Investigating the effect of hardness cations on coagulation: The aspect of neutralisation through Al(III)-dissolved organic matter (DOM) binding

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ABSTRACT

Hardness cations are ubiquitous and abundant in source water, while the effect of hardness on the performance of coagulation for dissolved organic matter (DOM) removal in water treatment remains unclear due to the limitation of methods that can characterise the subtle interactions between DOM, coagulant and hardness cations. This work quantified the competition between coagulant Al^{3+} and hardness cations to bind onto DOM using absorbance spectroscopy acquired at different Al^{3+} concentrations in the absence and presence of Ca^{2+} or Mg^{2+} . The results indicate that, in the presence of either Mg^{2+} or Ca^{2+} , an increasing depression of the binding of Al^{3+} -DOM could be observed in the differential spectra of DOM with the increasing of Mg^{2+} or Ca^{2+} at a level of 10, 100 and 1000 μM , with the observation being more significant at higher pH from 6.5 to 8.5. The results of zeta potentials of DOM indicate that the competition of hardness cations results in the negative DOM being less efficiently neutralised by Al^{3+} . This study demonstrates that the removal of DOM by coagulation would significantly deteriorate with the presence of hardness cations, which would compete with coagulant Al^{3+} to neutralise the unsaturated sites in DOM.

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1. Introduction

Dissolved organic matter (DOM) can cause taste, odour and colour problems in potable water, and bacterial regrowth in distribution systems. DOM is also deemed to be the precursor of disinfection byproducts such as trihalomethanes and haloacetic acids, which are found to be carcinogenic and genotoxic (Duirk et al., 2011; Richardson et al., 2007). The removal of DOM has been a major concern in the area of modern drinking water treatment (Han et al., 2013; Pommerenk and Schafran, 2005). Enhanced coagulation has been proposed as a best-available technology for DOM removal (USEPA, 1998) because coagulants, for example Al^{3+} ion and its (hydro)oxides, have a strong affinity to negatively-charged DOM. Thus DOM could be removed by charge neutralisation and/or adsorption onto amorphous hydroxide precipitate

(Duan and Gregory, 2003; Yan et al., 2008a).

Hardness cations Ca^{2+} and Mg^{2+} are ubiquitous in all kinds of source water (Benjamin, 2010; Stumm and Morgan, 1996), while studies into the effect of the presence of hardness ions on the mechanism and efficiency of coagulation are limited. This is partially because it had been deemed that the binding of Ca^{2+} and Mg^{2+} by DOM was mediated primarily by non-specific Donnan electrostatic interactions, and their binding to unsaturated carboxyl and phenolic groups in DOM was negligible (Ahn et al., 2008). Recent studies have found that Ca^{2+} and Mg^{2+} are likely to be co-ordinated to carboxyl groups of DOM and also slightly to phenolic groups, especially in high pH conditions (Iglesias et al., 2003; Lu and Allen, 2002; Tipping, 1993; Yan et al., 2015). Although the affinity of DOM to hardness cations is weak compared with coagulant Al^{3+} , the competition between hardness cations and Al^{3+} to bind onto DOM cannot be neglected in view of the abundance of hardness cations in the environment. This may be several orders more than the coagulant dosage used in water treatment (Benjamin, 2010; Stumm and Morgan, 1996). In fact, this phenomenon has been observed in water treatment facilities—that the performance

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of coagulation for DOM removal is poor for source water with high hardness, for example, groundwater and some water with high alkalinity and hardness—but it had been mostly attributed to high alkalinity and/or pH problems because, in most cases, high alkalinity/pH and hardness are concomitant (USEPA, 1998; Yan et al., 2008a).

Some of the challenges in elucidating the nature and extent of the effect of hardness cations on coagulation are associated with the lack of available methods to probe the complicated water chemistry processes, preferably at coagulation-relevant concentrations of coagulant and DOM (Chandra et al., 2013; Gupta et al., 2002). Previous studies demonstrated that the presence of Al^{3+} affects the binding of heavy metals such as Cu^{2+} , Cd^{2+} , Pb^{2+} , Cr^{3+} et cetera using ion-selective electrodes (ISE), voltammetry, Donnan membrane separations and other techniques to measure the speciation of interested metal ions (Chappaz and Curtis, 2013; Gustafsson et al., 2014; Marsac et al., 2012; Pinheiro et al., 2000). The available method for free Al^{3+} measurement, Fluoride-ISE, is indirect and time-consuming (Kinniburgh et al., 1999) and is not suitable for the study of the competition between hardness ions and Al^{3+} in coagulation.

Recent research has shown that the binding of metal ions, including Al^{3+} , Ca^{2+} , Mg^{2+} to DOM could be characterised through tracking the changes of ultraviolet and visible (UV–Vis) absorbance spectroscopy induced by metal binding, and each metal ion can produce metal-specific features in differential absorbance spectra (Yan and Korshin, 2014). This approach has been successively used to quantify not only the binding between each metal and DOM (Yan and Korshin, 2014), but also the competition between different metal ions for reactive binding sites in DOM (Gao et al., 2015; Yan et al., 2016).

This study employed this approach to track the competition between coagulant Al^{3+} and hardness cations Ca^{2+} and Mg^{2+} for DOM in the pH range 6.5–8.5. In combination with measuring the zeta potentials (ZPs) of DOM at various hardness cations and Al^{3+} concentrations, the effect of hardness cations on coagulation would be elucidated partially, specifically in the aspect of neutralisation in the coagulation mechanism.

2. Materials and methods

2.1. Reagents and chemicals

All the chemicals were of reagent grade, except where specifically noted. All solutions were prepared using Milli-Q water (18.2 M Ω cm, Millipore Corp., MA, USA). Suwannee River humic acid (SRHA) (standard number 2S101H) was purchased from the International Humic Substances Society (IHSS) and used as representative DOM (Maurice, 2015). The SRHA solutions were prepared with the concentration of 5.0 mg L^{−1} as dissolved organic carbon (DOC). DOC was measured with a Shimadzu TOC-Vcsh carbon analyser. The residual cations in SRHA solutions can be ignored compared with the concentration of hardness cations and Al^{3+} added in the experiment (Yan et al., 2016). Ionic strength of SRHA solutions (0.01 M) was controlled by adding requisite amounts of NaClO_4 background electrolyte. Stock Al^{3+} , Ca^{2+} and Mg^{2+} solutions were prepared using $\text{Al}(\text{ClO}_4)_3$, $\text{Ca}(\text{ClO}_4)_2$ and $\text{Mg}(\text{ClO}_4)_2$ salts purchased from Aldrich Chemical Company (Milwaukee, WI). ZPs in solutions were determined in the fulvic acid module by a zeta-sizer (Nano ZS90, Malvern Corp., UK).

2.2. Titrations

Titrations were carried out similarly to prior publications (Yan et al., 2016). Aliquots of stock Al^{3+} solution were added by

requisite volumes into a series of 100 mL-jars in the absence or presence of 10, 100 and 1000 μM Ca^{2+} or Mg^{2+} . Total Al^{3+} concentrations were varied from zero to 23.9 μM , which is below its precipitation level determined at pre-experiment stage. The pH of the solutions was controlled by adding tiny amounts of HClO_4 or NaOH . After the addition of metal stock solution and a 30-min equilibrium time, aliquots were taken from solutions with varied metal concentrations, then the corresponding absorbance spectra were recorded by a Hitachi U-3900 UV/Vis spectrophotometer at a wavelength from 200 to 600 nm, with a 5 cm cell.

Numeric processing of DOM absorbance spectra was done as described in previous studies (Gao et al., 2015; Yan et al., 2016). This procedure is described in the Supporting Information (SI) section.

3. Results and discussion

3.1. Effect of hardness cations on differential spectra of Al^{3+} -DOM binding

Absorbance of SRHA at various Al^{3+} concentrations in the absence and presence of 10, 100 and 1000 μM Ca^{2+} or Mg^{2+} was recorded. Consistent with the results of prior studies (Gao et al., 2015; Yan et al., 2013a, 2016), the intensity of SRHA absorbance decreased near-exponentially with wavelength and the changes of SRHA absorbance induced by the addition of $\text{Al}^{3+}/\text{Ca}^{2+}/\text{Mg}^{2+}$ were inconspicuous in the zero-order spectra. The differential spectra caused by metal binding were calculated using Eq (1) in SI. Selected data are shown in Fig. 1 and Fig. S1.

The differential spectra obtained at varying Al^{3+} and $\text{Ca}^{2+}/\text{Mg}^{2+}$ concentrations were of obvious features. A prominent peak located at 380 nm and several weak peaks located at a lower wavelength could be found in all cases, but the shape and intensity changed significantly with the concentration of Ca^{2+} , Mg^{2+} and Al^{3+} , especially in lower wavelength ranges and at higher concentrations of hardness cations (Fig. 1). The intensity of differential absorbance below the wavelength of 300 nm becomes more and more negative with the increase of Ca^{2+} or Mg^{2+} . This is because the differential spectra caused by hardness cations have negative peaks in low wavelength ranges, as shown in Fig. 1 and in the literature (Yan and Korshin, 2014). These observations are more obvious with the increasing of pH values from 6.5 to 8.5 (Fig. S1). This demonstrates that the pH value affected the interaction in Al^{3+} - $\text{Ca}^{2+}/\text{Mg}^{2+}$ -SRHA system significantly, which will be further discussed in following sections.

3.2. Deconvolution of the contributions of Al^{3+} and hardness cations in differential spectra

As differential spectra of DOM associated with its interactions with different metals have metal-specific features (Yan and Korshin, 2014; Yan et al., 2016), the differential spectra generated in Al^{3+} - Ca^{2+} -SRHA and Al^{3+} - Mg^{2+} -SRHA systems could be numeric deconvoluted into the contribution of each metal ion using Eq (4) in SI, as in a previous publication (Yan et al., 2016). Selected data are shown in Fig. 2 and Fig. S2.

This demonstrates that the numeric sum of the differential spectra for each cation, in the absence of competition cation, meets well with the differential spectra generated in the actual Al^{3+} - Ca^{2+} -SRHA system or Al^{3+} - Mg^{2+} -SRHA system at low concentrations of Al^{3+} and/or $\text{Ca}^{2+}/\text{Mg}^{2+}$. When the concentration of Al^{3+} and hardness cations increases, the deviation becomes more and more significant, which indicates the occurrence of competition between coagulant cation (Al^{3+}) and hardness cations (Mg^{2+} or Ca^{2+}) (Fig. 2). However, all of the differential spectra generated in the actual Al^{3+} - $\text{Ca}^{2+}/\text{Mg}^{2+}$ -SRHA system can be deconvoluted by Eq (4)

Fig. 1. Differential spectra of the Al^{3+} - $\text{Mg}^{2+}/\text{Ca}^{2+}$ -SRHA system generated at varying total Al^{3+} concentrations reference to SRHA absorbance spectra before the addition of metal ions at pH 7.5. (a) in absence of hardness cations; (b), (c) and (d) for Ca^{2+} at 10, 100 and 1000 μM , respectively; (e), (f) and (g) for Mg^{2+} at 10, 100 and 1000 μM , respectively. Ionic strength 0.01 M, DOC concentration 5.0 mg L^{-1} .

through introducing the two calculation factors: α (for calculation of Mg^{2+} or Ca^{2+}); and β (for calculation of Al^{3+}); indicating the

depression caused by competition for Al^{3+} and $\text{Ca}^{2+}/\text{Mg}^{2+}$, respectively. The results demonstrate that the presence of hardness

Fig. 2. Deconvolution the differential spectra generated in Al^{3+} - Ca^{2+} / Mg^{2+} -SRHA system. The concentrations of Al^{3+} and Ca^{2+} at: (a) 0.18 and 10 μM ; (b) 3.2 and 100 μM ; (c) 23.9 and 1000 μM , respectively. The concentrations of Al^{3+} and Mg^{2+} at: (d) 0.18 and 10 μM ; (e) 3.2 and 100 μM ; (f) 23.9 and 1000 μM , respectively. Ionic strength 0.01 M, pH 7.5 and DOC concentration 5.0 mg L^{-1} .

cations strongly depresses the differential spectra generated from Al^{3+} ($\beta < 0.7$ in most cases), while the depression of differential spectra of hardness cations caused by Al^{3+} competition is slight ($\alpha > 0.95$ in most cases), and can be ignored except at high hardness cations and Al^{3+} concentrations. These tendencies are more obvious at higher pH conditions where the affinity for Mg^{2+} and Ca^{2+} to DOM is stronger (Fig. S2).

These results can also be ascertained by calculating the Al-differential spectra reference to SRHA absorbance spectra measured after the addition of corresponding concentrations of Ca^{2+} or Mg^{2+} (Fig. S3), rather than before the addition of hardness cations (Fig. 1). The intensity of Al-differential spectra in the absence and presence of various levels of Ca^{2+} or Mg^{2+} is significantly different, but the shapes are almost similar to the Al-differential spectra in the absence of hardness cations (Fig. 1(a)) in general.

3.3. Quantify the effect of hardness cations on Al^{3+} -DOM interaction

In the previous studies the spectral parameter $\Delta S_{350-400}$ has been proven to have a strong linear relationship with the amount of metal ions bound onto DOM (Gao et al., 2015; Yan et al., 2014, 2013b, 2016). $\Delta S_{350-400}$ was calculated using Eq (3) in SI reference to the $S_{350-400}$ in the presence of a corresponding concentration of hardness cations to quantify the amount of Al^{3+} binding onto SRHA. Results are shown in Fig. 3. $\Delta S_{350-400}$ values increase rapidly with the addition of Al^{3+} , then the curve gradually turned smooth in all cases, which indicates the complexity between Al^{3+} and DOM tended towards saturation as the concentration of Al^{3+} increased up to about 23.9 μM . $\Delta S_{350-400}$ values decrease a lot in the presence of Ca^{2+} or Mg^{2+} compared with the absence of Ca^{2+} or Mg^{2+} . This phenomenon is more obvious with an increase of

Fig. 3. Correlations of between spectral parameter $\Delta S_{350-400}$ and the total concentrations of Al^{3+} in the absence and presence of hardness cations at various pH values. (a), (b) and (c) for Ca^{2+} at pH 6.5, 7.5 and 8.5, respectively; (d), (e) and (f) for Mg^{2+} at pH 6.5, 7.5 and 8.5, respectively. Ionic strength 0.01 M and DOC concentration 5.0 mg L^{-1} .

hardness cations concentration and pH.

The data of $\Delta S_{350-400}$ values at Al^{3+} concentration 23.9 μM in Fig. 3 are combined in Fig. 4 as an example to compare the effect of hardness cations and pH on Al^{3+} -SRHA binding. It demonstrates that the amount of SRHA-bound Al^{3+} ions were cut down by 2.7%, 25.7% and 42.7% in the presence of 10, 100 and 1000 μM Ca^{2+} , respectively, at pH 6.5 compared with that in the absence of Ca^{2+} . This observation is more obvious at pH 7.5 and 8.5, where the amount of SRHA-bound Al^{3+} ions were cut down by 63.6% and 97.6%, respectively, in the presence of 1000 μM Ca^{2+} compared to in the absence of Ca^{2+} and at pH 6.5. The amount of SRHA-bound Al^{3+} ions in the condition of pH 6.5 is almost five times higher than that in the condition of pH 8.5. This means the affinity of Al^{3+} to DOM in high pH/alkalinity water would be seriously deteriorated, which is consistent with the previous studies that the pH/alkalinity has a significant impact

Fig. 4. Comparison of the spectral parameter $\Delta S_{350-400}$ at total concentration of Al^{3+} 23.9 μM and at various pH and in absence and presence of Ca^{2+} or Mg^{2+} . Ionic strength 0.01 M and DOC concentration 5.0 mg L^{-1} .

on the performance of coagulation in DOM removal in water treatment (Yan et al., 2008b).

The results of $\Delta S_{350-400}$ in case of Mg^{2+} have similar tendencies to Ca^{2+} with the changes of hardness cation level and pH in general. At pH 6.5 the compression effects of Ca^{2+} and Mg^{2+} are comparative. However, when the pH values increase to 7.5 or 8.5 the compression effect of Mg^{2+} is more significant than Ca^{2+} . This finding is consistent with a previous study which demonstrated Mg^{2+} has stronger affinity to DOM at high pH values compared with Ca^{2+} (Yan et al., 2015).

3.4. Effect of hardness cations on ZPs

The ZPs at different concentrations of total Al^{3+} in the absence or presence of hardness cations were measured. The data in case of Mg^{2+} at pH 6.5 are shown in Fig. 5. Due to the limitation of zeta potential in the analyser's sensitivity, it cannot find obvious differences in ZP with and without the addition of Mg^{2+} from 10 to 1000 μM . On the other hand, it indicates that the ability of Mg^{2+} to neutralise DOM is weak. The ZPs increase with the concentration of Al^{3+} and are lower in the presence of higher concentrations of Mg^{2+} . This indicates that DOM is less efficiently neutralised by Al^{3+} due to the presence of hardness cations. The result is consistent with the data in Fig. 3 that the presence of Mg^{2+} could depress the binding between Al^{3+} and DOM.

4. Perspective

This study demonstrates that the presence of hardness cations will compete with coagulant Al^{3+} to bind onto DOM and will result in inefficiently neutralising DOM, especially in high pH conditions. It is well known that the performance of coagulation for DOM removal is poor for water with high alkalinity and pH. In most cases this has been attributed to the effect of pH/alkalinity on the hydrolysis of coagulant. Water with high alkalinity/pH would lead metal coagulants to overhydrolyse after dosing, resulting in the formation of high polymeric hydroxyl complexes and gel, which is less efficient in DOC removal compared with medium polymer, which is formed at moderate and weak acid conditions. The results in this study demonstrate that the affinity of Al^{3+} to DOM is significantly affected by both pH and the presence of hardness cations. The effect of hardness cations on the performance of coagulation for high alkalinity/pH water cannot be negligible, although the problems of high alkalinity/pH and hardness are concomitant in most cases. This study provides a new view for interpreting the mechanism and performance of coagulation for water with high alkalinity/pH and hardness, as well as for optimising the

coagulation process in drinking water treatment. It demonstrates that the affinity of Al to DOM is weak at high pH and in the presence of hardness cations; that the contribution of neutralisation for DOM removal is limited; and that more effort should be paid to DOM removal through adsorption and sweeping, or with alternative coagulants. Moreover, enhanced softening with Mg precipitation may be an alternative option, especially for water with high Mg concentration, which has extremely high affinity to DOM at high pH (Yan et al., 2015). This is beyond the scope of this paper, but is worth further study in future.

Due to the fact the particles and gel in the solution would influence the measurement of UV–Vis absorbance, this study was only carried out at the Al^{3+} concentration below 23.9 μM , which is lower than coagulant dose used in real water treatment—20–100 μM . The result shown in Fig. 3 demonstrates that the binding between DOM and Al^{3+} would be nearly saturated, as the concentration of Al^{3+} is close to 23.9 μM . The further increase of the coagulant Al would hydrolyse to form polymer and gel, which would remove DOM through the other mechanism of adsorption. In order to comprehensively determine the contributions of the two mechanisms—neutralisation and adsorption—to DOM removal in coagulation, further study is needed to investigate the effect of the degree of neutralisation of DOM on its removal by adsorption—in other words, to study the complicated interaction in $Al_{(ion)}-DOM-Al_{(gel)}$ ternary system.

5. Conclusion

The results presented above support the following conclusions:

- (1) This study demonstrates that the effects of competitive binding of coagulant Al^{3+} and hardness cations, Mg^{2+} and Ca^{2+} , by DOM could be quantified using the method of differential spectroscopy.
- (2) An increasingly significant depression of the binding of Al^{3+} -DOM can be observed in the differential spectra of DOM with an increase to the Mg^{2+} or Ca^{2+} level, which is more significant at higher pH and for Mg^{2+} , while the effect of Al^{3+} on Ca^{2+}/Mg^{2+} -DOM binding was slight.
- (3) The negative DOM is less efficiently neutralised by Al^{3+} in the presence of hardness cations due to the competition of hardness cations with coagulant Al^{3+} .
- (4) This study provides a new view for interpreting the mechanism and performance of coagulation in high hardness and alkalinity/pH water, but further study is needed to investigate the complicated interaction in the $Al_{(ion)}-DOM-Al_{(gel)}$ ternary system to comprehensively determine the contributions of the two mechanisms—neutralisation and adsorption—to DOM removal by coagulation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2017.02.041>

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Fig. 5. Zeta potential values at varying concentrations of coagulant Al^{3+} in absence and presence of Mg^{2+} . Ionic strength 0.01 M and DOC concentration 5.0 mg L^{-1} .

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