

Impact of carboxylic acid ultrafiltration recycle streams on coagulation

Christopher C. Boyd, Steven J. Duranceau and Jayapregasham Tharamapalan

ABSTRACT

This research identified unintended consequences of integrating ultrafiltration and its required ancillary cleaning systems within conventional surface water treatment facilities. Carboxylic acids, used in ultrafiltration membrane chemically enhanced backwashes, were demonstrated to interfere with ferric chloride and alum coagulation if recycled into coagulation basins at sufficient acid to coagulant (A/C) molar ratios. Tricarboxylic citric acid and monocarboxylic acetic acid were shown to interfere with conventional coagulation process performance. Significant changes in settled water turbidity, true colour and metal concentrations were observed in jar tests designed to simulate full-scale water treatment plant operations. A threshold A/C molar ratio for coagulation interference was identified for three surface waters in the United States based on sedimentation basin performance goals established by the US Environmental Protection Agency. Citric acid interfered with coagulation at A/C molar ratios as low as 0.028; whereas acetic acid negatively influenced coagulation at A/C molar ratios in excess of 18.0.

Key words | acetic, carboxylic, citric, coagulation, recycle, ultrafiltration

Christopher C. Boyd
Steven J. Duranceau (corresponding author)
Jayapregasham Tharamapalan
 University of Central Florida,
 Department of Civil, Environmental and
 Construction Engineering,
 4000 Central Florida Blvd,
 POB 162450,
 Engineering Building 2,
 Suite 211, Orlando,
 FL 32816-2450,
 USA
 E-mail: Steven.Duranceau@ucf.edu

ABBREVIATIONS

A/C	Acid to coagulant
Al	Aluminium
Alum	Aluminium sulphate
ASTM	American Society for Testing and Materials
CEBs	Chemically enhanced backwashes
CIP	Clean-in-place
EPA	Environmental Protection Agency
FBRR	Filter Backwash Recycle Rule
Fe	Iron
LC	Lake Claire
LM	Lake Manatee
M	Moles
NaOH	Sodium hydroxide
NOM	Natural organic matter
NTU	Nephelometric turbidity unit
PCU	Platinum cobalt units
SD	Sacramento Delta
SI	Supplemental information

UF	Ultrafiltration
WTP	Water treatment plant

INTRODUCTION

Conventional surface water treatment involves the use of coagulation, flocculation, sedimentation and filtration to remove colloids, dissolved solids and suspended particles from raw water. Traditionally, the filtration of settled water has been accomplished with sand or media filter beds, but the replacement of conventional filters with ultrafiltration (UF) membrane systems is growing in popularity. UF membranes can consistently produce filtered water with turbidity values below 0.05 NTU (Duranceau 2001). In the coming years, more water systems may consider retrofitting existing water treatment facilities with UF systems to meet tightening water quality regulations. However, consideration must be

given to the management of UF membrane fouling and the resulting waste streams.

Reversible fouling of UF systems is resolved by regular backwashing of the membranes to remove particulate matter. However, backwashing alone is often insufficient to maintain membrane performance as foulants accumulate on the membrane surface (AWWA 2011). Many studies have investigated the differing types and mechanisms for irreversible UF membrane fouling (Howe & Clark 2002; Kimura *et al.* 2004; Lee *et al.* 2004; Chen *et al.* 2007). Other studies have been conducted to research the use of chemical cleanings to manage irreversible membrane fouling (Strugholtz *et al.* 2005; Mavredaki *et al.* 2007; Zondervan & Roffel 2007). Chemical cleanings may be used to remove organic, biological or scaling type foulants via chemically enhanced backwashes (CEBs) or chemical clean-in-place (CIP) procedures.

Maintenance of UF membranes through backwashes and CEBs generates a waste stream that requires management and may constitute a significant volume of water. It is generally advantageous for public water systems to practise the recycle of backwash water to improve water recovery and reduce waste disposal costs. In 2001, the US Environmental Protection Agency (EPA) finalized the Filter Backwash Recycle Rule (FBRR) governing the recycling of spent filter backwash streams (US EPA 2001). The FBRR requires that spent filter backwash be treated by the existing processes in the treatment works. For public water systems governed by this rule, spent filter backwash may be blended with raw water ahead of the coagulation basin. However, this rule did not consider the impact that ultrafiltration membrane processes and their accompanying cleaning systems would have on the performance of conventional treatment.

It is important to consider the interactions between chemicals present in spent filter backwash recycle streams and existing water treatment processes. Studies have been conducted to evaluate the impacts of filter backwash recycle on water treatment plant (WTP) performance and water quality (Tobiason *et al.* 2003; Gottfried *et al.* 2008; McCormick *et al.* 2010). However, insufficient consideration has been given to the possibility of chemical reactions between the UF cleaning chemicals present in filter backwash recycle streams and traditional hydrolyzing

metal coagulants. It has been reported that the recycle of backwash water containing citric acid, a common membrane cleaning chemical, upsets the coagulation process and increases settled water turbidity values (Boyd 2011; Lyons & Sangines 2010). Citric acid is used frequently in the water treatment industry for cleaning membranes fouled with metal scales or organo-metallic type foulants (Porcelli & Judd 2010).

Using a concept for an alternative chemical as investigated by Duranceau and co-workers (Gupton *et al.* 1988), the influence of citric acid and acetic acid UF recycle streams on settled water quality were evaluated in this work via jar tests designed to simulate full-scale WTPs. Citric and acetic acids are carboxylic acids that act as ligands capable of coordinating to metal ions via carboxyl functional groups. Acetic acid is a monodentate ligand that possesses only one carboxyl functional group, whereas the multidentate ligand citric acid possesses three carboxyl groups. In water treatment, the coagulation process involves the addition of a hydrolyzing metal salt such as aluminium sulphate (alum) or ferric chloride (FeCl_3) to surface water. However, carboxylic acids can interfere with the intended function of iron- or aluminium-based metal coagulants by replacing typical hydrolysis products with metal-ligand complexes. The chemical interactions of iron and aluminium metals with carboxylic acids have been reviewed extensively in the literature (Hamm *et al.* 1954; Violante & Violante 1980; Wang *et al.* 1983; Motekaitis & Martell 1984; Thomas *et al.* 1991; Kuan *et al.* 2005).

The deprotonated forms of carboxylic acids are capable of complexing with aqueous metals. When filter backwash streams containing carboxylic acids are recycled, acid speciation is influenced by the coagulation basin pH. Ferric chloride and alum coagulants operate most effectively over narrow pH ranges. The typical pH range for alum is between 5.5 and 7.7, while ferric chloride has a broader pH range between 5.0 and 8.5 (MWH 2005). At the pH values desired during coagulation, both acetic acid and citric acid are present in deprotonated forms. The thermodynamic stability of complexes formed with acetic acid versus citric acid can be predicted by the chelate effect. The chelate effect states that metal complexes derived from multidentate ligands will be more thermodynamically stable than those formed with monodentate ligands (Martell & Hancock 1996). Therefore,

citric acid complexes are predicted to have increased stability relative to acetic acid complexes.

METHODS AND MATERIALS

In this research, a jar testing experiment was designed to investigate the impacts of citric acid and acetic acid on coagulation, flocculation and sedimentation basin performance. The jar tests evaluated settled water quality impacts for three different surface waters and simulated operations at two surface WTPs in the United States. The Lake Manatee WTP (Manatee County, FL) is a conventional alum coagulation plant that treats water from the Lake Manatee Reservoir (LM), and the Mission San Jose WTP (Fremont, CA) practises ferric chloride coagulation ahead of ultrafiltration for the treatment of Sacramento Delta (SD) water. Raw water from each of these facilities, along with surface water from Lake Claire (LC) on the University of Central Florida campus (Orlando, FL), was collected for the jar tests.

Jar testing and water sampling procedures

Jar tests were conducted in 2 L square B-ker² jars using a Phipps and Bird jar tester equipped with flat paddle impellers. Jars filled with raw surface water were first spiked with either citric or acetic acid prior to coagulant addition and pH adjustment at the start of rapid mix. The alum and ferric chloride coagulants evaluated during testing were provided by the Lake Manatee and Mission San Jose WTPs, respectively. Mixing times and speeds for LM and SD jars were selected to model actual operations at the Lake Manatee and Mission San Jose WTPs. Jar testing parameters for LC jars were based on ASTM International standard D2035–80 (ASTM 2003). Velocity gradient values for LC, LM and SD jar tests during rapid mix were approximately 120, 145 and 380 s⁻¹, respectively.

It was an experimental goal to maintain relatively consistent pH and temperature values between jars with the same water source, coagulant and carboxylic acid so that the effects of varying acid concentration on settled water quality could be identified. Titrations were performed to determine the appropriate sodium hydroxide (NaOH) dose for pH adjustment, and raw water was allowed to reach

approximately ambient temperature prior to jar testing. Temperature and pH measurements were taken during the slow mix sequence with average temperatures of 20.8 ± 0.9 and 20.6 ± 1.2 °C for the ferric chloride and alum jars, respectively. Additionally, an organic flocculant aid (Cedar-Floc 510; CedarChem, LLC) used at the Lake Manatee WTP was added to LM jars to facilitate floc agglomeration and settling. A uniform settling time of 15 minutes was utilized for LC, LM and SD jar tests (ASTM 2003).

At the conclusion of the 15-minute settling period, samples were collected from each jar for turbidity, true colour and metals testing. Turbidity measurements (SM 2130 B) were taken immediately after sample collection. The measurement of iron or aluminium metals was determined by Ion Coupled Plasma Optical Emissions Spectroscopy (SM 3120 B). In the case of LM jar tests, remaining sample volumes were filtered through glass microfibre filters for true colour measurement (SM 2120 C). SD and LC jar samples were filtered through 0.45 µm membrane filters prior to true colour measurement and the collection of dissolved metals samples. Natural organic matter (NOM) removal efficiencies were not evaluated for the coagulants, because the addition of organic carboxylic acids adds to the NOM concentration present in the raw water.

Laboratory quality control

Laboratory quality control measures were taken to monitor and assess the data collection process. Sample collection, storage and analytical equipment maintenance activities were conducted in accordance with the recommendations of the *Standard Methods for the Examination of Water and Wastewater* (APHA 2005). Analytical grade reagents were used where applicable. Approximately one out of every five samples was duplicated to monitor precision, and accuracy was assessed by preparation of laboratory-fortified matrix spikes.

RESULTS

A series of jar testing experiments were conducted to investigate the influence of citric acid and acetic acid on

conventional surface water treatment coagulation. The alum and ferric chloride coagulants selected for testing are commonly used in the water treatment industry and provide a comparison between aluminium and iron hydrolyzing metal salts. Jar testing with LM and LC surface waters evaluated both coagulants, whereas water from the SD was tested with only ferric chloride. Where applicable, coagulant doses and jar testing parameters were selected based on the actual operating conditions at the corresponding full-scale WTPs. For experiments where no existing WTP conditions could be simulated, a series of jar tests were performed to identify an acceptable coagulant dose and pH based on settled water turbidity and true colour values.

Raw water quality

A major goal of coagulation in surface water treatment is to remove NOM from drinking water to limit the formation of disinfection by-products (DBPs) during subsequent disinfection. In 1998, the US EPA addressed the issue of NOM removal with the promulgation of the Disinfectants/Disinfection By-Products Rule (D/DBPR) (US EPA 1998). The D/DBPR deals with the practice of enhanced coagulation for increasing NOM removal efficiencies from raw surface water (AWWA 2000). The surface water sources selected for this study possessed varying concentration of NOM and required different coagulant doses to achieve enhanced coagulation. The Lake Manatee and Lake Claire waters represented typical Florida surface waters high in NOM, whereas the Sacramento Delta water contained relatively low NOM concentrations. Table 1 presents the raw water quality parameters measured for the different source waters. The differences in raw water characteristics between the three surface waters allowed for the testing of carboxylic acid coagulation interference over a range of coagulant doses.

Acid to coagulant (A/C) molar ratio

The results for the jar testing experiments are presented in terms of the acid to coagulant (A/C) molar ratio for each combination of acid and coagulant tested. The A/C molar ratio provides a basis for comparing water quality trends between jars containing different coagulant doses and can

Table 1 | Raw surface water quality characteristics

WTP	TOC (mg/L C)	True colour (PCU)	Alkalinity (mg/L as CaCO ₃)	Turbidity (NTU)
Lake Manatee ^a	16.8	154	25.5	2.35
Sacramento Delta ^a	3.30	–	40.0	11.7
Lake Claire	12.4	58	37.2	–

^aWater quality data courtesy of Manatee County Utilities and ACWD.

serve as a tool for water purveyors to assess the possible coagulation impacts of UF carboxylic acid recycle streams on their treatment process. A range of A/C molar ratios were tested to identify changes in settled water quality with increasing carboxylic acid concentration. Tables 2 and 3 present the coagulant doses and carboxylic acid ranges evaluated in this experiment. Molecular weights of 594.4 and 162.2 g/gmol were used in the calculation of the A/C molar ratio for the alum and ferric chloride coagulants, respectively. Citric and acetic acid have molecular weights of 192 and 60 g/gmol, respectively.

Settled water quality impacts of carboxylic acids

Settled water turbidity, true colour and iron or aluminium concentration values are important for the characterization of conventional surface water treatment performance. Variations in these water quality parameters could lead to the decreased performance of downstream processes or deteriorations in treated water quality. During this research, water samples were collected to identify the impacts of carboxylic acids on coagulation at increasing A/C molar ratios. Turbidity and true colour measurements were taken for LM, LC and SD jars. Additionally, jars dosed with ferric chloride were tested for total iron, whereas alum jars were tested for total aluminium. LC and SD jars were also evaluated for dissolved iron or aluminium species to quantify the transition from solid to aqueous metal complexes at elevated carboxylic acid concentrations.

Turbidity

Figure 1 presents the settled water turbidity trends for ferric chloride jars spiked with either citric or acetic acid. The

Table 2 | Citric acid

Water source	Coagulant	Target pH	Coagulant dose (mg/L)	Acid concentrations (mg/L)	A/C molar ratios (M citric/M coagulant)
Lake Claire	FeCl ₃	6.5	120	0–50	0.000–0.352
Lake Manatee	FeCl ₃	4.5	75	0–70	0.000–0.788
Sacramento Delta	FeCl ₃	6.5	26	0–4	0.000–0.130
Lake Claire	Alum	6.5	140	0–50	0.000–1.11
Lake Manatee	Alum	6.0	100	0–70	0.000–2.17

Table 3 | Acetic acid

Water source	Coagulant	Target pH	Coagulant dose (mg/L)	Acid concentrations (mg/L)	A/C molar ratios (M acetic/M coagulant)
Lake Claire	FeCl ₃	5.5	120	0–2,000	0.000–45.1
Lake Manatee	FeCl ₃	5.0	75	0–2750	0.000–106
Sacramento Delta	FeCl ₃	6.5	26	0–1,000	0.000–104
Lake Claire	Alum	5.5	140	0–2,000	0.000–142
Lake Manatee	Alum	5.5	100	0–3750	0.000–347

observed turbidity trends are distinctly different between the two carboxylic acids, and citric acid spiked jars yielded higher maximum turbidities than acetic acid spiked jars at comparable A/C molar ratios. In citric acid spiked jars, settled water turbidity values remained relatively constant until a critical A/C molar ratio was obtained. Sharp increases in settled water turbidity values were observed for LC, LM and SD jars at A/C molar ratios of 0.028, 0.169 and 0.032, respectively. The settled water turbidity then began to decline with increasing A/C molar ratio. In contrast, acetic acid spiked LM and SD jars displayed a gradual increase in settled water turbidity beginning at A/C molar ratios of 18.0 and 52.0, although the increase was subtle for SD jars. A change in settled water turbidity was not observed for LC jar tests, because these tests were conducted over a narrow range of A/C molar ratios.

The turbidity trends for alum jars in the presence of citric acid corresponded to those observed with ferric chloride. Settled water turbidity values rose sharply for LC and LM samples at A/C molar ratios of 0.088 and 0.310 before gradually decreasing with increasing citric acid concentration. Turbidity values increased in LM jars spiked with acetic acid at an A/C molar ratio of 49.5 and exhibited

similar trends to citric acid spiked jars, with settled water turbidity reaching a maximum value before declining. An appreciable change in settled water turbidity was not observed for LC jars. Figure 2 presents the settled water turbidity trends for alum jars spiked with either citric or acetic acid. As with the ferric chloride coagulant, alum jars dosed with citric acid had higher maximum turbidities than those dosed with acetic acid.

True colour

Figure 3 presents the true colour trends for ferric chloride jars spiked with either citric or acetic acid. The true colour values for LC, LM and SD jars spiked with citric acid increased at A/C molar ratios of 0.070, 0.169 and 0.065, respectively. In the case of acetic acid, LM jars exhibited a linear increase in true colour values starting at an A/C molar ratio of 57.9. However, noteworthy changes in the true colour did not occur in LC or SD jars over the range of acetic A/C molar ratios tested. LC and SD true colour values are not included in Figure 3, because the majority of data points are below the detection limit established for the method. Citric acid spiked jars yielded

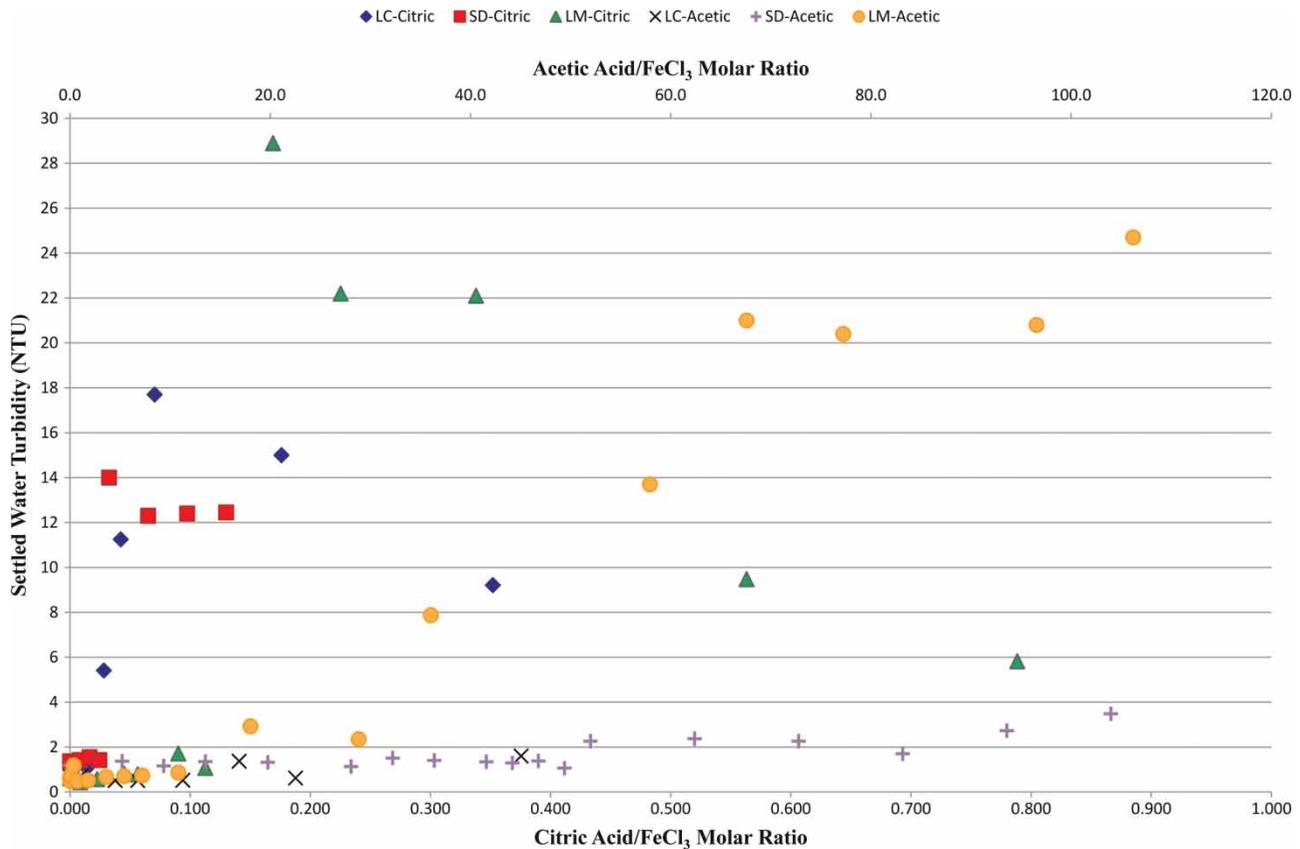


Figure 1 | Turbidity trends for ferric chloride jars.

higher maximum true colour values in the settled water than acetic acid jars.

The true colour trends for the alum jar tests are presented in Figure 4. Maximum true colour values for alum jars were lower than those observed with ferric chloride. The presence of citric acid in LC and LM jars resulted in true colour increases at A/C molar ratios of 0.553 and 0.310, respectively. Significant increases in true colour for acetic acid spiked jars were observed in LM samples at an A/C molar ratio of 149, but true colour values for LC jar tests remained relatively consistent with increasing A/C molar ratio. As was the case during ferric chloride jar tests, jars dosed with citric acid possessed higher maximum true colour values than acetic acid jars.

Total metal concentration

Figure 5 presents the trends for total iron concentrations in settled water samples coagulated with ferric chloride.

For citric acid jars, a significant increase in the total iron concentration was observed in LC, LM and SD jars at A/C molar ratios of 0.028, 0.090 and 0.032, respectively. As the concentration of citric acid was increased, floc formation and settling were observed to be negligible. The total iron concentration did not appreciably increase for LC and SD jars spiked with acetic acid over the range of A/C molar ratios tested. However, a linear increase in the total iron concentration was observed for LM jars starting at an A/C molar ratio of 36.0. Maximum total iron concentrations were greater for jars dosed with citric acid than acetic acid.

The total aluminium trends for LC and LM jars coagulated with alum are presented in Figure 6. Maximum settled water aluminium concentrations were greater for citric acid spiked jars than for acetic acid jars over the carboxylic acid concentration ranges tested. Citric acid jar tests conducted with LC and LM surface waters exhibited sudden increases in the total aluminium concentration at A/C molar ratios of 0.088 and 0.310, respectively. The

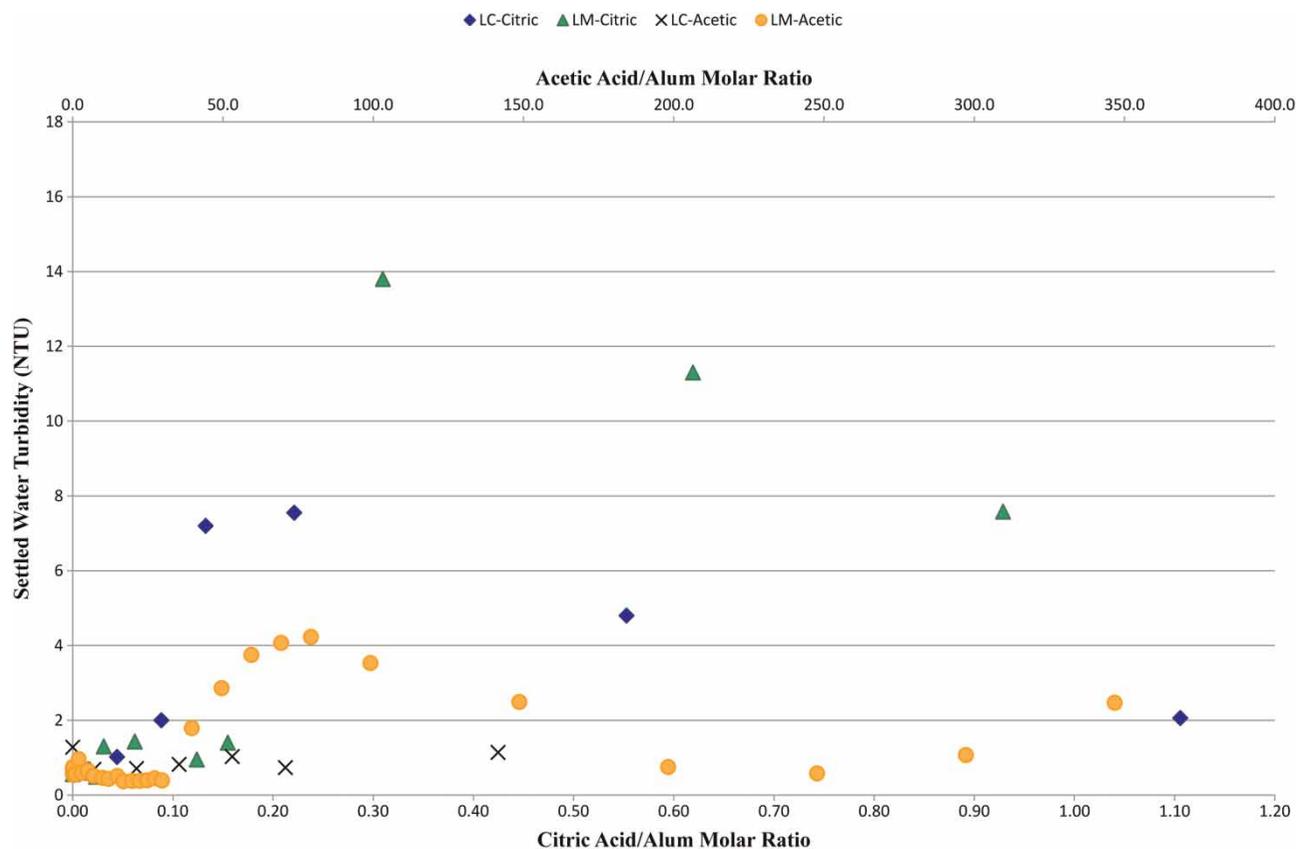


Figure 2 | Turbidity trends for alum jars.

total aluminium concentration for LC jars spiked with acetic acid increased at an A/C molar ratio of 142, and an approximately linear rise in the total aluminium concentration was observed for LM jar tests with acetic acid beginning at an A/C molar ratio of 39.6.

Dissolved metal concentration

Settled water samples from LC and SD jar tests were evaluated for both total and dissolved iron content. For LC jars dosed with ferric chloride and spiked with citric acid, increases in the total iron concentration were observed prior to an increase in the dissolved iron fraction. Dissolved iron concentrations in LC and SD jars began to increase at A/C molar ratios of 0.070 and 0.032, respectively. The fraction of dissolved iron then continued to rise with increasing A/C molar ratio. Increases in the dissolved iron concentration were observed for LC jars at an A/C molar ratio of 45.1 but were negligible for SD jars spiked with acetic acid.

Figure SI 7 (see the Supplemental Information section, available online at <http://www.iwaponline.com/jws/061/005.pdf>) presents the trends for dissolved iron in ferric chloride jars.

The influences of citric and acetic acid on the dissolved aluminium concentration were evaluated in LC jar tests with alum. For citric acid spiked jars, the dissolved aluminium concentration increased at an A/C molar ratio of 0.221. This increase in the dissolved aluminium concentration occurred subsequent to an increase in the total aluminium concentration at an A/C molar ratio of 0.088. Acetic acid addition to LC jars yielded an increase in the dissolved aluminium concentration at an A/C molar ratio of 142. Figure SI 8 presents the trends for dissolved aluminium in alum jars.

DISCUSSION

The purpose of this study was to evaluate the settled water quality impacts of carboxylic acids on conventional surface

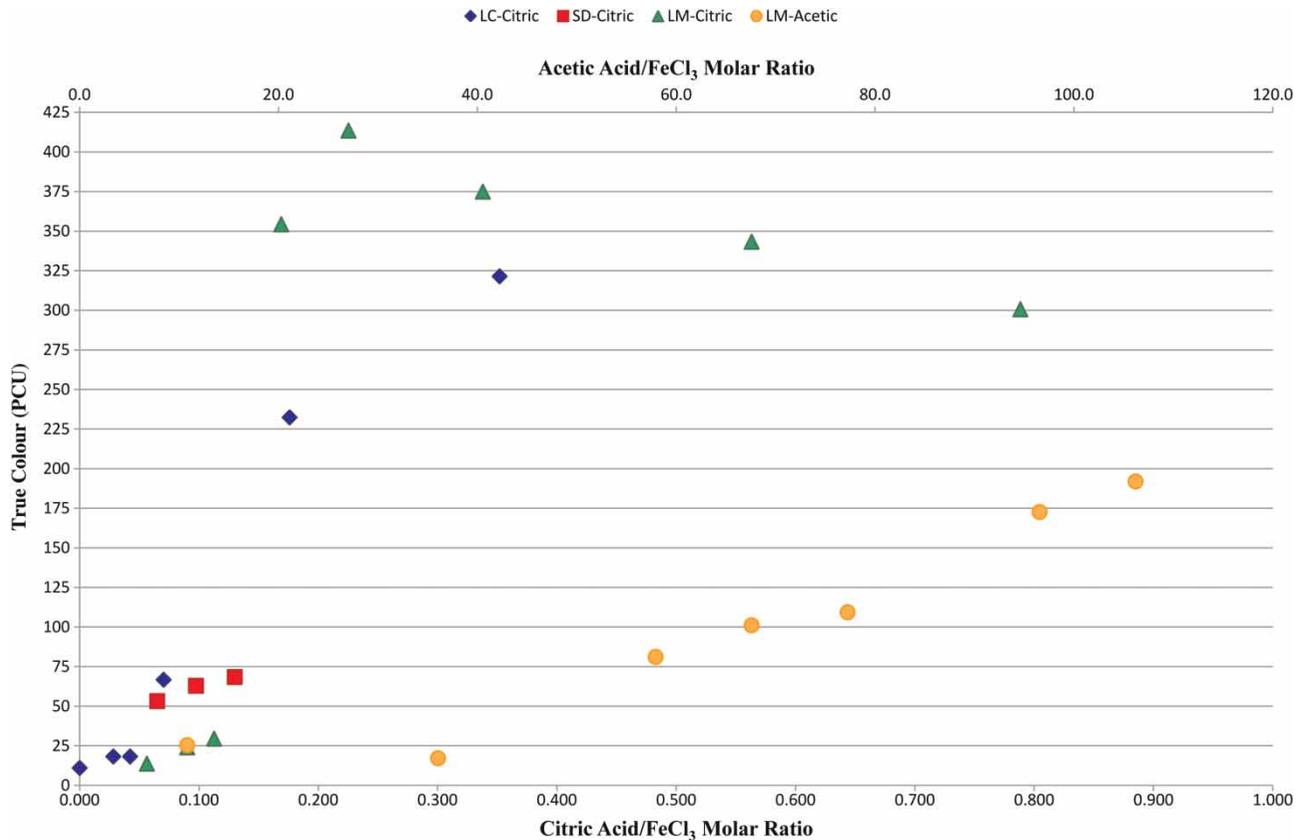


Figure 3 | True colour trends for ferric chloride jars.

water treatment coagulation-flocculation-sedimentation processes. The results of jar testing experiments designed to simulate full-scale WTP operations indicate that settled water turbidity, true colour, total and dissolved metal concentrations are adversely affected by the presence of carboxylic acids. This research demonstrates that at a sufficient A/C molar ratio, carboxylic acids can interfere with metal hydrolysis and floc agglomeration to produce small flocs with poor settling characteristics. Given the potential negative influence of carboxylic acids on coagulation, the impact of coagulation interference should be considered in the design and operation of surface water treatment facilities utilizing a carboxylic acid for UF membrane chemical maintenance.

Definition of coagulation interference

Trends in the settled water quality data indicate a carboxylic acid concentration range over which there is minimal impact on settled water quality. However, a threshold A/C

molar ratio exists beyond which significant deteriorations in settled water quality are observed. For this study, the coagulation interference threshold has been defined in terms of settled water turbidity values, because this metric provides an easily quantifiable way to assess coagulation-flocculation-sedimentation process performance. The US EPA has recommended individual sedimentation basin performance goals for surface water treatment facilities. For facilities with average annual raw water turbidity values greater than 10 NTU, the settled water turbidity goal is less than 2 NTU 95% of the time (US EPA 1998). Therefore, the coagulation interference threshold values presented herein are the A/C molar ratios at which settled water turbidity values exceed 2 NTU.

Coagulation interference thresholds

Citric acid was found to interfere with alum and ferric chloride coagulation at significantly lower A/C molar ratios than

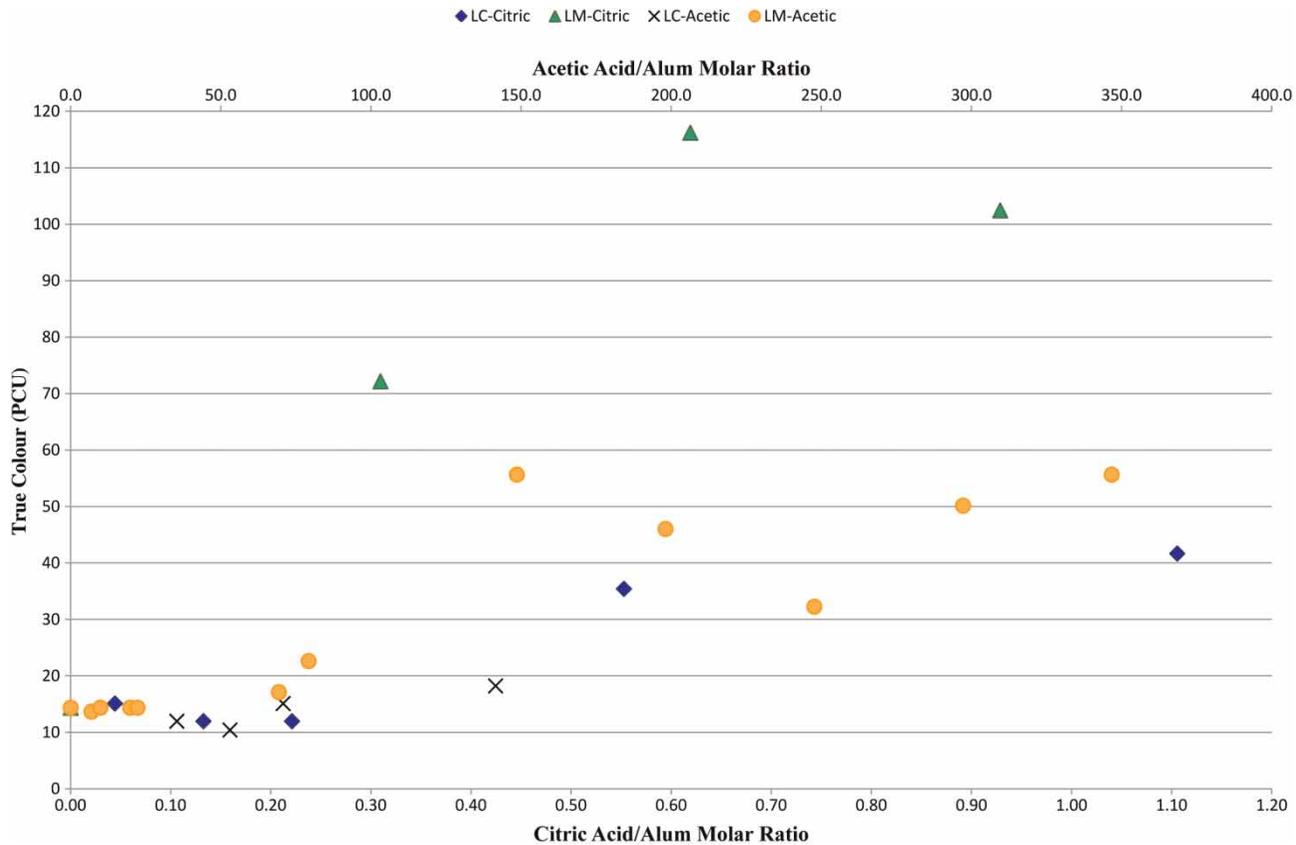


Figure 4 | True colour trends for alum jars.

acetic acid. This result is in accordance with the predictions of the chelate effect, which states that metal complexes formed with citric acid will be more thermodynamically stable than those formed with acetic acid. Therefore, tridentate citric acid will require lower acid concentrations than monodentate acetic acid to form complexes with the iron or aluminium metals added for coagulation. Tables 4 and 5 present the coagulation interference threshold values identified for citric and acetic acid with LC, LM and SD surface waters. As can be seen from the data, the citric acid concentrations required for coagulation interference are lower than those determined for acetic acid. Citric acid interfered with coagulation for the different surface waters between A/C molar ratios of 0.028 and 0.310, whereas acetic acid negatively influenced coagulation between A/C molar ratios of 18.0 and 52.0. A/C molar ratios were not identified for the LC acetic acid experiments, because the 2 NTU settled water turbidity goal was not exceeded within the acetic acid concentration ranges tested.

Correlations between settled water quality parameters

The results for citric acid jar tests show strong correlations between settled water quality parameters. Table SI 6 (available online at <http://www.iwaponline.com/jws/061/005.pdf>) presents the results for LC jar tests with ferric chloride. The observed turbidity increase to 5.41 NTU at the coagulation interference threshold corresponded to an increase in the total iron concentration from 1.72 to 9.57 mg/L. Turbidity values then began to decline indicating a transition from solid to aqueous metal species. Between A/C molar ratios of 0.176 and 0.352, the turbidity decreased from 15 to 9.21 NTU with corresponding increases in the dissolved iron concentration from 16.52 to 26.11 mg/L as Fe. True colour values for the LC citric acid jar tests did not increase significantly until an A/C molar ratio of 0.070. At this ratio, the dissolved iron concentration also increased from 0.16 to 3.06 mg/L as Fe. Changes in true colour values generally occurred at A/C molar ratios greater than the coagulation interference

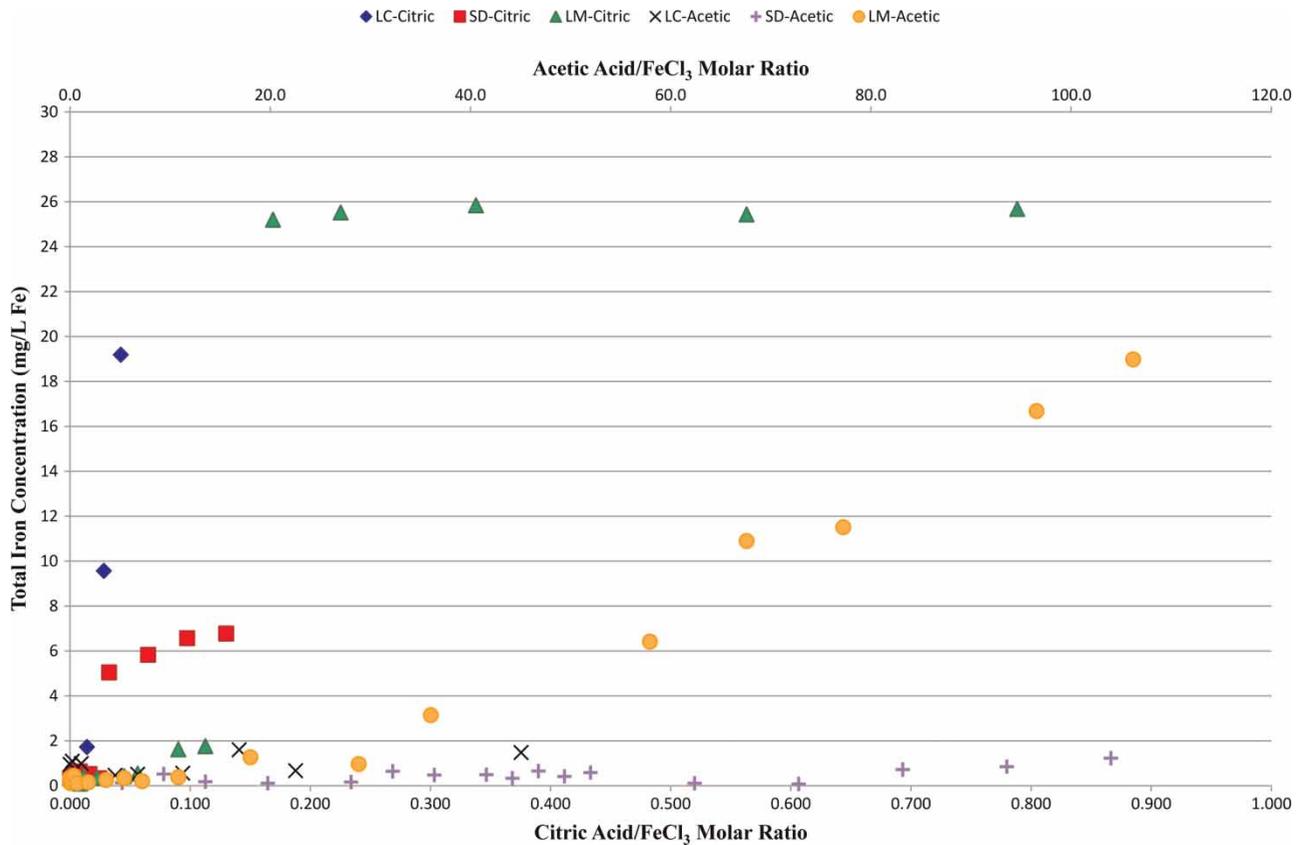


Figure 5 | Total iron trends for ferric chloride jars.

thresholds identified on the basis of settled water turbidity. This result agrees with the total iron concentration data and indicates that the metal species present at the coagulation interference threshold are predominately solids that are filtered out during the true colour analysis.

Correlations between settled water quality parameters were not as clear for the acetic acid jar tests, and coagulation interference thresholds were not identified for two of the five acid-coagulant combinations over the range of A/C molar ratios tested. Table SI 7 presents the results for LM jar tests with ferric chloride, which did display similar settled water quality correlations to the citric acid spiked jars. LM settled water turbidity values exceeded the coagulation interference threshold at an A/C molar ratio of 18.0, corresponding with an increase in the total iron concentration from 0.38 to 1.27 mg/L as Fe. As was also the case with citric acid spiked jars, an appreciable increase in the true colour was not observed until an A/C molar ratio in excess of the coagulation interference threshold established based on settled water turbidity.

Factors influencing the coagulation interference threshold

Coagulation and coagulant dose are influenced by factors such as pH, temperature and NOM concentration. Solution pH affects metals solubility, NOM surface charge and the speciation of carboxylic acids, whereas temperature affects both floc strength and the solubility of aluminium metal (MWH 2005). The coagulant dose required to achieve sweep floc is a function of the NOM concentration (O'Melia *et al.* 1999). The LC, LM and SD surface waters selected for this experiment contained different NOM concentrations and, therefore, required different coagulant doses to achieve sweep floc.

Flocculation is influenced by mixing speed, the number of particle collisions and the differential settling of heterogeneous flocs. Flocculant aids are organic polymers that may be added during the slow mix sequence to improve floc agglomeration and settling (MWH 2005).

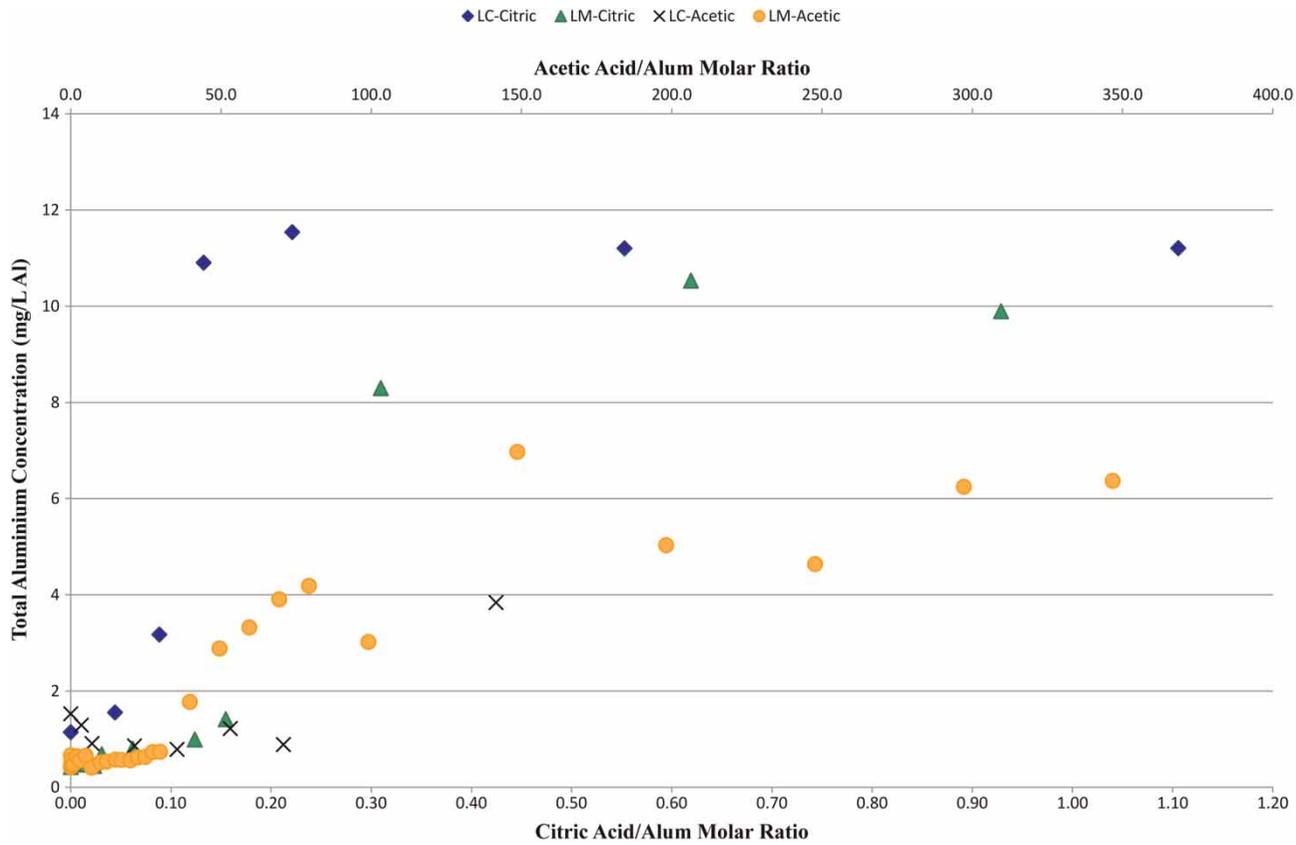


Figure 6 | Total aluminium trends for alum jars.

Table 4 | Coagulation interference threshold values for citric acid

Water source	Coagulant	Coagulant dose (mg/L)	Flocculant aid (mg/L)	Acid concentration (M citric/M coagulant)	A/C molar ratio (mg/L)
Sacramento Delta	FeCl ₃	26	No	0.032	1
Lake Manatee	FeCl ₃	75	Yes	0.169	15
Lake Claire	FeCl ₃	120	No	0.028	4
Lake Manatee	Alum	100	Yes	0.310	10
Lake Claire	Alum	140	No	0.088	4

Table 5 | Coagulation interference threshold values for acetic acid

Water source	Coagulant	Coagulant dose (mg/L)	Flocculant aid (mg/L)	A/C molar ratio (M acetic/M coagulant)	Acid concentration (mg/L)
Sacramento Delta	FeCl ₃	26	No	52.0	500
Lake Manatee	FeCl ₃	75	Yes	18.0	500
Lake Claire	FeCl ₃	120	No	N/A	N/A
Lake Manatee	Alum	100	Yes	49.5	500
Lake Claire	Alum	140	No	N/A	N/A

A flocculant aid was added to LM jars to simulate operations at the Lake Manatee WTP. The addition of the flocculant aid appeared to have a positive effect on coagulation interference with citric acid when compared to LC and SD surface waters. However, the results were inconclusive due to the variable nature of mixing intensities, pH and temperature between LC, LM and SD jars. Further research is needed to identify the effects of flocculant aid addition on settled water quality in the presence of carboxylic acids.

It was an experimental goal to maintain constant pH and temperature within each set of jars for a given surface water-coagulant-carboxylic acid combination. However, factors such as pH, temperature, mixing speed and mixing time were not held constant across the different surface waters tested. Jar testing parameters were selected based on settled water turbidity and true colour removal in preliminary jar tests or actual operating conditions at the full-scale WTPs. Differences in surface water quality, and thus the required coagulation parameters, preclude direct comparison of the coagulation interference thresholds identified for the LC, LM and SD surface waters. The variable nature of surface water quality and WTP operations necessitates jar testing to identify the coagulation interference threshold for a specific water source.

CONCLUSION

In this study, citric and acetic acid were evaluated in terms of their respective abilities to interfere with surface water coagulation. The results indicate that carboxylic acids adversely affect settled water turbidity, true colour and metal concentrations at an appreciable A/C molar ratio. Citric acid interfered with coagulation at A/C molar ratios as low as 0.028, whereas acetic acid negatively influenced coagulation at A/C molar ratios in excess of 18.0. This study attempts neither to establish a definitive A/C molar ratio for coagulation interference, nor to quantify the changes in NOM removal resulting from upsets to the coagulation process. The coagulation interference threshold is dependent on a variety of factors, including pH, temperature and mixing conditions and should be evaluated for each surface water source and water treatment facility. Surface

water purveyors considering the recycle of CEB streams should assess the possible impacts of carboxylic acids on treatment objectives.

The Supplemental Information section is available online at <http://www.iwaponline.com/jws/061/005.pdf>.

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