

Effect of Copper(II) on Natural Organic Matter Removal During Drinking Water Coagulation Using Aluminum-Based Coagulants

Guojing Liu¹, Xiangru Zhang², Jeffrey W. Talley^{1*}

ABSTRACT: Coagulation has been proposed as a best available technology for controlling natural organic matter (NOM) during drinking water treatment. The presence of heavy metals such as copper(II) in source water, which may form copper–NOM complexes and/or interact with a coagulant, may pose a potential challenge on the coagulation of NOM. In this work, the effect of copper(II) on NOM removal by coagulation using alum or PAX-18 (a commercial polymerized aluminum chloride from Kemiron Inc., Bartow, Florida) was examined. The results show that the presence of 1 to 10 mg/L of copper(II) in the simulated waters improved the total organic carbon (TOC) removal by up to 25% for alum coagulation and by up to 22% for PAX-18 coagulation. The increased NOM removal with the presence of copper(II) in the waters can most likely be ascribed to the formation copper–NOM complexes that may be more adsorbable on aluminum precipitates and to the formation of copper(II) co-precipitates that may also adsorb NOM. The presence of 1 to 5 mg/L of copper(II) in the waters containing 3 mg/L NOM as carbon was reduced below the maximum contaminant level goal (1.3 mg/L as copper) using either coagulant. The results suggest that the presence of copper(II) in source water may not adversely affect the NOM removal by coagulation. A good linear correlation was observed between the TOC removal efficiency and the log-total moles of the precipitated metals, which include the metal ion from a coagulant and the divalent metal ion(s) in source water. *Water Environ. Res.*, **79**, 593 (2007).

KEYWORDS: drinking water, coagulation, natural organic matter, copper(II), complexation.

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Introduction

Modern drinking water utilities are required to remove natural organic matter (NOM) because of aesthetic and health concerns (Amirtharajah et al., 1993; Edwards and Amirtharajah, 1985; Letterman et al., 1999; U.S. EPA, 1999). Natural organic matter is a complex mixture of acidic organic molecules that originates from a variety of natural sources (Letterman et al., 1999). The presence of NOM may result in discoloration, bad tastes, and disinfection byproducts (DBPs) in drinking water (Randtke, 1988; Richardson, 1998; Zhang and Minear, 2002). According to the Disinfectants/

Disinfection Byproducts Rule, organic carbon precursor removal is required if total organic carbon (TOC) of the finished water is greater than 2.0 mg/L (U.S. EPA, 1999). Coagulation has been proposed as one of the best available technologies for TOC control (Singer and Harrington, 1993) and is an accepted water treatment practice when combined in series with sedimentation and filtration processes (Letterman et al., 1999). It is known that coagulation can significantly remove NOM, which could lead to the formation of commonly known low-molecular-weight DBPs during disinfection. A recent study showed that coagulation can significantly reduce the formation of high-molecular-weight chlorinated DBPs also (Zhang et al., 2005).

The effectiveness of NOM removal by coagulation can be affected by coagulant type, coagulant dosage, NOM properties, pH, mixing effects, and temperature (Letterman et al., 1999). The presence of cations in raw water may also have a significant effect on the coagulation of NOM. Randtke (1988) reported that magnesium (0.25 mM) and calcium (0.25 mM) can broaden the pH range for effective removal of NOM (4.8 mg/L as carbon) and lower the required coagulant dosage, presumably by complexing with organic functional groups. These studies, however, were limited to the naturally enriched alkali and alkaline cations. With modern industrial development, a large quantity of heavy metals is being introduced to the aquatic environment. It is estimated that over 60 water systems in the United States have copper levels in source water greater than 1.3 mg/L, the maximum contaminant level goal (MCLG) set by the U.S. Environmental Protection Agency (U.S. EPA) (Washington, D.C.) (U.S. EPA, 2002). Aside from the adverse health effects, copper(II) can also interact with NOM to form stable inner and outer complexes (Lu and Johnson, 1997; Tipping, 2002) and can increase the adsorption of humic substances (a major component of NOM) onto the mixed bed of silica and α -aluminum oxide (α -Al₂O₃) (Oden et al., 1993). Therefore, the presence of copper(II) in raw water may pose a potential challenge for NOM removal during drinking water coagulation.

Aluminum-based coagulants, such as alum [Al₂(SO₄)₃·nH₂O] and polyaluminum chloride (PAX-18), are widely used coagulants in the water treatment industry. The aluminum-based coagulants are effective in removing NOM because (1) their hydrolysis products can neutralize the negative charges on NOM, and (2) the metal hydroxide precipitates can adsorb NOM and remove it from water. The predominant mechanism for NOM coagulation is dependent on the coagulation pH. Neutralization is typically dominant when the solution is slightly acidic (pH 5.0 to 5.5); when the coagulation pH

¹ Department of Civil Engineering and Geological Sciences, University of Notre Dame, Indiana.

² Department of Civil Engineering, Hong Kong University of Science and Technology, Hong Kong, China.

* Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick Hall, University of Notre Dame, Notre Dame, IN 46556; e-mail: jtalley1@nd.edu.

is near neutral, the adsorption of NOM on insoluble hydroxides is expected (Edwards and Amirtharajah, 1985).

Tipping (1981) and Jekel (1986) found that the relationship between residual TOC concentration and iron or aluminum hydroxides formed during coagulation can be expressed with the Langmuir isotherm. Edwards (1997) and Kastl et al. (2004) used the isotherm to predict NOM removal by coagulant dose, assuming that the coagulants added are all transformed to insoluble metal hydroxides.

The primary objective of this work was to investigate the effect of copper(II) on NOM removal during coagulation. The aluminum and copper concentrations remaining in the coagulated waters were also examined. The performances of the two aluminum-based coagulants, alum and PAX-18, were compared. The relationship between NOM removal and total moles of metals precipitated during coagulation was studied.

Material and Methods

Materials. All chemicals were of analytical grade. Milli-Q water was supplied by the Millipore MR3 water purifier system (Billerica, Massachusetts). Suwannee River NOM (SRNOM), a well-characterized NOM, was purchased from the International Humic Substances Society. The copper(II) stock solution (40 000 mg/L) was prepared by dissolving a given amount of copper(II) perchlorate hexahydrate $[\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}]$ (Sigma-Aldrich, St. Louis, Missouri) in Milli-Q water. The $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was used because perchlorate is typically a weakly binding ion and is considered not to bind to metals (Boyanov et al., 2003). In an earlier study, the removal efficiencies of NOM or copper(II) by coagulation were compared between two different anions (perchlorate $[\text{ClO}_4^-]$ and chloride $[\text{Cl}^-]$) that were introduced with the addition of copper(II). The result indicates that the effect of the introduced anions on NOM or copper(II) removal by coagulation is insignificant (Liu et al., 2004). Alum $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ from Sigma-Aldrich and polyaluminum chloride (PAX-18) from the Kemiron Inc. (Bartow, Florida) were used as coagulants. The basicity of PAX-18 was $42 \pm 2\%$.

The glassware used in the study was soaked overnight in a 10% hydrochloric acid solution, rinsed with deionized water and Milli-Q water, and then baked at 450°C for over 5 hours before use.

Jar Tests. The simulated water containing 3 mg/L SRNOM as carbon (the average TOC level in source water) was freshly made in a 10-L glass container. The alkalinity of the simulated water was controlled by adding sodium bicarbonate to 29 mg/L as calcium carbonate, representing a low alkalinity level (U.S. EPA, 1999). Aliquots of the simulated water were spiked with varying amounts of the copper(II) stock solution, resulting in copper(II) concentrations of 1 to 10 mg/L, which is the possible range of copper(II) in waters with NOM and low alkalinity. Other potentially significant ions (i.e., calcium, magnesium, and silicate) were not included in the simulated waters for the sake of simplifying the reaction mixture. The interaction between copper(II) and NOM has been reported to be rapid (Lin et al., 1995). Our preliminary test showed that the mixing time periods of 5 minutes and 24 hours resulted in the same TOC, copper(II), and aluminum concentrations remaining in solutions after coagulation, suggesting that the interaction between NOM and copper(II) has reached equilibrium within 5 minutes. The simulated waters were thus well-mixed for 5 minutes before coagulation.

A standard jar test apparatus equipped with six paddles was used to simulate the coagulation process. The paddles of the jar test

apparatus were wrapped with Teflon tape to prevent the possible deposition of copper onto the paddle surface. Each time before use, the paddles were cleaned for 1 to 2 hours using an ultrasonic cleaner and then rinsed with deionized water and Milli-Q water. The 1-L water sample was rapidly mixed at 100 r/min for 3 minutes, followed by a slow mix at 30 r/min for 30 minutes. Coagulant was added during the rapid mix condition. Because the spiked copper(II) could slightly reduce the pH value of the SRNOM waters, the waters that contained copper(II) were adjusted (after coagulant addition) using 2-M sodium hydroxide to the same pH level as the water that did not contain copper(II). Floccs were allowed to settle for 1 hour before 150 mL of supernatant was collected for analysis.

The critical coagulant dosage (CCD) and the corresponding pH for coagulating the water containing NOM only were determined and then were applied to the coagulation of the waters containing both NOM and copper(II). The CCD was determined as the coagulant dose where the maximum ratio of the amount of TOC removed (TOC_{rem}) to the amount of aluminum added (Al_{add}) was attained. The ratio of TOC_{rem} to Al_{add} can be used to evaluate the efficiency of an aluminum-based coagulant in removing NOM. The coagulant efficiency is considered to be high, as the ratio of TOC_{rem} to Al_{add} is high.

Sample Collection and Analysis. A vacuum filtration apparatus with a 0.45- μm Gelman Supor membrane (Gelman Sciences, Ann Arbor, Michigan) was used to filter the supernatant. Filtration membranes may affect the TOC measurement by adsorbing NOM from the sample or leaching organic compounds from the membranes themselves (Karanfil et al., 2003). To ensure the reliable measurement of TOC, a series of membranes, including Gelman Supor and Gelman GN6, were tested for the leaching of organic matter and the adsorption of SRNOM. The Gelman Supor membrane was found to be the best option because of its low leaching and low adsorption property. The membrane was rinsed with 500 mL Milli-Q water before use. During sample filtration, an initial 25 mL of the filtrate was wasted to minimize the effect of the SRNOM loss to the membrane.

The TOC was measured using a Shimadzu TOC-5050 analyzer (Shimadzu, Kyoto, Japan). The TOC analysis may be affected by sample pH (Van Hall et al., 1965). Our preliminary tests showed that sample pH had the least effect on the TOC analysis when it was within the range 2.0 to 2.5. Additionally, hydrochloric acid (2 M) was found to be the most effective acid for pH adjustment among the four acids (hydrochloric acid, nitric acid, sulfuric acid, and phosphoric acid) tested. Therefore, all the filtrates were acidified to $\text{pH } 2.3 \pm 0.1$ using 2-M hydrochloric acid and sparged with TOC-grade air for 5 minutes before analysis. The TOC in each sample was analyzed in triplicate, and the corresponding relative standard deviation (RSD) was less than 5%.

As a simple surrogate measure for the TOC in waters (APHA et al., 1998), UV absorbance (UV_{254}) was also used to measure NOM at the beginning of this study. However, the presence of 1 to 10 mg/L of copper(II) was found to increase the UV_{254} absorbance of 3 mg/L SRNOM as carbon by 8.8 to 12%, suggesting that UV_{254} absorbance is not a good surrogate for the TOC in waters containing copper(II).

The total concentrations of copper and aluminum in the filtrates were measured simultaneously using a Perkin Elmer optima 2000DV inductively coupled plasma-optical emission spectrometer (ICP-OES) (Perkin Elmer, Wellesley, Massachusetts). Yttrium from SPEX Certipre (Metuchen, New Jersey) was used as the internal standard for the metal analysis. The detection limits of

Table 1—pH change with coagulant dose during coagulation of water containing 3 mg/L SRNOM as carbon and 29 mg/L alkalinity as calcium carbonate.

Dose of coagulant (mg Al/L)	Alum coagulation pH (± 0.1)	PAX-18 coagulation pH (± 0.1)
0	7.9	7.9
0.81	7.3	7.6
1.62	6.9	7.3
2.43	6.7	7.4
3.24	6.6	7.2
4.05	6.1	7.0
6.48	4.9	6.8

copper and aluminum using the ICP-OES were less than 3 $\mu\text{g/L}$. The RSDs for the triplicate measurements of copper and aluminum were less than 2%, unless the metal concentrations were below 20 $\mu\text{g/L}$.

For all work, a minimum replication of 20% on experimental procedures was performed. Replication experiments showed that the average relative errors of TOC, copper, and aluminum concentrations in the experimental protocol were within 6 to 10%.

Results and Discussion

Critical Coagulant Dosage for Natural Organic Matter Coagulation. To determine the CCD for NOM coagulation, the simulated water containing 3 mg/L SRNOM as carbon was coagulated with a series of doses of alum or PAX-18. No acid or base was added to adjust the pH during coagulation. The pH change with the coagulant dose was monitored and is shown in Table 1.

The ratios of TOC_{rem} to Al_{add} at various coagulant doses are presented in Figure 1. For either coagulant, the ratio of TOC_{rem} to Al_{add} initially increased with increasing the coagulant dose and then decreased abruptly at a certain coagulant dose. For the alum coagulation, the maximum ratio of TOC_{rem} to Al_{add} was attained at the coagulant dose of 1.62 mg/L as aluminum. For the PAX-18 coagulation, the maximum ratio of TOC_{rem} to Al_{add} was attained at the coagulant dose of 2.43 mg/L as aluminum. Therefore, the CCD for the coagulation of SRNOM in the simulated water was set at 1.62 mg/L alum as aluminum or 2.43 mg/L PAX-18 as aluminum, where the corresponding coagulation pH was 6.9 or 7.4.

Figure 1 also shows that the ratio of TOC_{rem} to Al_{add} during the alum coagulation generally was higher than that during the PAX-18 coagulation at the same coagulant dose (milligrams per liter as aluminum), suggesting that alum is more efficient in removing SRNOM from the simulated water than PAX-18. The NOM removal by coagulation is strongly dependent on coagulation pH and aluminum hydrolysis species (Dempsey et al., 1984; Edwards and Amirtharajah, 1985). Because alum is more acidic than PAX-18, the alum coagulation resulted in a lower pH (Table 1), which is closer to the optimum pH (5.8 to 7.5) for NOM removal by aluminum-based coagulation (Edwards and Amirtharajah, 1985). To test the possible effect of aluminum hydrolysis species on NOM removal efficiency, additional experiments were performed by coagulating the water containing the same initial TOC (3 mg/L SRNOM as carbon) and a higher alkalinity (90 mg/L as calcium carbonate). The pH values and TOC removal efficiencies for a series of coagulant doses are listed in Table 2. The pH value for the alum coagulation was approximately the same as that for the PAX-18 coagulation, when coagulant doses in the range 0.81 to 4.05 mg/L

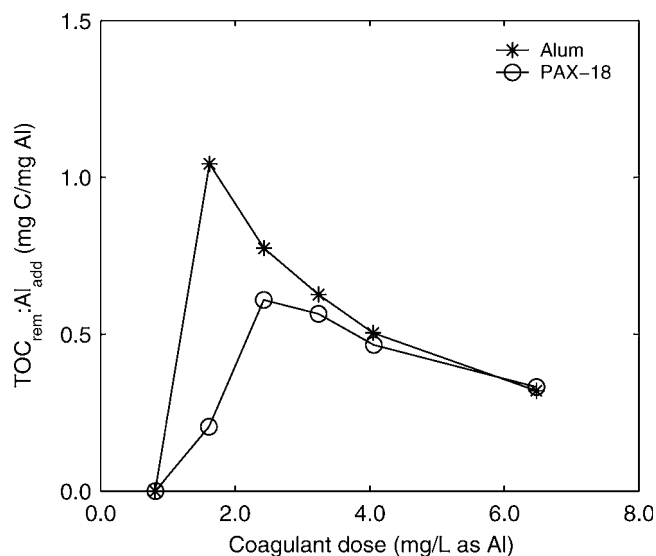


Figure 1—Change of ratio of TOC_{rem} to Al_{add} with coagulant dose during the coagulation using alum or PAX-18.

as aluminum were applied. However, the alum coagulation resulted in a TOC removal of 3 to 63%, whereas the PAX-18 coagulation resulted in a TOC removal of 0 to 48% only. Unlike alum, polyaluminum chloride can produce aluminum polymers besides aluminum monomer during hydrolysis (Van Benschoten and Edzwald, 1990). The results appear to indicate that the difference in aluminum hydrolysis species from using the two coagulants could partly account for the different NOM removal efficiencies.

Effect of Copper(II) on Total Organic Carbon Removal by Coagulation. The effect of copper(II) on NOM coagulation was investigated by coagulating the low alkalinity waters that contained 3 mg/L SRNOM as carbon and 1 to 10 mg/L copper(II). The coagulants (alum and PAX-18) were used at the corresponding CCDs, as determined above (i.e., 1.62 mg/L as aluminum for coagulation with alum, and 2.43 mg/L as aluminum for coagulation with PAX-18). Because the spiked copper(II) could reduce the pH of the simulated waters, the waters containing copper(II) were adjusted (after coagulant addition), using 2-M sodium hydroxide, to the same pH level as the water that did not contain copper(II). The pH values for coagulation with alum and PAX-18 were 6.9 and 7.4, respectively.

Table 2—Coagulation pH and TOC removal efficiency after coagulation of waters containing 3 mg/L SRNOM as carbon and 90 mg/L alkalinity as calcium carbonate.

Coagulant	Coagulant dose (mg Al/L)	Coagulation pH (± 0.1)	TOC removal efficiency (%)
Alum	0.81	7.8	3.18
	1.62	7.7	4.33
	2.43	7.6	53.8
	4.05	7.4	62.7
PAX-18	0.81	7.9	0.00
	1.62	7.7	0.00
	2.43	7.6	0.00
	4.05	7.5	48.9

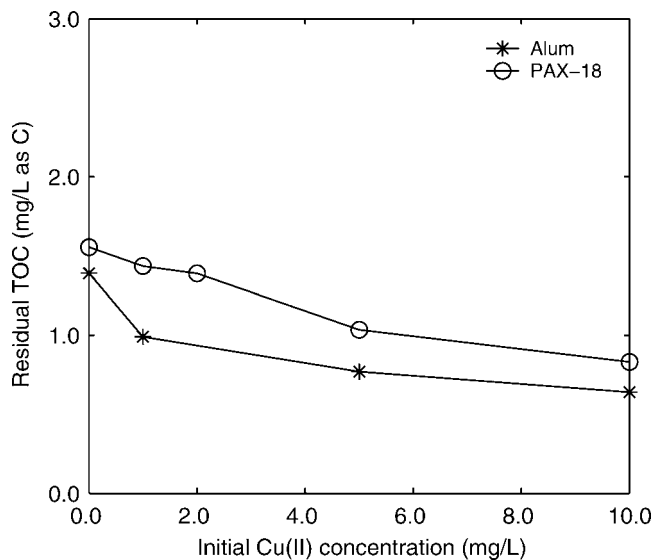


Figure 2—Effect of copper(II) on TOC removal by coagulation using alum or PAX-18.

The relationship of the residual TOC to the initial copper(II) concentration during the coagulation of 3 mg/L SRNOM as carbon is presented in Figure 2. The residual TOC concentration decreased with increasing the initial copper(II) concentration. The presence of 1 to 10 mg/L of copper(II) enhanced TOC removal by up to 25% for the alum coagulation and by up to 22% for the PAX-18 coagulation. The maximum TOC removal was achieved when the initial copper(II) concentration was 10 mg/L. The results suggest that the presence of copper(II) in source water (because of natural occurrence or anthropogenic pollution) may not adversely affect the NOM removal by coagulation, but might be beneficial instead. Because all the coagulations were conducted at pH 6.9 or 7.4, the adsorption of the NOM on aluminum precipitates should be the predominant mechanism controlling NOM removal (Edwards and Amirtharajah, 1985). Thus, the increased NOM removal during coagulating the waters containing copper(II) can possibly be accounted for as follows:

- (1) Copper(II) can form complexes with NOM (Lu and Johnson, 1997; Tipping, 2002), and the newly formed copper–NOM complexes may be more adsorbable onto aluminum precipitates than NOM itself. When studying the subsurface interactions of humic substances with copper(II), Oden et al. (1993) observed a significant increase in the adsorption of Suwannee River (Georgia) fulvic acid onto the silica and α - Al_2O_3 mixed bed with the presence of copper(II).
- (2) Copper(II) can co-precipitate with the coagulant to form copper precipitates, such as copper hydroxide $[\text{Cu}(\text{OH})_2]$, copper carbonate $[\text{CuCO}_3]$, and copper aluminum oxide $[\text{CuAl}_2\text{O}_4]$ during coagulation (Karthikeyan et al., 1999), and these copper precipitates may adsorb NOM.
- (3) Copper(II) could facilitate the formation of aluminum precipitates by displacing a fraction of aluminum that would be bound to NOM as the soluble Al–NOM, allowing more aluminum to precipitate.

To examine whether the presence of copper(II) could facilitate the formation of aluminum precipitates by displacing a fraction of

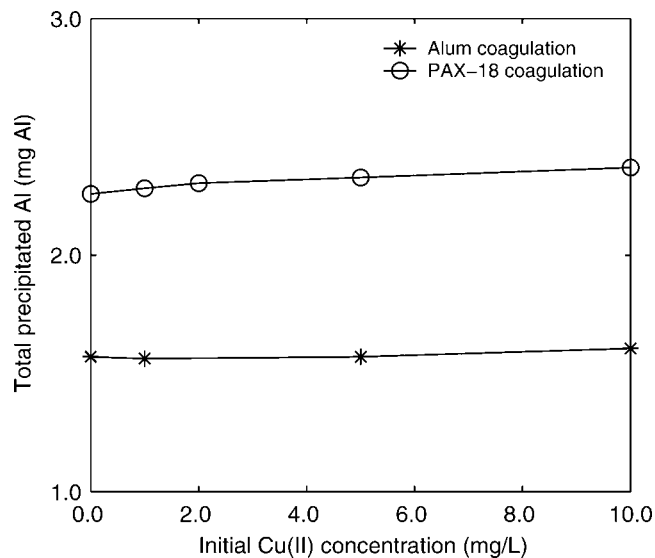


Figure 3—Effect of copper(II) on the total mass of aluminum precipitates formed during the coagulation of 3 mg/L SRNOM as carbon with alum or PAX-18.

aluminum in the complex Al–NOM, the total mass of aluminum precipitates formed during coagulation was calculated by subtracting the mass of aluminum remaining in solution from the total mass of aluminum added. The results are presented in Figure 3. The total mass of aluminum precipitates formed during the alum coagulation scarcely changed with increasing the initial copper(II) concentration in the simulated waters. The presence of 1 to 10 mg/L copper(II) in the simulated waters increased the total mass of aluminum precipitates by only less than 5.3% during the PAX-18 coagulation. The slim increase in aluminum precipitates could hardly account for the improved TOC removal as observed. Such a weak effect of copper(II) on aluminum precipitation also indicates that the NOM did not affect the aluminum precipitation considerably at the CCDs. Control tests by coagulating the simulated waters without SRNOM using the same coagulant dose showed that the total mass of aluminum precipitates formed during coagulating the water without SRNOM was approximately the same as that formed during coagulating the water with SRNOM (data not shown). This ruled out the speculation that more aluminum precipitation facilitated by copper(II) could be a major contribution to the increased NOM removal.

The copper(II) concentrations remaining in the solutions after coagulation are presented in Figure 4. The copper(II) removal efficiencies for the coagulation with alum and PAX-18 were 63.5 to 78.0% and 80.0 to 100%, respectively. For the PAX-18 coagulation, the 1 to 10 mg/L of copper(II) in the simulated water was reduced below the U.S. EPA MCLG, whereas, for the alum coagulation, the copper(II) concentration remaining in the solution after coagulation satisfied the U.S. EPA MCLG when the initial copper(II) concentrations were less than 5 mg/L. Accordingly, 1 to 5 mg/L of copper(II) in the simulated waters containing 3 mg/L SRNOM as carbon could be reduced below the U.S. EPA MCLG by coagulation using either coagulant.

Relationship Between Natural Organic Matter Removal and Metal Precipitation During Coagulation. The TOC removal efficiency and total moles of precipitated metals during coagulation were calculated using eqs 1 and 2, respectively.

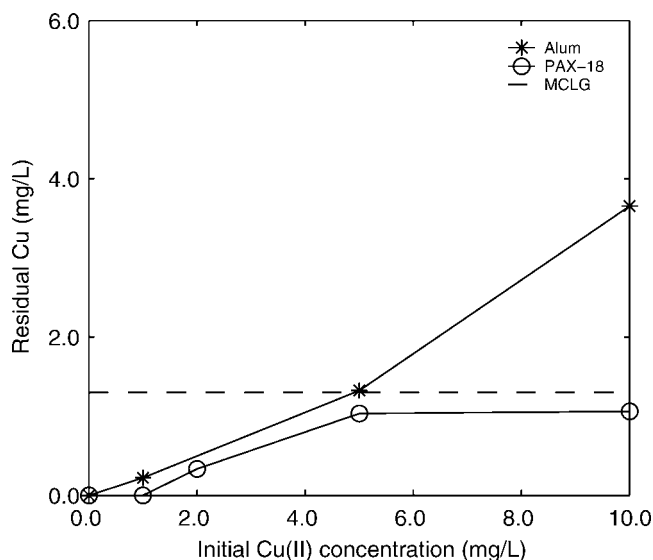


Figure 4—Copper(II) concentration remaining in the solutions after coagulation of 3 mg/L SRNOM as carbon with alum or PAX-18.

$$R = \frac{TOC_i - TOC_r}{TOC_i} \quad (1)$$

Where

R = TOC removal efficiency, and

TOC_i = initial TOC concentration (mg/L as carbon) in the simulated water, and

TOC_r = TOC concentration remaining in the solution after coagulation (mg/L as carbon), respectively.

$$M_{pre} = [([Al]_{add} - [Al]_r) + ([Cu]_i - [Cu]_r)] \cdot V \quad (2)$$

Where

M_{pre} = total amount of metals precipitated during coagulation (mol),

$[Al]_{add}$ = amount of coagulant as aluminum added per unit volume (M),

$[Al]_r$ = aluminum concentration remaining in the solution after coagulation (M),

$[Cu]_i$ = initial copper(II) concentration in the simulated water (M),

$[Cu]_r$ = copper(II) concentration remaining in the solution after coagulation (M), and

V = volume of the simulated water used for each coagulation test (L).

With the absence of copper(II) in the simulated water, M_{pre} represents the total amount of aluminum precipitated during coagulation. With the presence of copper(II) in the simulated water, M_{pre} represents the sum of the total amount of aluminum and copper in the precipitates formed during coagulation. It is of note that the forms of copper in the precipitates may include the direct precipitates (i.e., copper carbonate $[CuCO_3(s)]$ and copper hydroxide $[Cu(OH)_2(s)]$); the co-precipitates (i.e., copper carbonate aluminum hydroxide $[CuCO_3 \cdot Al(OH)_3(s)]$ and copper aluminum oxide $[CuAl_2O_4(s)]$); and the complex adsorbed on the aluminum pre-

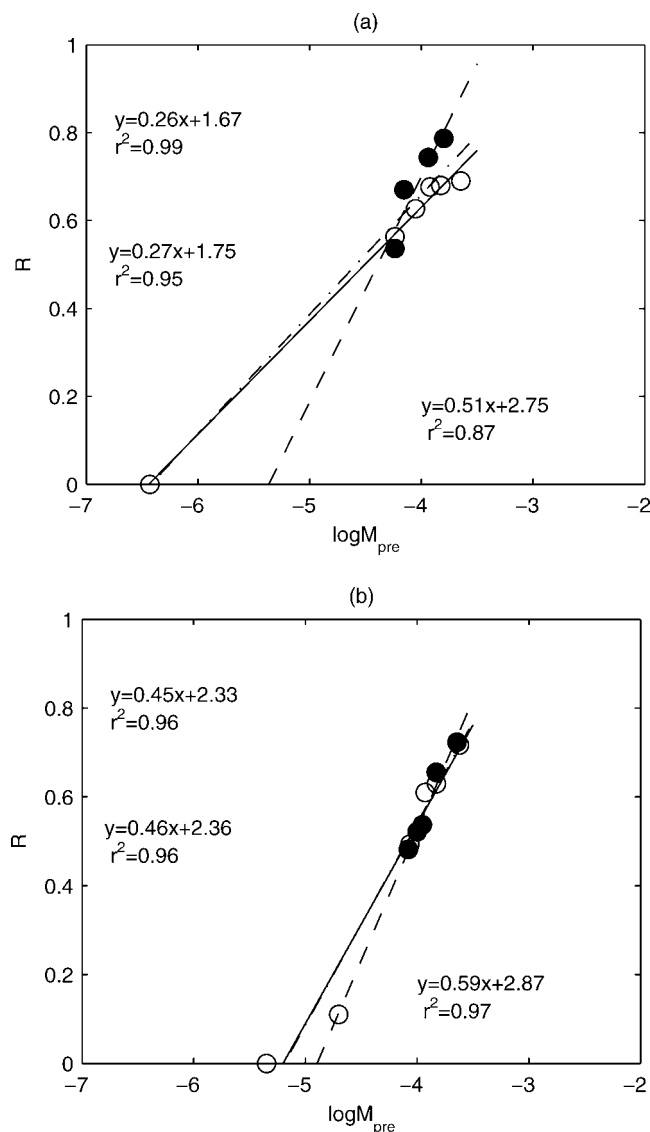


Figure 5—Correlation between TOC removal efficiency (R) and log-total moles of the precipitated metals ($\log M_{pre}$) during coagulation of the waters with copper(II) (●) or without copper(II) (○) using (a) alum or (b) PAX-18. The solid line and upper left corner regression equation and r^2 include the coagulations of the water without copper(II) at a series of coagulant doses. The dashed line and lower right corner regression equation and r^2 include the coagulations of the waters with 1 to 10 mg/L copper(II) at the CCD. The dashed dotted line and middle left regression equation and r^2 include all the coagulations tested.

cipitates (i.e., copper–NOM–aluminum hydroxide $[Cu(II)\text{--}NOM\text{--}Al(OH)_3(s)]$).

Various possible regression relationships between R and M_{pre} were examined. It was found that there was a linear correlation of R and $\log M_{pre}$, as shown in Figure 5. The solid line and upper left corner regression equation and r^2 include the coagulations of the water without copper(II) at a series of coagulant doses. The dashed line and lower right corner regression equation and r^2 include the

coagulations of the waters with 1 to 10 mg/L copper(II) at the CCD. The dashed dotted line and middle left regression equation and r^2 include all the coagulations tested.

For the correlation that includes the coagulations of the water without copper(II) at different coagulant doses, the linear correlation coefficients of R and $\log M_{pre}$ were 0.99 and 0.96 for the coagulation with alum and PAX-18, respectively, indicating a good linear correlation at a significance level of 0.05. Tipping (1981) and Jekel (1986) used the Langmuir isotherm to describe the relationship between residual TOC and precipitated metal hydroxides during the coagulation with iron- or aluminum-based coagulants. Their studies provide one way to predict TOC removal with precipitated metal hydroxides during coagulation. Our study suggests that a new simple relationship may also be used to model NOM removal during coagulation.

For the correlation that includes the coagulations of the waters with 1 to 10 mg/L copper(II) at the CCD, the linear correlations of R and $\log M_{pre}$ during the coagulation using alum (r^2 0.87) and PAX-18 (r^2 0.97) were good at a significance level of 0.05. To calculate the total moles of metals precipitated during coagulation (M_{pre}), both aluminum and copper in the precipitates were considered. If copper in the precipitates were not included in the calculation of M_{pre} , the linear correlation coefficients (r^2) of R and $\log M_{pre}$ would become smaller—0.35 and 0.93 for the coagulation using alum and PAX-18, respectively. Apparently, the increased TOC removal with the presence of copper(II) was related, to a great extent, to the copper(II) removal out of the waters, and copper(II) involved the TOC removal by ultimately consisting of part of the precipitates. The forms of the precipitates other than NOM–Al(OH)₃(s) may most likely include the following: Cu(II)–NOM–Al(OH)₃(s), NOM–CuCO₃·Al(OH)₃(s), and NOM–CuAl₂O₄(s), NOM–Cu(OH)₂(s).

For the correlation that includes all the coagulations tested, the linear correlation coefficients of R and $\log M_{pre}$ were 0.96 and 0.90 for the coagulation using alum and PAX-18, respectively. While differing in the water composition [i.e., copper(II) concentration] and differing in the coagulant dose, the linear correlations between R and $\log M_{pre}$ were still good. This suggests that, whether copper(II) is present in water or not, the TOC removal efficiency by coagulation can be predicted as a function of the total moles of precipitated metals, which includes not only the metal ion from a coagulant, but also the divalent metal ion(s) in source water.

Conclusions

The effect of copper(II) on SRNOM removal by coagulation was studied. The presence of 1 to 10 mg/L of copper(II) in the simulated waters significantly enhanced the TOC removal during the coagulation with alum or PAX-18. The increased NOM removal with the presence of copper(II) in the waters can most likely be ascribed to the formation of copper–NOM complexes that may be more adsorbable on aluminum precipitates and to the formation of copper(II) co-precipitates that may also adsorb NOM. The presence of 1 to 5 mg/L of copper(II) in the waters containing 3 mg/L SRNOM as carbon was reduced below the U.S. EPA MCLG using either coagulant. The results suggest that the presence of copper(II) in source water because of natural occurrence or anthropogenic pollution may not adversely affect the NOM removal by coagulation. A good linear correlation was observed between the TOC removal efficiency and the log-total moles of the precipitated metals, which include the metal ion from a coagulant and the divalent metal ion(s) in source water.

Credits

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