Removal of disinfection by-products precursors by polyaluminum chloride coagulation coupled with chlorination

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ABSTRACT

The effect of coagulation coupled with chlorination (i.e., pre-, inter-, and post-chlorination) on the formation of disinfection by-products (DBPs) and the removal efficiency of DBPs precursors were investigated. Compared with coagulation coupling with pre-chlorination, coagulation coupled with inter-chlorination could lead a higher removal efficiency of dissolved organic carbon (DOC), specific ultraviolet absorbance (SUVA) and chloroacetic acids formation potential (CAAsFP). The CAAsFP/DOC value of residual DOC showed that coagulation with inter-chlorination has a beneficial effect on CAAs precursors removal. More DBPs were produced during inter-chlorination than that of pre-chlorination at pH 7.5, while less DBPs were produced during inter-chlorination than that of pre-chlorination at pH 5.5. In addition, the precipitate of humic acid (HA) after coagulation was chlorinated to study the kinetics of chlorine decay. The results showed that coagulated-HA had a higher reactivity with chlorine than aqueous-HA at pH 7.5. Furthermore, the trends of zeta potential during coagulation process suggested that the distribution of chlorine species had significant influence on the removing of DBPs precursors by coagulation coupled with chlorination.

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1. Introduction

Natural organic matters (NOM) react with chlorine during disinfection to produce a number of halogenated disinfection by-products (DBPs) in drinking water treatment [1]. Water supplies require removal of such DBP precursors. Enhanced coagulation is suggested by the United States Environmental Protection Agency (USEPA) as an effective method to remove DBPs precursors during water treatment process [2,3].

Water treatment plants frequently use pre-treatment oxidations, such as chlorine, ozone, and chlorine dioxide as the oxidants to control the amount of nuisance aquatic growths [4]. Additionally, these oxidants have been shown to behave as coagulant aids in some waters. However, some studies have suggested that oxidation prior to coagulation tends to hinder dissolved organic carbon (DOC) removal [5,6]. Bose and Reckhow [7] reported that ozone applied to raw water reacted preferentially with humic fraction of NOM which was readily removed from water by coagulation. Ozonation of humic fraction resulted in a decline removal of DOC through coagulation. However, hydrophilic neutral fraction was

hardly removed by coagulation. Prior ozonation of such organics resulted in an increase removal of DOC through coagulation. Accordingly, a strategy for staged coagulation with intermediate ozonation (coagulation–oxidation–coagulation) was proposed for water treatment to use the beneficial effects of ozone on NOM removal. Singer et al. [8] reported that coagulation coupled with intermediate ozonation was more effective on removing specific ultraviolet absorbance (SUVA) and decreasing DBPs formation than that of coagulation alone.

Coagulant could interact with NOM to change the oxidation reactivity of NOM. There were many researches involved in studying the impact of prior oxidation on coagulation and comparing the NOM removal by coagulation with and without prior oxidation. Staged coagulation with intermediate oxidation (coagulation–ozonation–coagulation) [7] was also studied. And the removal efficiency of DOC and SUVA is substantially enhanced. But this method is not practical for the treatment plant to replace the conventional coagulation at the present time. Dosage of the oxidants during coagulation (inter-oxidation) might be an effective method for the improvement of conventional coagulation to increase DBP precursors removal in practical. However, coagulation coupled with inter-oxidation was rarely studied.

In this paper, we employed sodium hypochlorite as oxidant, humic acid (HA) as NOM to study the effect of inter-oxidation on the

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DBPs precursors removal in coagulation process. The major objectives were to identify and study (1) the effect of chlorination on the humic acid structure; (2) the reaction mechanism of sodium hypochlorite (NaOCl) with humic acid in the presence of polyaluminum chloride (PACl), and (3) the removal efficiency of DBPs precursors by PACl coagulation coupled with inter-chlorination. The results of this study might provide new method of enhanced coagulation and useful information involved in these processes.

2. Materials and methods

2.1. Experimental materials

- (1) *Natural organic materials*. Isolated humic acid from soil was used as source of NOM. Soil collected from a wetland at the edge of a lake in North China has a high content of organic material.
- (2) *Polyaluminum chloride*. The electrolysis process was employed to prepare PACl [9], which contains significant quantities of the active species Al_{13} polymer [10]. Speciation of the PACl was determined by Ferron method [11]. The total aluminum concentration (Al_T) of PACl was 13.57 g/L. The chemical species of hydrolyzed $Al(III)$ were divided into three types: Al_a 2.7%, Al_b 89.9% and Al_c 7.4%, with OH/Al molar ratio (simplified as B values) of 2.36.
- (3) Kaolinite particles were calcined in a muffle furnace at $500^\circ C$ for 4 h to remove organic impurities, then size fractionated by sedimentation at pH 7.5 to produce monodisperse suspension.

2.2. Experiment procedures

Isolated humic acid was dissolved in 0.1 M NaOH and filtered through a $0.45\ \mu m$ filter, then diluted to Milli-Q water with a sodium bicarbonate of 2 mM, potassium nitrate of 3.5 mM and kaolinite for an approximate turbidity of 20 NTU. Jar test were carried out in a jar test apparatus (MY3000-6, Meiyu Inc., Qianjiang). 0.1 M HCl and 0.1 M NaOH were used to adjust the pH to required value. The contents of the jars were rapid mixed at paddle speed of 300 rpm for 2.5 min, followed by slow mixing at 30 rpm for 20 min, and settling for 2 h. The supernatant was collected for measurement of DOC, pH, UV_{254} .

Three coagulation processes were performed at pH 5.5 and 7.5 in the PACl underdosing and conventional situations, which were as follows: (1) chlorine dosed 30 min before PACl; (2) chlorine dosed simultaneously with PACl and (3) chlorine dosed 2.5 min after PACl. DBPs yields were determined after coagulation to calculate the DBPs produced in coagulation processes.

Water samples after coagulation were chlorinated with sodium hypochlorite (NaOCl) with a Cl_2 of 20 mg/L at pH 7, $20^\circ C$ for 72 h, buffered by $KH_2PO_4/NaOH$ in 40 mL vials to determine the DBPs formation potential (DBPsFP). DBPsFP here is defined as the formation potential of residual DOC (DBPs produced in pre-chlorination or inter-chlorination were not included):

$$\text{Total DBPs} = \text{Pre-DBPs} + \text{DBPsFP} \quad (1)$$

In addition, water samples after coagulations were concentrated by vacuum rotary evaporation at $40^\circ C$. The concentrated samples were used for gel permeation chromatography to determine the molecular weight distribution of humic acid both after chlorination and coagulation.

2.3. Analytical methods

pH was measured by Orion 720 APLUS Benchtop meter (Thermo Orion Co., USA). Zeta potentials were measured by a Zetasizer 2000

(Malvern, UK). Turbidity was measured by 2100N IS Turbidimeter (HACH Co., USA). Quantification of HA was accomplished by measuring UV absorbance of samples at 254 nm by a U-3010 UV-vis spectrophotometer (Hitachi Co., Japan) equipped with 10 mm quartz cells and measuring DOC by a multi-N/C 3000 analyzer (Analytik Jena AG, Germany). Chlorine concentration was measured by *N,N*-diethyl-phenylenediamine (DPD) photometry methods.

Gel permeation chromatography (GPC) was performed with a HPLC system (L-2000, HITACHI Co., Japan). The column employed for GPC was TSK-GEL (Toshiba, G3000PWXL, $7.8\ mm \times 30\ cm$, and particle size $6\ \mu m$). The eluent was phosphate buffer (2.4 mM NaH_2PO_4 , 1.6 mM Na_2HPO_4 , pH 6.8, 0.01 M CH_3COONa) with a flow rate of 0.6 mL/min. The sample volume was $20\ \mu L$. Sodium-*p*-styrene sulfonates (PSS 1.37 kDa, PSS 4.6 kDa, PSS 6.2 kDa, and PSS 15.65 kDa) were used as molecular mass calibration standards.

Trichloromethane (TCM) was analyzed by liquid/liquid extraction with hexane and gas chromatography/electron capture detector (GC/ECD) (Agilent 6890N Series, USA) according to USEPA Method 551.1 [12]. Chloroacetic acids (CAAs, including di-, and tri-chloroacetic acids) were analyzed by liquid/liquid extraction with methyl *tert*-butyl ether (MTBE) followed by derivatization with acidic methanol and measured by GC/ECD according to USEPA methods 552.2 [13].

3. Results and discussion

3.1. Effect of chlorination on humic acid structure

Gel permeation chromatography–UV detection was applied to study the structure change of humic acid after chlorination. The comparison of the humic acid structure before and after chlorination is shown in Fig. 1. For the fractions with different molecular weight (MW), the changes of UV_{254} after chlorination do not follow the same trends. A reduction of UV_{254} is observed for the fractions with a retention time of 9.00 and 11.50 min, while there is no reduction for the fractions with a retention time range of 11.50–11.90 min. According to the separation mechanism of GPC, higher MW compounds are eluted earlier. A direct reason for this difference is that part of higher MW humic acid are oxidized and transformed into lower MW compounds. The reduction of UV absorbance of higher MW is due to that larger size humic acid is oxidized into smaller size which elute later from the column or the destruction of chromophores. This implies that chlorination do not only destruct chromophores that absorb UV radiation, but also changes the MW distribution of humic acid. The results present in Fig. 1 are similar to that reported by other researcher [14].

GPC–UV profiles of humic acid after coagulation are also shown in Fig. 1. For the humic acid solution with a DOC level of 3.6 mg/L,

Fig. 1. GPC–UV analysis of humic acid before and after chlorination (pH 7.0 ± 0.2 , DOC 3.6 mg/L, chlorine 3.0 mg/L (as Cl_2) and PACl 0.4 mg Al/mg DOC). Note: retention times of peaks a–e are 9.00, 11.50, 12.36, 13.30 and 14.67 min, respectively.

Fig. 2. Impact of dosage points of chlorine (as HOCl/OCl⁻) on humic acid removal by PACI coagulation at pH 5.5 ± 0.2. DOC 3.6 mg/L, chlorine 3.0 mg/L (as Cl₂), turbidity 20 NTU. (A) DOC removal and (B) SUVA removal.

Table 1
Quotient E_2/E_3 value of humic acid with different MW

	Retention time (min)				
	11.50	11.90	12.36	13.30	14.67
E_2/E_3 (HA)	5.17	6.00	8.78	8.24	7.38
E_2/E_3 (HA + NaClO)	6.00	6.58	8.22	8.55	5.88
$\Delta E_2/E_3$	+0.83	+0.58	-0.56	+0.31	-1.50

almost 72% of DOC can be removed after PACI coagulation. The profiles indicate that coagulation remove the humic acid component selectively. Higher MW humic acid compounds tend to be a higher removal, while lower MW humic acid compounds turn out to be the opposite. After coagulation, the major components of larger size humic acid are removed, while residual humic acid components are relatively with smaller size. These components become the major DBPs precursors during disinfection process.

Another evidence of structure changes of NOM is the evolution of E_2/E_3 (the ratio of 250/365 nm) value after chlorination. Humic acid with different MW may contain different functional groups. The quotient E_2/E_3 correlates with the molecular size and aromaticity of aquatic humic solutes: when the quotient E_2/E_3 increases, the aromaticity and molecular size of aquatic humic solutes decreases [15]. As shown in Table 1, it is observed that the quotient E_2/E_3

increases for the compounds with retention time 11.50, 11.90 and 13.30 min and decreases for the compounds with retention time 12.36 and 14.67 min. The increase of E_2/E_3 is presumably a manifestation of oxidation and halogenation reactions, reflecting changes in the chromophores that can be destructed by chlorine [16]. But this oxidation does not usually lead to complete mineralization of NOM [17]. However, the decrease of E_2/E_3 in the lower MW region was probably attributed to the fragment from larger size molecules which contain low E_2/E_3 value.

These results suggest that the DOC removal by coagulation will be hindered if the chlorination is applied to humic acid before coagulation, because larger sizes humic acid molecules will transform into smaller sizes after chlorination. Bose and Reckhow [7] suggested two-stage coagulation with intermediate oxidation make optimal use of the beneficial effects of oxidation on NOM removal.

3.2. Removal of DOC and SUVA by PACI coagulation coupled with chlorination

Coagulations coupled with chlorination for NOM removal were carried out at pH 5.5 and 7.5, and the results are presented in Figs. 2 and 3, respectively. Chlorine dosed 30 min before PACI (coagulation with pre-chlorination) leads a decrease of DOC removal at

Fig. 3. Impact of dosage points of chlorine (as HOCl/OCl⁻) on humic acid removal by PACI coagulation at pH 7.5 ± 0.2. DOC 3.6 mg/L, chlorine 3.0 mg/L (as Cl₂), turbidity 20 NTU. (A) DOC removal and (B) SUVA removal.

the two pH values. These phenomena are similar to those reported by other researchers [5,18]. Organic matters adsorbed on the particle surface can be oxidized into lower molecular size and released into solution (Figs. 2A and 3A). Moreover, the formation of the small organics can inhibit the coagulation and decrease the DOC removal.

The trends of DOC removal vary with different pH values. A higher DOC and SUVA removal efficiency is observed when chlorine is dosed 2.5 min after PACI dosing (coagulation with inter-chlorination) at pH 5.5 (see Fig. 2). However, DOC removal decreases when using coagulation coupled with chlorination (pre- and inter-) at pH 7.5 (Fig. 3A). The SUVA removal efficiency by PACI coagulation without chlorine is less than that of coagulation coupled with inter-chlorination (Figs. 2B and 3B). SUVA was indicative parameters for the aromaticity in NOM [8,19]. So it can be concluded that the aromatic structure of NOM are destructed by chlorine, resulting in the reduction of DBPsFP of NOM. According to the report of Morris [20], the proportion of HOCl and OCl⁻ is affected by the pH of solution. It can be concluded that during the coagulation process coupled with chlorination, the effect of pH on the DOC removal efficiency results from the different mechanisms and pathway of chlorination reaction.

3.3. Reaction between chlorine and humic acid during coagulation process

To study the effect of chlorine on the humic acid during coagulation progress, coagulated-HA solution and aqueous-HA solution were prepared and were chlorinated. Humic acid was coagulated with PACI in a dosage of 0.3 mg Al/mg DOC (a conventional situation) and settled. And then, the precipitate was transferred to Milli-Q water to obtain a TOC concentration of 4.8 mg/L (DOC ≤ 0.30 mg/L). The DOC contained in precipitate was calculated through residual DOC concentration in the supernatant. Aqueous humic acid was also prepared with a DOC of nearly 4.8 mg/L. NaHCO₃ (2 mM) were added to these two different humic acid phases. Chlorine with an initial concentration of 3.0 mg/L (as Cl₂) was added to these two solution. Degradations of chlorine in these two humic acid phases are presented in Fig. 4. A higher degradation rate is observed in the coagulated-HA solution in the first 30 min

Fig. 4. Degradation of chlorine for aqueous-HA and coagulated-HA (chlorine 3.0 mg/L (as Cl₂), PACI 0.3 mg Al/mg DOC, NaHCO₃ 2 mM, temperature 25 °C and pH 7.5 ± 0.2).

and the residual chlorine become changing slightly after 30 min. However, The concentration of chlorine remaining in aqueous-HA solution after 60 min reaction.

These results indicate that parts of coagulated-HA have higher reactivity, while others might not react with chlorine. Coagulation increases the concentration of HA in a micro-environment and forms a solid–water interface. The negative charge density of the aggregates is lower than aqueous-HA due to the charge neutralization of PACI. Thus, OCl⁻ can be concentrated near the surface of the aggregates and react with HA, resulting in the high reaction rate between chlorine and coagulated-HA. In contrast, negatively charged functional groups of aqueous-HA can hamper HOCl/OCl⁻ collision because of electrostatic repulsion. Thus, the chlorination reaction will be relatively restrained in aqueous-HA solution. Another reason for the high reactivity is probably due to the catalysis of aluminum species. Previous researcher [21] reported that aluminum could catalyze the oxidation process of

Fig. 5. Yields of DBPs produced during coagulation coupled with chlorination (DOC 3.6 mg/L, Chlorine 3.0 mg/L (as Cl₂), NaHCO₃ 2 mM and temperature 25 °C).

sodium hypochlorite with polyamide membrane. The aggregates can provide interface for the catalytic reaction.

Since coagulated-HA solution is heterogeneous, humic acid is presented as “solid state”. Chlorine can hardly react with compounds entrapped in aggregates. Then, higher reaction rate of chlorination primarily occurred covering the interface of these “solid state” HA. Thus, the negative surface charges density of coagulated-HA increased after reaction with chlorine. With the increasing charge density, higher reaction rate slowed down, and furthermore, negatively charged functional groups on surface benefit its subsequent adsorption and precipitation by PACI, leading a better removal of SUVA.

For the further study, attention is drawn to the production of DBPs during pre- and inter-chlorination processes. CAAs and TCM production were determined and the results are presented in Fig. 5. Both CAAs and TCM productions are higher during the process of chlorine dosed 2.5 min after PACI at pH 7.5. This indicates that the presence of PACI has enhanced the formation of CAAs and TCM at pH 7.5. As in the present result, PACI species change the organic charge, which may increase the reactivity of humic acid with chlorine. However, the opposite results are found at pH 5.5. CAAs and TCM productions are lower when chlorine dosed 2.5 min after PACI. This study indicates that pH value shows greatly influence on the reaction between humic acid and chlorine in the presence of PACI.

The pH adjustment affects the distribution of HOCl and OCl⁻. Hypochlorous acid is a weak acid which dissociates in aqueous solution [20].

At low pH values, hypochlorous acid (HOCl) is a predominant species. Increasing pH value will lead a high proportion of hypochlorite (OCl⁻) species.

Fig. 6. Influences of pH on zeta potentials of the particles during coagulation process in the presence of chlorine (chlorine 3.0 mg/L (as Cl₂), NaHCO₃ 2 mM, temperature 25 °C, PACI 0.4 mg Al/mg DOC at pH 7.5 and 0.2 mg Al/mg DOC at pH 5.5).

For the purpose of demonstrating the above conclusion, a special experiment was performed in which zeta potentials of particles were measured during coagulation process with inter-chlorination at different pH condition. Since the reaction activity between HA and chlorine was influenced by zeta potential of HA, different PACI dosages were chosen at different pH (pH 5.5 and 7.5) to make the initial zeta potentials nearly the same. The results are presented in Fig. 6. Progressive decrease of zeta potential at pH 7.5 is consistent with the phenomena in Fig. 4, indicating a high reaction rate between chlorine and humic acid. There is, however, only a slight decrease of zeta potential at pH 5.5, implying the low reactivity rate between coagulated-HA and HOCl. These differences result in the

Fig. 7. Comparison of CAAsFP/DOC after different coagulation processes (chlorine 3.0 mg/L (as Cl₂), NaHCO₃ 2 mM, temperature 25 °C, PACI = 0.4 mg Al/mg DOC at pH 7.5 and 0.2 mg Al/mg DOC at pH 5.5).

dissimilar formation of DBPs during coagulation process at pH 5.5 and 7.5 (see Fig. 5).

The results of the above experiments indicate that, while coagulation coupled with inter-chlorination, the removal efficiency of DOC is affected by the oxidant species, as well as the NOM chemical structure. On the basis of overall results, it is proposed that the formation of aggregates during coagulation process inhibits the reaction between chlorine and the organics that has been entrapped in the aggregates. At pH 7.5, higher reaction rate of chlorination occurred covering the interface of these aggregates. The duration of coagulation process was about 20–30 min, during which the higher reaction rate occurred (see Fig. 4). As a result, more DBPs were produced during the coagulation process at pH 7.5 (see Fig. 5). While at pH 5.5, HOCl is prevalent. Although the formation of aggregates increased the concentration of HA in micro-environment and the zeta potential, the reactivity of HOCl with coagulated-HA was less influenced by zeta potential than that of ClO^- with coagulated-HA (see Fig. 6). Therefore, the reaction rate of chlorine with coagulated-HA was not increased. Furthermore, HA was entrapped in the aggregates and could not contact with chlorine. Thus, less DBPs were produced during the coagulation process at pH 5.5 (see Fig. 5). The aggregates can “protect” humic acid with larger size which is readily removal by PACl coagulation. Organic matter with smaller size which is hardly removal from water appears to change the specific organic charge by reacting with chlorine, causing an increased removal of DOC.

3.4. Removal of CAAs precursors by PACl coagulation coupled with chlorination

Coagulations were performed at PACl optimum dosage (0.2 mg Al/mg DOC at pH 5.5 and 0.4 mg Al/mg DOC at pH 7.5). The CAAs formation potential (CAAsFP) of residual DOC after coagulation are presented in Fig. 7. CAAs concentrations ($\mu\text{g/L}$) are normalized per unit of DOC (mg/L). CAAsFP/DOC values follow the rank order: chlorine dosed 30 min before PACl > chlorine dosed simultaneously with PACl > chlorine dosed 2.5 min after PACl. The results indicate that coagulation coupled with inter-chlorination has a beneficial effect on CAAs precursors removal. A hypothesis here is that DBPs precursors transform into intermediate products by reaction with chlorine. The intermediate products can readily be coagulated by PACl and entrapped in the aggregates. As a result, further chlorination reaction tends to be restrained (see Section 3.3).

4. Conclusions

Coagulation with inter-chlorination showed higher removal of DOC, SUVA and CAAs precursors than that of coagulation with pre-chlorination. Coagulation process increased the concentration of HA in a micro-scale ambience and formed a solid-water interface, resulting in the change of chlorination reactivity.

Higher degradation rate of HA was observed in PACl coagulated-HA solution than in aqueous-HA solution. More DBPs were produced in inter-chlorination than in pre-chlorination at pH 7.5, while the opposite result was obtained at pH 5.5. Since pH affects the distribution of HOCl and OCl^- . These phenomena indicated that the HOCl reacted with coagulated-HA at low reactivity, while OCl^- could react with coagulated-HA quickly for its different charge properties.

Based on these results, inter-oxidation with pH control was proposed to apply during coagulation process to make efficiently use of oxidant and reduce DOC and DBPs precursors.

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