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Effects of Ca(OH)$_2$ assisted aluminum sulfate coagulation on the removal of humic acid and the formation potentials of tri-halomethanes and haloacetic acids in chlorination

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Abstract

The effects of addition of calcium hydroxide on aluminum sulphate (or alum) coagulation for removal of natural organic matter (NOM) and its subsequent effect on the formation potentials of two major types of regulated disinfection byproducts (DBPs), haloacetic acids (HAAs) and trihalomethanes (THMs), have been examined. The results revealed several noteworthy phenomena. At the optimal coagulation pH (i.e. 6), the coagulation behavior of NOM water solutions versus alum dose, showed large variation and a consequent great change in the formation potentials of the DBPs at certain coagulant doses. However, with addition of a relatively small amount of Ca(OH)$_2$, although the zeta potential of coagulated flocs remained almost the same, NOM removal became more consistent with alum dose. Importantly, also the detrimental effect of charge reversal on NOM removal at the low coagulant dose disappeared. This resulted in a steady decrease in the formation potentials of DBPs as a function of the coagulant dose. Moreover, the addition of Ca(OH)$_2$ broadened the pH range of alum coagulation and promoted further reduction of the formation potentials of the DBPs. The enhancement effects of Ca(OH)$_2$ assisted alum coagulation are especially pronounced at pH 7 and 8. Finally, synchronous fluorescence spectra showed that the reduction in DBPs formation potential by Ca(OH)$_2$-assisted alum coagulation was connected to an enhanced removal of small hydrophobic and hydrophilic HA molecules. Ca(OH)$_2$-assistance of alum coagulation appeared to increase substantially the removal of the hydrophilic HA fraction responsible for HAAs formation, prompting further reduction of HAA formation potentials.

Key words: enhanced coagulation; alum; disinfection byproducts; humic acids

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Introduction

Chlorination is an effective disinfection method in water treatment for inactivating microorganisms to safeguard the public health against waterborne diseases. However, reactions of chlorine with natural organic matter (NOM) in water may result in formation of harmful disinfection by-products (DBPs), such as trihalomethane (THMs) and haloacetic acids (HAAs) (Malliarou et al., 2005; Hua and Reckhow, 2007). To minimize the formation of DBPs, ‘enhanced coagulation’ and ‘precipitative softening’ processes have been introduced to increase the removal efficiency of NOM (the DBP precursors) by the United States Environmental Protection Agency (US EPA) in the Stage 1 Disinfectant and Disinfection Byproducts Rule in conventional water treatment processes (US EPA, 1998).

Removal of natural organic matter (NOM) by hydrolyzing metal salt coagulants has been studied extensively at laboratory and full treatment plant scales (Chowdhury et al., 1997; Edwards, 1997; Yan et al., 2006). Studies showed that disinfection byproduct formation can be reduced through increased NOM removal by enhanced coagulation. Such enhanced coagulation effects have also been observed by examining the speciation and yield of THMs and HAAs after coagulation and lime softening (Shorney et al., 1999). The coagulation effects on removal of total organic carbon (TOC) or dissolved organic carbon (DOC) from water have been observed to be dependent on coagulant dosage, final pH, and the concentration and nature of NOM in raw waters, as well as raw water alkalinity (Krasner and Amy, 1995; Chowdhury et al., 1997; Edwards, 1997; White et al., 1997). A significantly enhanced removal of THMs at a high dose of alum has been observed at pH 5.5 compared with that at ambient pH (Vrijenhoek et al., 1998). Further, it has been reported that enhanced coagulation and the subsequent sedimentation and filtration processes in water treatment remove mostly the hydrophobic NOM with large molecular weights and that the hydrophilic NOM fractions are less amenable to removal through such conventional...
treatment processes (Sharp et al., 2006). However, a recent study suggested that optimized removal of DOC could not assure the greatest removal of THMs precursors and that the removal efficiencies could be dramatically different when coagulation proceeded above neutral pH (Iriarte-Velasco et al., 2007). At the same time, the study also indicated that hydrophilic NOM could be better removed from higher alkalinity-hardness waters. Despite these complexities, compared with other methods, such as advanced oxidation processes, enhanced coagulation is still the most feasible technology for DBP mitigation (Gerrity et al., 2009).

The proposed mechanisms of enhanced coagulation for NOM removal include enhanced adsorption, precipitation and charge neutralization based on optimization of pH or increase of coagulant dose. In addition, a certain degree of NOM removal has been reported by softening or enhanced softening via adsorption or co-precipitation by CaCO$_3$ or Mg(OH)$_2$ precipitates at high pH (e.g. the formation of calcium-fulvate) (Liao and Randtke, 1986; Roalson et al., 2003). Also in enhanced softening pre-addition of a dose of aluminum sulfate or ferric sulfate before lime was found to increase TOC removal and hence benefit DBP reduction.

The objective of this study is to examine the possibility of enhanced removal of humic acid by Ca(OH)$_2$ addition in aluminum sulfate coagulation and the consequent effects on the reduction in formation of the two major regulated by-products, THMs and HAAs in water supply.

1 Experimental

1.1 Materials

Ultra-pure water was produced by a Milli-Q ultra-pure water apparatus (18.2 MΩ·cm at 25°C) (Millipore, USA). Aluminum sulfate (Al$_2$(SO$_4$)$_3$:18H$_2$O), Ca(OH)$_2$, NaHCO$_3$ are of analytical grade (Xi’an Chemicals Ltd., China). Stock solutions of aluminum sulfate (0.1 mol/L) were stored in a refrigerator at 4°C and used for a maximum of two weeks. A sodium hypochlorite (NaClO) solution (chemically pure) was purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Ascorbic acid (C$_6$H$_8$O$_6$, analytical grade) was obtained from Tianli Chemical Ltd. (Tianjin, China). The pH adjustment was carried out using HCl and NaOH (analytical grade, Xi’an Chemicals Ltd., China).

Humic acid (HA) was purchased as a commercial product (Technical grade, Sigma-Aldrich, USA). A stock solution was prepared by dissolving 1 g of dry humic acid product in 1 little ultra-pure water at 70°C, and the filtrate from 0.45 μm membrane filter (Mixed Cellulose Esters Membrane Filters (MCE), Xinya Shanghai Ltd., China) stored for use. The dissolved organic carbon (DOC) concentration of the humic acid solutions was measured using a TOC analyser (Shimadzu TOC-VCPH, Japan).

1.2 Instruments and methods

Zeta potentials of the coagulated suspensions were measured with a Zetasizer nano particle analyzer (Nano ZS, Malvern, UK). pH was measured with a pH meter (PHS-3C, Dapu, China). Haloacetic acids were determined using a method developed in this laboratory based on ultra-performance liquid chromatography tandem mass spectrometry (Acquity TQD, Waters, USA) (Duan et al., 2011). Trihalomethanes were detected using the US EPA method 524.2 based on purge & trap gas chromatography-mass spectrometry (GC/MS) (6890N-5973N, Agilent, USA). Fluorescence spectra of solutions were measured using a JASCO FP-6500 (Japan) fluorescence spectrometer. Synchronous fluorescence spectra were obtained at a wavelength difference between excitation and emission (∆λ) of 60 nm. The value for ∆λ was selected for the maximum structured fluorescence intensity, in the scan range of excitation wavelength (λ$_{excitation}$) from 250 to 550 nm for the humic acid solution, after a series of trials with ∆λ, at 20, 40 and 60 nm. Note that this value was also used in a previous study (Duarte et al., 2003).

Humic acid solutions were prepared using Milli-Q water with 1 mmol/L NaHCO$_3$ for an alkalinity background. Coagulation experiments were performed in a 500 mL beaker following a standard jar-test procedure. In the experiments, a certain pre-determined amount of HCl or NaOH was first added into 300 mL of the humic acid solution, followed by addition of Ca(OH)$_2$. Then, a dose of alum was finally added into the solution, leading to a designated final solution pH. Immediately after addition of the alum, the solution was stirred for 60 sec at 500 r/min, followed by slow stirring at 100 r/min for 15 min. A sample of 5 mL was taken for detection of zeta potentials immediately after the fast mixing; a final pH value was taken at the end of the slow mixing and reported with an error of ±0.05. A 250-mL sample was taken from the supernatant at the end of the settling period, filtered through a 0.45-μm membrane filter, and analyzed for DOC to evaluate the separation efficiency of coagulation. The dosages of alum and calcium hydroxide were calculated as mg/L Al$_2$(SO$_4$)$_3$ and Ca(OH)$_2$, respectively. The filtrate was chlorinated in a 150-mL amber flask by addition of NaClO solution (6 mg/L as Cl$_2$) and allowed for 20-hr reaction. Then, 100 mg of ascorbic acid powder was added into the flask to quench any further the reactions.

All the experiments were repeated three times. Average values of the triplicate measurements for each condition were reported. The relative standard deviations (RSD) of the triplicate DOC and HAA measurements: < 2.5 % and < 7 %, respectively. A typical set of synchronous fluorescence spectra of water samples for each of the two coagulation conditions was reported. The experiments were carried out at the ambient water temperature 21 ± 2°C.

2 Results and discussion

2.1 Influences as a function of pH

The influences of solution pH on Ca(OH)$_2$ assisted alum coagulation for NOM removal were examined at an optimal alum dose of 80 mg/L and a Ca(OH)$_2$ dose of 30 mg/L.
Several coagulation mechanisms have been proposed and discussed in literature. Sorption of DOC to metal hydroxide surfaces formed during coagulation was considered to be the mechanism for enhanced coagulation. Removal of DOC during alum coagulation is also thought to be facilitated by surface complexing of the fraction of sorbable DOC on the metal hydroxide surfaces (Edwards, 1997). In addition, a precipitation and charge neutralization model (PCN) has also been proposed for the coagulation mechanisms of particulates and NOM (Dentel, 1997). In addition, a precipitation and charge neutralization model (PCN) has also been proposed for the coagulation mechanisms of particulates and NOM (Dentel, 1997). It should be pointed out that at the optimum pH value (pH 6) and the highest alum dose (80 mg/L) in our experiments, enhancement of alum coagulation for HA removal by addition of Ca(OH)$_2$ was observed even at a very small dose of Ca(OH)$_2$ (the COD removal percentage were 79.1%, 79.5%, 79.9%, 80.2%, 80.6%, 81.3%, and 81.3% at 0, 5, 10, 20, 30, 40, 50, and 80 mg/L, respectively). The enhancement increased as the increase of Ca(OH)$_2$ dose, and appeared to reach its maximum at around the dose above 40 mg/L.

The disinfection byproduct (haloacetic acids and chloroform) formation results for the above coagulation systems were 79.1%, 79.5%, 79.9%, 80.2%, 80.6%, 81.3%, and 81.3% at 0, 5, 10, 20, 30, 40, 50, and 80 mg/L, respectively. The enhancement increased as the increase of Ca(OH)$_2$ dose, and appeared to reach its maximum at around the dose above 40 mg/L.
are presented in Fig. 2. Note that only chloroacetic acids were formed and detected since there were no bromide ions present in the solutions. It can be seen that formation of the chloroacetic acids (MCAA, DCAA, TCAA) was decreased for the chlorinated water treated by the Ca(OH)$_2$ assisted-alum coagulation followed by the microfiltration. At the optimum pH value (pH 6), and neutral pH value (pH 7), an appreciable reduction of HAAs formation was observed, which is large compared with the US EPA limits for the HAA5 (60 μg/L). However, the most striking reduction in the formation of chloroacetic acids occurred at pH 8, at which a great enhancement of HA removal was observed for the Ca(OH)$_2$-alum coagulation system (Fig. 1b). Surprisingly, formation of chloroacetic acids was increased at pH 9 even though the DOC was reduced by the addition of Ca(OH)$_2$. Gerrity et al. (2009) reported that the THMFP was lowest at an acidic pH (5.5) when a moderate dose of ferric chloride was used. The results here agree with this general observation by showing that the best reduction was observed at pH 6 for alum coagulation. However, the biggest merit may be that the addition of Ca(OH)$_2$ broadens the pH range for alum coagulation in terms of NOM removal and DBP reduction up to pH 8.

The trend of the enhanced reduction of chloroform formation in the coagulation system of alum with assistance of Ca(OH)$_2$ is similar to that for chloroacetic acids (Fig. 2c). Again, similarly to the situation for chloroacetic acids, the formation of chloroform appeared to be also increased significantly at pH 9.

2.2 Influences as a function of alum dose

The effect of Ca(OH)$_2$ addition on alum coagulation of the humic acid solutions was also examined at different alum dose up to 100 mg/L at the optimum coagulation pH (6) (Fig. 3). The benefits of the addition of a moderate dose of Ca(OH)$_2$ (30 mg/L) for enhanced humic acid removal in alum coagulation were clearly observed from the results, especially at a low (10 mg/L), and a medium (40 mg/L), alum dose. It is noteworthy that the coagulation effect for humic acid removal for alum (without Ca(OH)$_2$) at the dose of 40 mg/L deteriorated compared to that at a lower alum dose due to a charge reversal effect of the coagulated suspensions. Addition of Ca(OH)$_2$ eliminated such a negative effect and improved the humic acid removal. Again, since the charge of the flocs remains almost the same with addition of Ca(OH)$_2$, Gerrity et al. (2009) reported that the THMFP was lowest at an acidic pH (5.5) when a moderate dose of ferric chloride was used. The results here agree with this general observation by showing that the best reduction was observed at pH 6 for alum coagulation. However, the biggest merit may be that the addition of Ca(OH)$_2$ broadens the pH range for alum coagulation in terms of NOM removal and DBP reduction up to pH 8.

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![Fig. 2](image-url)  
**Fig. 2.** HAAs (a, b) and chloroform (c) concentrations versus pH. (a) humic acid containing water was chlorinated after coagulation by alum followed by microfiltration; (b) the same except coagulation by alum with addition of Ca(OH)$_2$ (30 mg/L); (c) with and without addition of Ca(OH)$_2$ (30 mg/L).
Fig. 3 Zeta potentials of the coagulated suspensions of humic acid solutions by alum with and without addition of Ca(OH)$_2$ (a) and DOC concentrations of these suspensions after microfiltration, versus alum dose (b). Ca(OH)$_2$: 30 mg/L; HA: 10 mg/L as DOC at pH 3.

Fig. 4 HAA concentrations versus alum dose. (a) the filtrate was chlorinated after microfiltration of coagulated humic acid solutions by alum; (b) the same except coagulation by alum in the presence of Ca(OH)$_2$.

of the spectra for the filtered water samples after alum coagulation in the presence of Ca(OH)$_2$ were much smaller than those without the presence of Ca(OH)$_2$ clearly due to the enhanced removal of fluorophore components of the humic acid fraction. This may be taken to indicate an overall enhanced removal of humic matter with addition of Ca(OH)$_2$ to the coagulation system. In addition, a shift of the spectra to lower wavelengths was also observed (see pH = 6 or the inset). It has been suggested that the spectra would shift to lower wavelengths for smaller fulvic molecules (Duarte et al., 2003). Humic acid fractions with a smaller size range (5–8 kDa) show relatively higher

Fig. 5 Synchronous fluorescence spectra of filtered coagulated waters (pure water spectra subtracted) at different pH values with (a) and without (b) addition of Ca(OH)$_2$. Al$_2$(SO$_4$)$_3$: 80 mg/L; Ca(OH)$_2$: 30 mg/L. Inset: solid line: no Ca(OH)$_2$; broken line: with Ca(OH)$_2$ at pH 6.
specific fluorescence intensity, especially for the characteristic peaks at $\lambda_{\text{excitation}}$ between 280 and 320 nm. A signal at $\lambda_{\text{excitation}}=280$ nm is probably due to lignin-derived structural moieties and aromatic amino acids (Sierra et al., 2005). It has also been reported that for water treated by coagulation, flocculation and settling, the fractions of small molecular weight ($<1$, or 1–10 kDa) of NOM are predominant, contributing significantly to the THMFP (Iriarte-Velasco et al., 2007), and that for filtered water the apparent molecular weight (AMW) is smaller than 10 kDa. The hydrophobic fraction was found to be more readily removed than the hydrophilic fraction of NOM by water treatment and the relative proportion of the hydrophilic fraction was thus increased (Kim and Yu, 2005). Phenolic acids of NOM surrogates produced a larger amount of DBPs (Reckhow et al., 1990), and compounds with attached carboxyl (–COOH) functional groups had lower halogen consumption and haloform formation (Westerhoff et al., 2004). Zhang et al. (2005) showed that coagulation could significantly reduce the formation of high MW chlorinated DBPs. Therefore, addition of Ca(OH)$_2$ in alum coagulation systems may enhance the removal of smaller humic acid molecules (either hydrophobic or hydrophilic). Further, by comparing the formation of chloroform and chloroaacetic acids (Fig. 2), it seems that the enhanced coagulation by addition of Ca(OH)$_2$ has a stronger reduction effect on chloroaacetic acids than on chloroform. Therefore, it is likely that addition of Ca(OH)$_2$ enhanced the removal of humic acids with hydrophilic molecular moieties. Low MW and hydrophilic NOM fractions tend to produce chloroaacetic acids (Hua and Reckhow, 2007), whereas the formation potential of THMs was highly influenced by the hydrophobic fractions of NOM (Reckhow et al., 1990; Vrijenhoek et al., 1998; Kim and Yu, 2005).

3 Conclusions

The effects of addition of Ca(OH)$_2$ on coagulation of humic acid-containing waters by alum were examined as a function of solution pH and alum dosage. Addition of Ca(OH)$_2$ improved alum coagulation in terms of DOC removal at almost all the tested pH values and alum doses. However, the most significant enhancement was seen at low and medium alum doses and at neutral and alkaline pHs. These results indicate that addition of Ca(OH)$_2$ in the alum coagulation system promoted co-precipitation between humic acid and the coagulants, resulting in enhanced humic acid removal from the water. The enhancement of alum coagulation by addition of Ca(OH)$_2$ leads to significant reduction in the formation of THMs and HAAs as disinfection byproducts. A comparatively greater reduction was observed for HAAs than for chloroform. The synchronous fluorescence spectra of the filtered coagulated waters indicate that the Ca(OH)$_2$ addition enhanced the removal of both the hydrophobic and hydrophilic fractions of humic acid with smaller molecular size. An enhancement in the removal of small hydrophilic humic acids facilitates a significant reduction of HAAs formation. Finally, addition of Ca(OH)$_2$ broadens the optimum pH range for alum coagulation, which should make the coagulation process more manageable and effective for the purpose of NOM removal and the reduction of DBPs in water treatment.

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