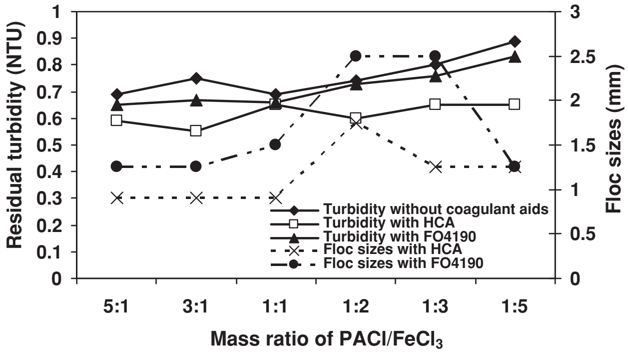

Fig. 4. Effect of coagulant aids of HCA and FO4190 on turbidity removal.

larger, with maximum floc sizes of 1.75 mm using HCA and of 2.5 mm using FO4190 under the PACl/$FeCl_3$ of 1:2. However, the coagulant aids used in this study can only increase the floc size without much improvement on the floc structure and the settling of particles, resulting in a certain number of flocs still remaining in the settled water, thus giving only marginal reductions in residual turbidity. This observation was also reported in the previous study [7], while the complete mechanism was still unclear. Since using HCA resulted in lower residual turbidity and HCA is more easily dissolved into the solution than FO4190, it was suggested to use HCA as the coagulant aid for the Tanggu's source water, in efforts to improve coagulation.

3.5. Coagulation optimization integrating combined coagulant dosage, order, ratio, and coagulant aid

Considering the effects of the coagulant dosage, order, ratio, and coagulant aid on the turbidity removal, we attempted to integrate all the optimized values for each parameter of the previous studies, i.e., dosing PACl followed by $FeCl_3$ (1:2 by mass) and using HCA as coagulant aid with different dosage, in order to evaluate the treatment efficiency of high algae and high alkalinity source water.

Compared to the single coagulant $FeCl_3$, combined coagulants (PACl/$FeCl_3$) showed superior coagulation performance in terms of turbidity and UV_{254} removal (Fig. 5). As the dosage increased from 10 to 30 mg/L, the pH decreased from 7.9 to 7.8 using combined coagulants and to 7.5 using single $FeCl_3$, with the corresponding residual turbidity of 0.86 and 0.42 respectively. These results confirmed that the combined PACl/$FeCl_3$ was less sensitive than single $FeCl_3$ to pH level during coagulation, and the final lower pH decreased the corrosive tendency in pipe network. When the single $FeCl_3$ dosage continued, the pH decreased to 7.2, resulting in further removal of turbidity, while not much improvement occurred when PACl was the coagulant. In addition, although the optimized combined PACl/$FeCl_3$ and single $FeCl_3$ showed similar algal removal (around 90%), compared to single $FeCl_3$, the combined PACl/$FeCl_3$ obtained a higher UV_{254} removal (77.4%), which can improve the removal efficiency of organic matter significantly.

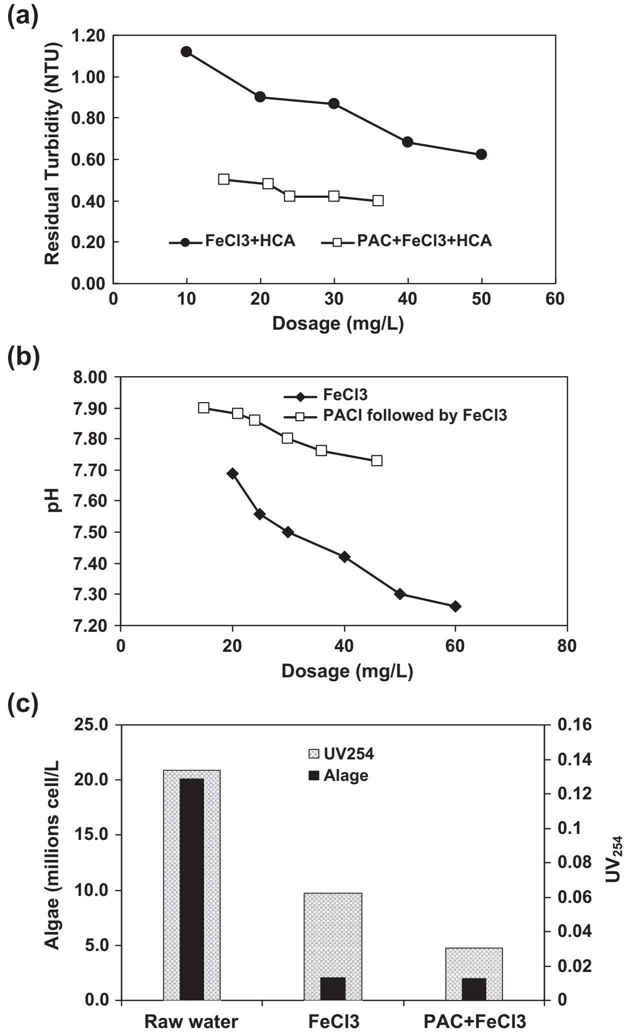

Fig. 5. Coagulation optimization integrating combined coagulant dosage, order, ratio, and coagulant aid. (a) Change of residual turbidity for different amounts of coagulant dosage. (b) Change of pH for different amounts of coagulant dosage. (c) UV_{254} concentration and algae content of raw water and settled water using single $FeCl_3$ and combined coagulants $FeCl_3$/PACl with the total dosage of 30 mg/L.

3.6. Floc structure examination through SEMs

The differences in coagulation performance using different coagulants are also confirmed through the floc structures observed by SEMs (Fig. 6). Using single $FeCl_3$ as coagulant, the flocs formed with porous structures, where particles and colloids (both organic and inorganic) were adsorbed or swept afterward as shown in Fig. 6(a). When adding HCA after the single $FeCl_3$ dosing, the flocs formed in the PACl test tends to exist as chain-like or reticulate structures as well as some porous structures can also be identified as seen in Fig. 6(b). It was believed that the chain-like and reticulate structures contributed to the lower turbidityin the settled water. When using the combined PACl/$FeCl_3$ with HCA, more compact floc structure was obtained (Fig. 6(c)). The mechanism for the

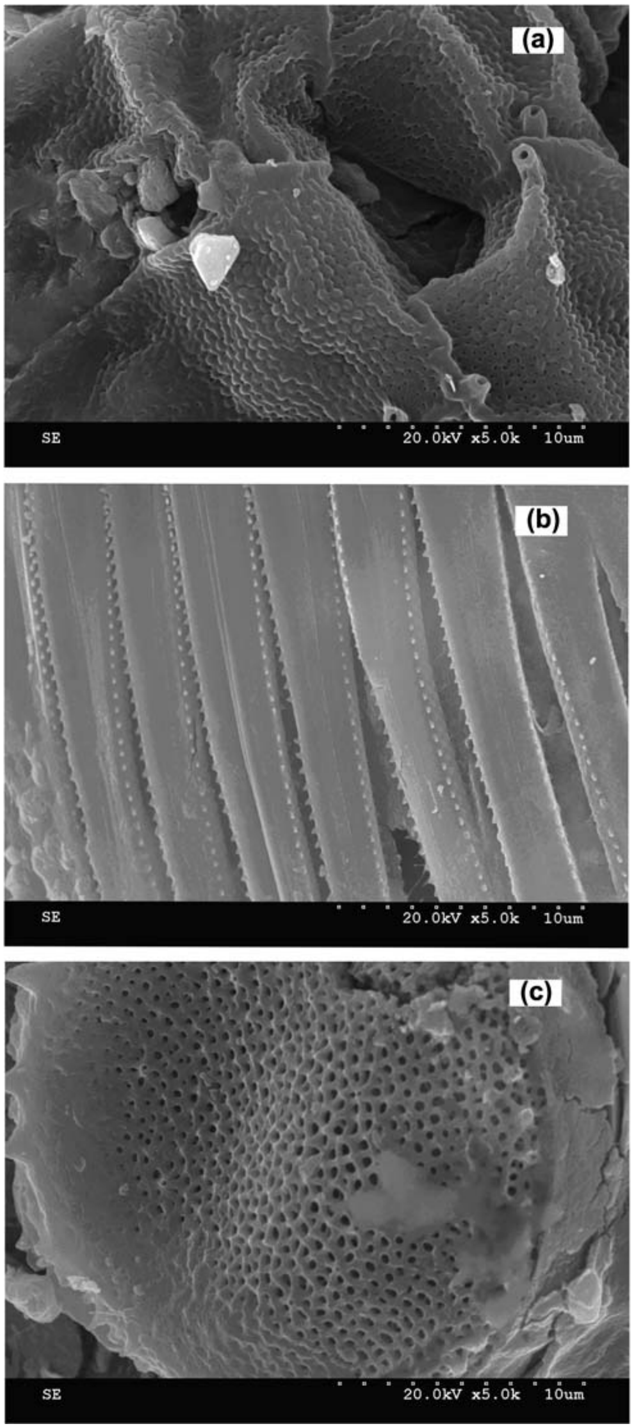

Fig. 6. SEMs for the flocs structure formed using different coagulants/coagulant aids, with the magnification of 5000. (a) Single $FeCl_3$, (b) single $FeCl_3 + HCA$, and (c) combined $PACl/FeCl_3 + HCA$.

enhanced coagulation using combined coagulant was probably that the chain-like and reticulate structures can adsorb Fe^{3+} or contribute to a combination settling with the ferric hydrolysis species to form the soluble reticular aluminum-ferric structures. This can also be verified to some extent, through the color of the flocs/structures using a combined coagulant of a mixture of yellow (Fe^{3+}) and white (PACl). There are also some uncompleted structures in Fig. 6(c), which showed the process of flocculation. The combined dosing way, addition of $FeCl_3$ after PACl, enhanced the coagulation with compact reticular structures [18], which can speed up the sedimentation of the whole flocs/structures. The mechanisms of coagulation by combined PACl and $FeCl_3$ are more complex and will be systematically investigated in future studies.

3.7. Combined coagulant performance in full-scale water treatment plant

In order to verify the enhanced coagulation using combined coagulant in full-scale WTPs, two approaches were compared in high algae and high alkalinity period (June to September). In the first approach, the combined $PACl/FeCl_3$ was used in WTP1, and single $FeCl_3$ in WTP2. In the second approach, the WTP3 coagulation performance of two consecutive years was compared, with only the single $FeCl_3$ used in the first year, while the combined coagulants of $PACl/FeCl_3$ used in the second year. The three WTPs use similar conventional treatment processes.

It was observed that WTP1 and WTP3 in the second year had a better removal efficiency of algae, turbidity, DOC, and UV_{254} than the WTP2 and WTP3 in the first year, respectively (Tables 2 and 3 and Fig. 7). Compared in terms of dosing $FeCl_3$ only, using the combined coagulant $PACl/FeCl_3$ can reduce the high iron and COD_{Mn} concentration, and increase the higher alkalinity in treated water, resulting in decreases of the corrosion of the distribution network. Further analysis showed that by using combined $PACl/FeCl_3$ operational costs can be reduced by more than 20%, as opposed to using single $FeCl_3$ (data not shown).

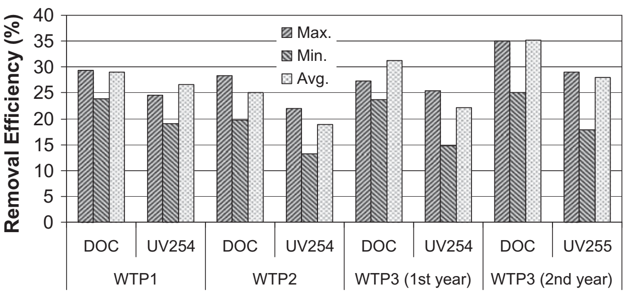

Fig. 7. Comparison of DOC and UV254 removal efficiencies of WTP1 and WTP2, and WTP3 in two consecutive years.

3.8. Mechanisms of the combined coagulant using PACl/$FeCl_3$

$FeCl_3$ and PACl, used as coagulants in drinking water treatment, have different effects on algal removal. Similar to aluminum salt, ferric salts are more pH dependent coagulants and the most effective range of pH is suggested to be 4.5–6 [17–20]. It has been noted that $FeCl_3$ is better than alum when removing medium size NOM fractions, and is also not as sensitive to temperature change [21,22]. The ferric-based coagulant associated with the optimized coagulation pH range produces treated water with less buffering capacity, and requires greater chemical addition for stabilization and corrosion control. However, PACl is composed of partially neutralized, pre-hydrolyzed aluminum chloride, and contains large amounts of high-charged and moderate-molar-mass hydrolysis species, such as Al_{13}, in the coagulation process [5,20]. These coagulation species are considered to be the most efficient Al-species due to their higher positive charge and larger size. The destabilization mechanisms of different aluminum species have been observed [20]. Compared to ferric salts, PACl is less temperature and pH dependent, thus, leading to smaller alkalinity consumption, lower dose requirement, and less sludge production. HCA, one of the effective coagulant aids, enhances the bridging ability of PACl to increase the efficiency of algal removal.

The effectiveness of coagulation using combined coagulant and coagulant aid is accredited to be due to the formation of the soluble reticular aluminum–ferric structures. Using single PACl, the reticular structures/flocs is dominated by aluminum-based salts, which are light and have a low settling efficiency [23]. However, by adding $FeCl_3$ after PACl, the formation of the reticular structure flocs is enhanced [21], which can speed up the sedimentation as a whole of the entire structures. This hypothesis was verified through the SEMs in the study.

In addition, alkalinity is one of important factors that affect the NOM removal. Usually, high pH water with lower alkalinity can be used to remove NOM more efficiently [20], as alkalinity influences the pH of coagulation after coagulant addition, and further control the hydrolyzed species of the metal coagulants. Higher alkalinity needs more extent of the hydrolysis process for larger polymer formation, and produces more precipitation. It was reported that DOC and UV_{254} correlated well with the hydrolyzing behavior of the coagulant, with the minimum solubility of $FeCl_3$ at pH 5.8, and the efficient DOC removal mostly occurs at a pH slightly less than that of the minimum solubility, which ensure the hydrolysis products are mainly medium polymers or monomers that have a high ability to remove DOC by complexation and charge neutralization [20]. On the other hand, PACl contains a high level of charged polymer pre-hydrolysis products that are stable even after being added into high alkalinity and high pH water [14]. Therefore, using combined coagulants of $FeCl_3$ and PACl performed better than using $FeCl_3$ alone for treating high algae and high alkalinity source water, which has been shown in our results shown in Figs. 5 and 7. Further study will measure the pre-formed medium polymer species (Al_b) of PACl to confirm our results.

4. Conclusion

High algae and high alkalinity source water from Luan River was treated using single $FeCl_3$, single PACl, and the combination of both as coagulants. The efficiencies of combination coagulation using PACl and $FeCl_3$ were much better than those when using single $FeCl_3$. The residual turbidity of the combination coagulation can reach to less than 0.5 NTU after 10-min settling, which was not observed in the conventional coagulation using single $FeCl_3$, even when increasing the coagulant dosage to as high as 60 mg/L.

The optimal coagulation dosage was determined as 30–35 mg/L of the combined PACl/$FeCl_3$, using PACl dosing followed by $FeCl_3$ with a PACl/$FeCl_3$ mass ratio of 1:2 and the addition of coagulant aid HCA. The treated water qualities, such as the residual turbidity, UV_{254}, and algal content in the combination coagulation using PACl and $FeCl_3$ were much better than those of the traditional coagulation under a 60 mg/L $FeCl_3$ dosage. The pH was maintained at 7.5 even though the total dosage increases, which was able to meet the water quality requirements for the treated water in the distribution network.

The flocs formed in the combination coagulation tests were larger in size and more compact in structure compared to those formed in single $FeCl_3$ or PACl coagulation tests. Thus, the optimized combination coagulation process can solve the problems of floc disturbance and subsequent filter clogging in the treatment processes, due to the high algae source water treatment.

The enhanced coagulation was studied in three full-scale Tanggu WTPs. The results showed that compared to single $FeCl_3$, combined coagulants of PACl/$FeCl_3$ was able to further reduce DOC and iron concentrations, and increase the high alkalinity in treated water, resulting in decreasing the corrosion of the distribution network.

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