



Effect of polyaluminum chloride on enhanced softening for the typical organic-polluted high hardness North-China surface waters

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ABSTRACT

The treatment of organic-polluted high hardness surface water by enhanced softening via precipitation using various coagulants, such as FeCl₃, AlCl₃ and polyaluminum chloride (PACl), was investigated in bench scale experiments. Higher removal of natural organic matter (NOM) (UV₂₅₄ removal reaches about 50%) is achieved by enhanced softening with coagulant addition conditions as compared with conventional coagulation at natural pH or by softening alone without coagulation. It is found that PACl could enhance the formation of Mg(OH)₂ precipitate to remove NOM efficiently at relative lower pH range (pH < 10). Under this circumstance, the pH for enhanced softening can be decreased significantly into the practical pH range for treatment plant operation. The efficiency of enhanced softening is affected significantly not only by pH, coagulant type and dose, but also by raw water quality such as NOM characteristics, magnesium content and hardness. NOM with more hydrophobic content and higher molecular weight may be removed more easily in some situations. For water with higher content of Mg²⁺, the inflexion pH for favorable UV₂₅₄ 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.

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1. Introduction

Natural organic matter (NOM) in source water can cause odor, taste, color, and bacterial regrowth problems during distribution for drinking water supply. More importantly, NOM is the precursor for health concerning disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs). The US Environmental Protection Agency (USEPA) has proposed more stringent maximum contaminant levels (MCLs) of 80 and 60 µg/L for THMs and HAAs, respectively in finished drinking water [1,2]. Removal of NOM in an effective way is one of the major challenges in modern drinking water industry. Enhanced softening, improving the removal of DBPs precursor by precipitative softening, was recommended by the USEPA as one of the best available technologies to control the formation of DBPs [1].

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 pro-

cess [3–6]. Even the use of high doses of lime (200 mg/L) 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 [7–9]. Altering the surface character of calcium carbonate precipitates by adding cationic polyelectrolytes is an alternative option to enhanced NOM removal during softening [10,11].

Unlike calcium carbonate, magnesium hydroxide precipitates as positively-charged particles with an amorphous structure and larger surface area [3,6]. It is found that a small increase in magnesium precipitation results in a significant NOM removal [12]. Systems that remove at least 10 mg/L Mg hardness as CaCO₃ are proposed to exempt from the enhanced softening requirements by the USEPA [1]. However, for typical concentrations of magnesium in raw water supplies, the precipitation of magnesium hydroxide requires high pH (above 11) condition, which is uncommon in water treatment practice [13]. It is not an attractive choice for softening plants. Addition of coagulant (e.g. activated silica, ferric chloride and organic polymers) during softening was proposed as alternative to enhanced NOM and particle removal [14].

Polyaluminum chloride (PACl) has been claimed by many investigators to be superior to the traditional coagulants for high alkalinity and pH water due to the fact that the prehydrolyzed

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polymer in PACI is positively charged and relatively stable at high pH range [15–17]. However, the influence of PACI on enhanced softening is still unclear. This paper investigates the performance of PACIs on enhanced softening compared with traditional coagulants such as AlCl_3 and FeCl_3 . The typical source waters from North-China were selected as examples because they are not only polluted seriously by recalcitrant synthetic organic contaminants [18], but also are of high alkalinity, pH and hardness.

2. Materials and methods

2.1. Materials

Four coagulants, AlCl_3 , FeCl_3 , PACI_1 , and PACI_{22} , were used in this study. AlCl_3 and FeCl_3 were of reagent grade. PACI_1 , commercial PACI product, was provided by a local factory (Beijing Wanshui Water Cleaning Agent CO., China), which was produced by dissolving $\text{Al}(\text{OH})_3$ solids. PACI_{22} (Basicity of 2.2, OH/Al molar ratio, simplified as B values), was prepared by the base titration method in laboratory at room temperature [19]. The Al species distribution in the PACIs and AlCl_3 samples was analyzed by Ferron (Sigma, UK) assay [15]. The chemical species of hydrolyzed Al(III) can be divided through the different reaction rates into three types: monomeric species (Al_a) (instantaneous reacted), medium polymer species (Al_b) (reacted less than 120 min), and species of sol or gel (Al_c) (no reaction within 120 min). The results are shown in Table 1.

Three water samples with different water quality were taken from the typical North-China rivers. One was collected from the Yellow River in Autumn (YW); the others were collected from the Luan River during Summer (LW_{Sum}) and Winter (LW_{Win}), respectively. The quality of the raw waters is presented in Table 2.

2.2. Jar testing

Jar tests were performed on a programmable jar test apparatus (Daiyuan Jar Test instruments, China). The operation procedures were as follows: 1 L of raw water was transferred into a 1.4-L square beaker with sampling port 3 cm below water surface; the jar tester was started at rapid mixing of 300 rpm; after 30 s coagulant was added followed by mixing speed of 250 rpm for 2 min; 40 rpm for 10 min; and then after 20 min of quiescent settling, samples were taken for water quality measurement. In the enhanced softening experiment, predetermined amount of NaOH were dosed 15 s before adding coagulant during rapid mixing period. Coagulants as well as acid and base reagents were dosed using pipettes, which were calibrated before each experiment.

2.3. Analysis

Dissolved organic carbon (DOC) was analyzed by a TOC Analyzer (Phoenix 8000 system, Tekmar-Dohrman Co., USA) using the method of sodium peroxydisulphate/orthophosphoric acid wet oxidation and UV radiation after filtered through 0.45 μm membrane. UV_{254} was measured by a spectrophotometer (UV-vis 8500, China) at a wavelength of 254 nm using a 1 cm quartz cell after filtered through a 0.45 μm membrane. Turbidity was measured using a

Table 1

The speciation distribution of coagulant-PACIs by Ferron method

	Al_{Total} (mol/L)	Al_a (%)	Al_b (%)	Al_c (%)
AlCl_3	0.200	91.9	8.1	0
PACI_1	0.207	40.0	38.5	21.5
PACI_{22}	0.101	17.8	61.5	20.7

2100N Turbidimeter (Hach, USA). pH was measured by a pHS-3C (Shanghai, China) pH meter, which was daily calibrated using pH 7.01 and pH 9.18 buffers. The hardness, alkalinity and chemical oxygen demand (COD_{Mn}) were measured by standard methods [20]. Metal elements (Ca, Mg and Al) were analyzed by ICP-OES after filtered through a 0.45 μm membrane (Agilent, USA). Dissolved organic matter (DOM) was characterized using resin absorbent and ultrafiltration (UF) fractionation methods described in the literature [18].

3. Results and discussion

3.1. Comparison of coagulant type on enhanced softening

Four typical coagulants, two metal salts, FeCl_3 and AlCl_3 , and two PACIs, PACI_1 and PACI_{22} , were selected to examine the effect of coagulant type on softening. NaOH was used as softening reagent instead of the traditional softening agents lime and soda (CaO and Na_2CO_3) to reduce the influence of Ca^{2+} addition on the softening process. The results of source water YW are shown in Fig. 1.

In Fig. 1a, all four coagulants follow a similar trend with residual turbidity increases against pH (adjusted by NaOH) until the maximum is reached at approximately pH 10. Further increase in pH (beyond 10) resulted in residual turbidities decrease. In order to evaluate the influence of coagulant on softening, samples were taken for water quality measurement only after 20 min of quiescent settling, in which CaCO_3 and $\text{Mg}(\text{OH})_2$ precipitates were still in the form of suspended solid and at that point of time the residual turbidities for all four coagulants were relatively high (based on predetermined test).

As shown in Fig. 1b, low UV_{254} removal is observed at pH below 9.5 and it is even lower than at natural pH (the lowest pH point in the figures), especially for the two metal salt coagulants. The higher the B values of the PACI, the better the UV_{254} removal at pH below 9.5. UV_{254} removal by FeCl_3 is more efficient than AlCl_3 and is less efficient compared with the two PACIs. When pH increased to above 10, the UV_{254} removal increases significantly for all four coagulants but the removal performance of each coagulant is reversed, better UV_{254} removal is observed for PACIs with lower B value and both metal coagulants out performed the PACIs with the removal efficient in the order of $\text{PACI}_{22} < \text{PACI}_1 \approx \text{FeCl}_3 < \text{AlCl}_3$.

The relative efficiency of COD_{Mn} removal by the four coagulants (Fig. 1c) shows the same trend as in the case of UV_{254} removal except that COD_{Mn} removal decreased more obviously at pH about 9.5, and that the increase of UV_{254} removal is more significant than that of COD_{Mn} removal when pH increases from about 9.25 to 10. This phenomenon may be linked with the inefficiency of turbidity removal at pH about 10.

Table 2

Water quality characteristics of water samples

	pH	Alkalinity (mg/L)	Hardness (mg/L)	Turbidity (NTU)	UV_{254}	COD_{Mn} (mg/L)	DOC (mg/L)	Mg (mg/L)	Ca (mg/L)
YW	8.67	160	345	11.5	0.133	6.0	5.4	45.5	98
LW_{Sum}	8.21	116	180	8.02	0.056	4.1	4.2	30.0	70
LW_{Win}	8.61	135	150	0.92	0.063	3.5	3.2	19.8	52

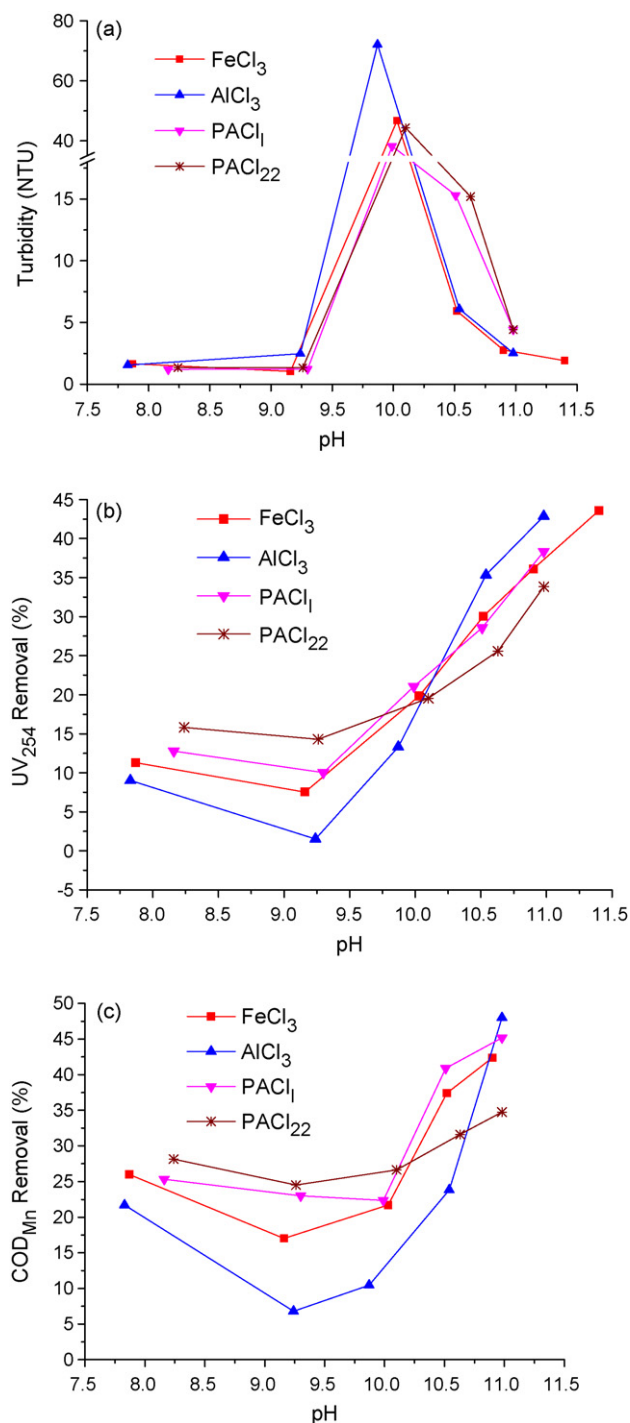


Fig. 1. The effect of coagulant type on enhanced softening with NaOH for the Yellow River water at dose of 0.08 mmol/L Al/Fe. (a) Turbidity removal; (b) UV₂₅₄ removal; (c) COD_{Mn} removal.

3.2. Effect of PACI on enhanced softening

The performance of coagulants during softening may be seriously affected by coagulant hydrolyzing process, particularly the interaction of coagulant hydrolyzed speciation and the concentration of Mg²⁺ and Ca²⁺ ions. The performance of DOC, turbidity, Ca²⁺ and Mg²⁺ removal with or without PACI₁ under softening conditions by pH adjustment using NaOH was investigated with source water LW_{Win}. The results are shown in Fig. 2.

The residual turbidities increase with pH (the dose of NaOH) and reach the maximum at about pH 10 for both softening with PACI and softening alone (without PACI) with 1 and 7 NTU, respectively. Once the pH increases beyond 10, the residual turbidities decrease. The residual turbidities are significantly lower for softening with PACI than without PACI in the studied pH range. Just the softening process alone (without PACI), only slight DOC removal is observed at pH below 10. The use of PACI as coagulant 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 turbidity and DOC are affected by the residual Ca²⁺ and Mg²⁺ contents. The balance of Ca²⁺ and CO₃²⁻, HCO₃⁻ is disturbed at pH about 9, and large amount of CaCO₃ precipitate is formed. During this process, the residual Ca²⁺ content decreases rapidly due to the precipitation of CaCO₃ and at the same time the residual turbidity increased (Fig. 2c). When pH increased to 10, Mg(OH)₂ precipitate starts to form and the residual content of Mg²⁺ decreases (Fig. 2d). As a result of this process, the residual turbidity and DOC also decrease.

The removal of NOM, as well as other contaminants, by softening is largely controlled by the surface properties of calcium carbonate and magnesium hydroxide particles. Precipitation and coprecipitation are two possible mechanisms proposed for NOM removal during softening [21–23]. No matter which type of mechanisms is responsible for NOM removal, adsorption of NOM onto solid phase is essential. However, only limited amounts of NOM can be adsorbed onto the calcium carbonate surface due to electrostatic repulsion arising from the high negative charge density of humic substances and the negatively-charged calcium carbonate surface [7–9]. In addition, calcium carbonate is precipitated as a dense crystalline solid with very low surface area (5 m²/g), as compared to other coagulants such as ferric chloride (230 m²/g), which results in less available sites for NOM adsorption [6].

Unlike calcium carbonate, magnesium hydroxide precipitates as positively-charged, gelatinous precipitate with high surface area, which makes it an excellent adsorbent for negatively-charged humic substances. A significant amount of NOM can be removed by precipitation of magnesium hydroxide.

PACI plays a complicated role in the process of NaOH softening. PACI can promote magnesium precipitation, and the residual Mg is lower than that of the NaOH softening without PACI (Fig. 2d). At the same time, the pre-formed positively charged polymer in PACI is relative stable at high pH [15]. The PACI can act as a coagulant to remove particle and NOM at high pH in the softening process and also it can act as cationic organic polymer to reform the surface electrostatic properties of the products of CaCO₃ precipitate [10]. In addition, the presence of PACI can reduce CaCO₃ precipitation [24] and resulted in higher residual Ca²⁺ level as compared with NaOH softening without PACI (Fig. 2c). Then the residual turbidity is lower and the NOM could be removed more efficiently.

3.3. Effect of coagulant dose and pH

The influence of coagulant dose and pH on the removal of turbidity and UV₂₅₄ by PACI₁ for source water YW is shown in Figs. 3 and 4, respectively. Coagulant dose and pH play significant roles in turbidity and UV₂₅₄ removal. The condition of combining optimum dose and optimum pH, higher UV₂₅₄ and turbidity removal is achieved. The best UV₂₅₄ removal is observed at a combination of high dose and high pH (Fig. 4).

3.4. Comparison of enhanced softening with PACI for LW and YW

The turbidity and NOM removal by enhanced softening with coagulant PACI₁ for three typical source waters were compared. The

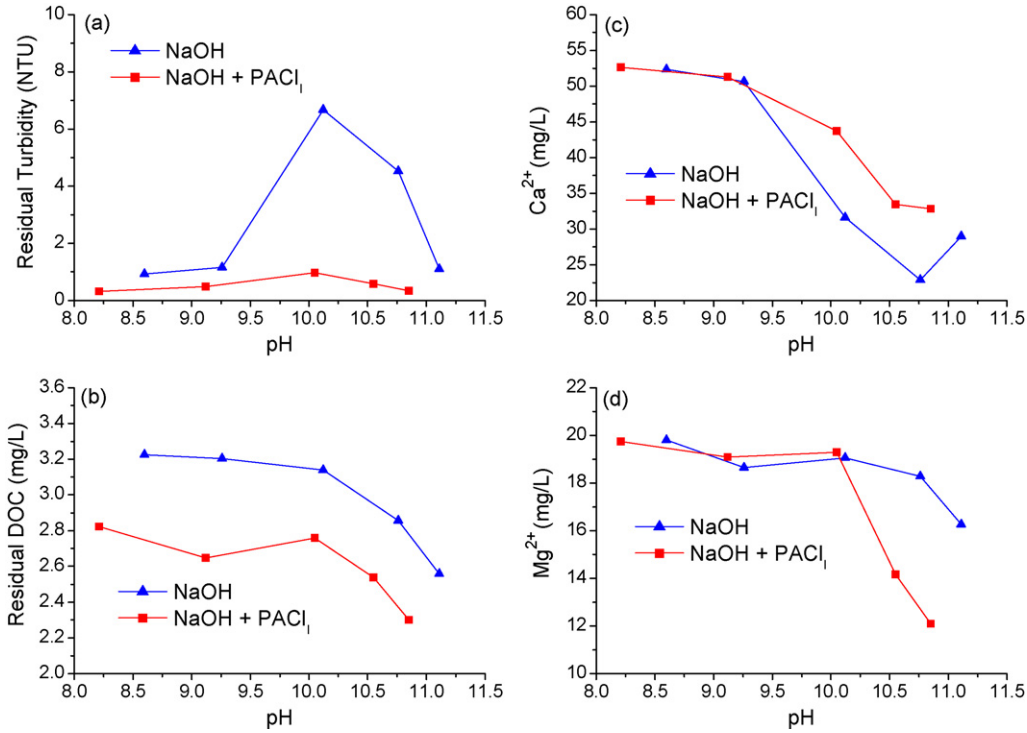


Fig. 2. The effect of PACl on softening by NaOH for the Luan River water in Winter.

results are shown in Fig. 5. It shows that the three source waters have the same enhanced softening behavior in general, such as the residual turbidity increases with the increase of pH (the dose of NaOH), and it reaches the maximum at pH about 10. When pH continuously increases, the residual turbidity drops. In the case of UV₂₅₄ removal, it decreases slightly firstly at pH below 10, then increases significantly when pH increases to above 10.

It also shows some significant difference among the three waters due to the water characteristics. The first is that the inflexion pH for favorable UV₂₅₄ removal is lower for the source water with higher content of Mg²⁺ (Table 2). The contents of Mg²⁺ are as high as 45.5, 30.0 and 19.8 mg/L for YW, LW_{Sum} and LW_{Win}, respectively; and the

inflexion pH values for favorable UV₂₅₄ removal are about 9.25, 9.75 and 10.0, correspondingly (Fig. 5b). Kvech and Edwards [24] have revealed that the presence of Al³⁺ can reduce significantly the solution of Mg²⁺ in synthetic water to about 27 mg/L from pH 9.25 to 10. The water with higher Mg²⁺ (above 27 mg/L) content can produce more Mg(OH)₂ precipitate to enhance NOM removal at a relatively lower pH range. The content of Mg²⁺ in source water YW is as high as 45.5 mg/L, it is a suitable water source for enhanced softening treatment with PACl and the UV₂₅₄ removal increases significantly at pH around 10, which has great practical value in water plant operation.

The relative effectiveness of NOM removal shows significant difference among the three source waters. The UV₂₅₄ removal for

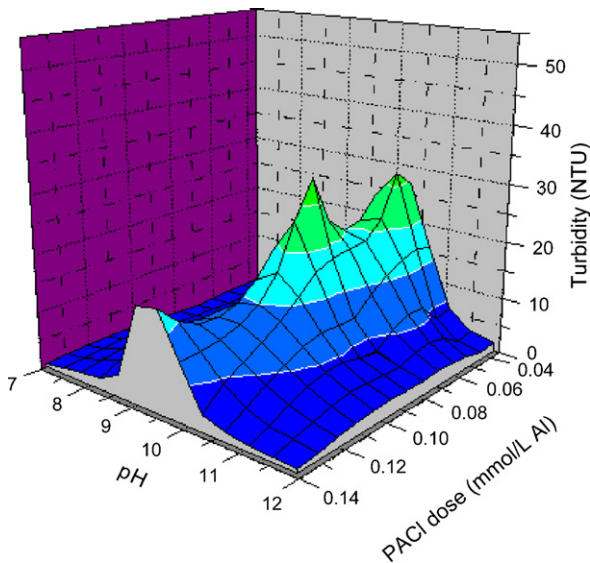


Fig. 3. The influence of coagulant dose and pH on turbidity removal by PACl for the Yellow River water.

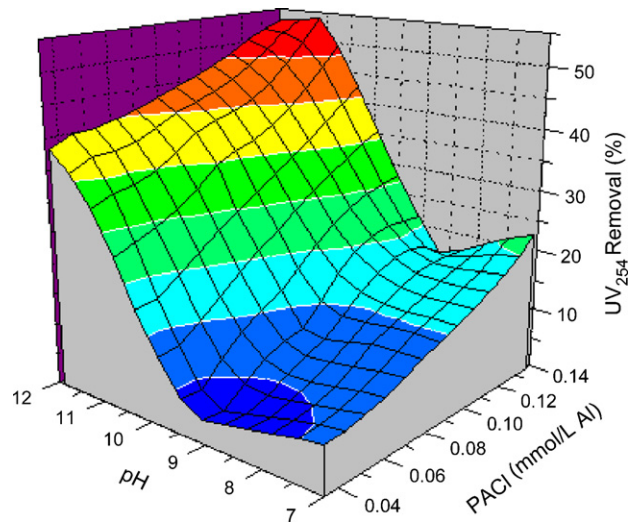


Fig. 4. The influence of coagulant dose and pH on UV₂₅₄ removal by PACl for the Yellow River water.

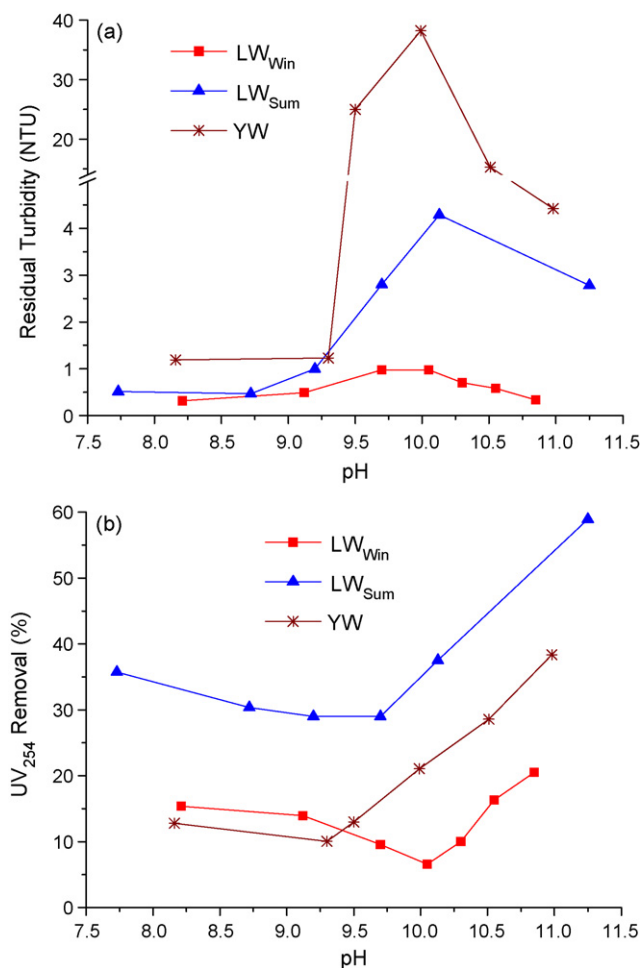


Fig. 5. The efficiency of enhanced softening with PACI for three source waters, the Yellow River water (YW), the Luan River water in Summer (LW_{Sum}), and the Luan River water in Winter (LW_{Win}). (a) Removal of UV₂₅₄; (b) removal of turbidity.

LW_{Sum} is not only the most efficient by coagulation at natural pH (the lowest pH point in the figures), but also by softening with PACI. Although UV₂₅₄ removal for YW is as low as the LW_{Win} by coagulation at natural pH, it is more efficient than LW_{Win} by enhanced softening with PACI at high pH. It could be due to the characteristics of organic contaminants.

The characteristics of DOM for the three source waters were determined by resin absorbent and UF fraction. The results are shown in Fig. 6. Although the percentage of hydrophobic DOC in YW is higher than LW_{Sum} and LW_{Win}, it is only about 60% of the total DOC. It is lower than that in the well-protected source water, more than 70% [25,26]. The LW_{Sum} and LW_{Win} are polluted seriously by low molecular weight DOM, especially the LW_{Sum} source accounting for about 65% overall DOM. It is unusually high compared with the commonly found value of no more than 40%. Although DOM with molecular weight lower than 1 kDa only accounts for 21% of the YW DOM, the fractions with molecular weight between 1 and 10K is extremely high (65%) [26,27]. Both rivers are highly polluted by recalcitrant synthetic organic matter, which is not easily removed by coagulation [25–27].

Although the percentage of hydrophobic and high molecular weight DOM in YW is higher than that in LW_{Sum}, the DOM in YW may be harder to remove by enhanced coagulation with PACI [18]. It was found that the coagulable DOM in YW was more heterogeneous than LW_{Sum}, and there was some DOM with high SUVA which

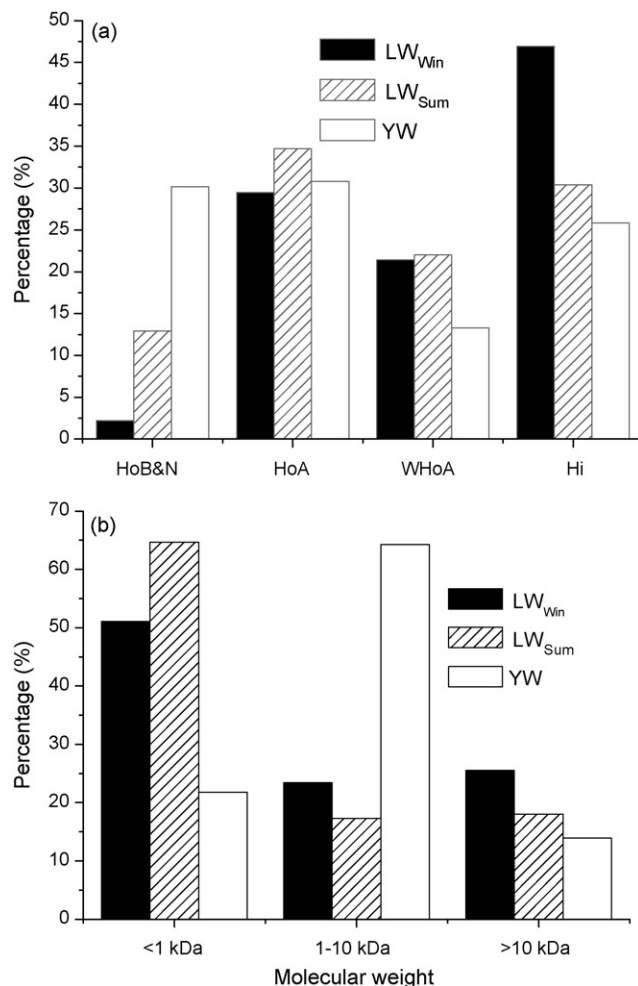


Fig. 6. Comparison of DOM fraction distribution by (a) resin absorbent and (b) ultrafiltration in the Yellow River water (YW), the Luan River water in Summer (LW_{Sum}), and the Luan River water in Winter (LW_{Win}). Hydrophobic basic and neutral (HoB&N), Hydrophobic acid (HoA), Weakly hydrophobic acid (WHOA), Hydrophilic (Hi).

could not be removed efficiently at moderate dose (generally high SUVA refers to the presence of easily removable DOM) [18]. While considering the two source waters from the Luan River, higher content of hydrophobic DOM in LW_{Sum} compared with LW_{Win}, the UV₂₅₄ is removed more efficiently by coagulation at natural pH and coagulation under softening condition. Which is agreed with the results from Thompson et al. [12] that magnesium precipitation effectively remove the hydrophobic fraction of the organic carbon.

4. Conclusion

The effect of coagulants on enhanced softening (using NaOH) for the typical North-China rivers is investigated in this paper and the main conclusions can be drawn as following.

- (1) PACI can enhance Mg(OH)₂ precipitate formation at relative low pH range (pH <10), and it is more efficient than FeCl₃ and AlCl₃ to improve the softening process for NOM and particle removal. Better NOM removal by enhanced softening with coagulant (achieved 50% UV₂₅₄ removal) compared with coagulation at natural pH, and even greater improvement is observed as compared with softening without coagulant. It is also worth notice

that the pH for enhanced softening could decrease significantly into the practical pH range for treatment plant operation.

- (2) From the results, it is shown that the efficiency of enhanced softening is affected by coagulant type and dose, and water quality such as content of Mg, hardness and NOM characteristics. It is of practical value that for organic-polluted water with high content of Mg, enhanced softening with PACl is a recommended treatment option.
- (3) There are several aspects of enhanced softening require further investigation, such as developing coagulant with high Mg^{2+} content, developing positive electrostatic coagulant to enhanced $Mg(OH)_2$ precipitation and surface modification of the surface charge of the $CaCO_3$ precipitate.

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References

- [1] USEPA, Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual, EPA, Office of Water and Drinking Ground Water, Washington, DC, 1998, pp. 20–50.
- [2] U. Iriarte-Velasco, J.I. Álvarez-Uriarte, J.R. González-Velasco, Enhanced coagulation under changing alkalinity-hardness conditions and its implications on trihalomethane precursors removal and relationship with UV absorbance, *Sep. Purif. Technol.* 55 (2007) 368–380.
- [3] A.P. Black, R.F. Christman, Chemical characteristics of fulvic acids, *J. Am. Water Works Assoc.* 53 (1961) 897–916.
- [4] S.J. Randtke, C.E. Thiel, M.Y. Liao, C.N. Yamaya, Removing soluble organic contaminants by lime-softening, *J. Am. Water Works Assoc.* 74 (4) (1982) 192–202.
- [5] M.J. Semmens, A.B. Staples, The nature of organics removed during treatment of Mississippi River water, *J. Am. Water Works Assoc.* 78 (2) (1986) 76–91.
- [6] S.J. Randtke, Organic contaminant removal by coagulation and related process combinations, *J. Am. Water Works Assoc.* 80 (5) (1988) 40–56.
- [7] P. Somasundaran, G.E. Agar, The zero point of charge of calcite, *J. Colloid Interface Sci.* 24 (1967) 433–438.
- [8] W. Stumm, *Chemistry of Solid Water Interface*, Wiley, New York, 1992.
- [9] G. Newcombe, C. Donati, M. Drikas, R. Hayes, Adsorption onto activated. Carbon: electrostatic and non-electrostatic interactions, *Water Supply* 14 (1994) 129–144.
- [10] M. Bob, H.W. Walker, Enhanced adsorption of natural organic matter on calcium carbonate particles through surface charge modification, *Colloid Surf. A* 191 (2001) 17–25.
- [11] M. Bob, Enhanced Removal of Natural Organic Matter During Lime-Soda Softening, Dissertation for Ph.D, Ohio State University, Columbus, 2003.
- [12] J.D. Thompson, M.C. White, G.W. Harrington, P.C. Singer, Enhanced softening: factors influencing DBP precursor removal, *J. Am. Water Works Assoc.* 89 (5) (1997) 64–79.
- [13] J. Leentvaar, M. Rebhum, Effect of magnesium and calcium precipitation on coagulation-flocculation with lime, *Water Res.* 16 (1982) 655–662.
- [14] E. Coro, S. Laha, Colour removal in groundwater through the enhanced softening process, *Water Res.* 35 (2001) 1851–1854.
- [15] D.S. Wang, W. Sun, Y. Xu, H.X. Tang, J. Gregory, Speciation stability of inorganic polymer flocculant-PACl, *Colloid Surf. A* 243 (2004) 1–10.
- [16] M.Q. Yan, D.S. Wang, J.H. Qu, W.J. He, C. Chow, Relative importance of hydrolyzed Al(III) species (Ala Alb and Alc) during coagulation with polyaluminum chloride: a case study with the typical micro-polluted source waters, *J. Colloid Interface Sci.* 316 (2007) 482–489.
- [17] B.A. Dempsey, H. Sheu, T.T.M. Ahmed, J. Mentink, Poly-aluminum chloride and alum coagulation of clay-fulvic acid suspensions, *J. Am. Water Work Assoc.* 77 (3) (1985) 74–80.
- [18] M.Q. Yan, D.S. Wang, S.J. You, J.H. Qu, H.X. Tang, Enhanced coagulation in a typical North-China water plant, *Water Res.* 40 (2006) 3621–3627.
- [19] D.S. Wang, H.X. Tang, Modified inorganic polymer flocculant-PFSi: Its preparation, characterization and coagulation behavior, *Water Res.* 35 (2001) 3418–3428.
- [20] APHA AWWA WEF, Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, Washington, DC, 1995, pp. 253–258.
- [21] M.Y. Liao, S.J. Randtke, Removing fulvic acid by lime softening, *J. Am. Water Works Assoc.* 77 (8) (1985) 78–88.
- [22] D.A. Skoog, D.M. West, *Fundamentals of Analytical Chemistry*, 2nd ed., Reinhart, New York, 1982.
- [23] I.M. Kolthoff, The formation and properties of crystalline precipitates, *J. Phys. Chem.* 36 (1932) 860–881.
- [24] S. Kvech, M. Edwards, Solubility controls on aluminum in drinking water at relatively low and high pH, *Water Res.* 36 (2002) 4356–4368.
- [25] D.M. Owen, G.L. Amy, Z.K. Chowdhury, R. Paode, G. McCoy, K. Viscosil, NOM characterization and treatability, *J. Am. Water Works Assoc.* 87 (1) (1995) 46–63.
- [26] J.A. Leenheer, J.P. Croue, Characterizing aquatic dissolved organic matter, *Environ. Sci. Technol.* 37 (2003) 18A–26A.
- [27] G.L. Amy, R.A. Sierka, J. Bedessem, D. Price, L. Tan, Molecular size distributions of dissolved organic matter, *J. Am. Water Works Assoc.* 84 (6) (1992) 67–75.