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

Yuxuan Zhou [a], Mingquan Yan [a, *], Ruiping Liu [b], Dongsheng Wang [b], Jiuhui Qu [b]

[a] Department of Environmental Engineering, Peking University, The Key Laboratory of Water and Sediment Sciences, Ministry of Education, Beijing 100871, China
[b] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, CAS, POB 2871, Beijing 100085, China

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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.

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 haloactic 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 anamorphous 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 coordinated 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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* Corresponding author. Department of Environmental Engineering, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China.
E-mail address: yanmq@pku.edu.cn (M. Yan).

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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+}, Cd^{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 MΩ 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 $Al(ClO_4)_3$, $Ca(ClO_4)_2$ and $Mg(ClO_4)_2$ salts purchased from Aldrich Chemical Company (Milwaukee, WI). ZPs in solutions were determined in the fulvic acid module by a zetasizer (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 Al^{3+}/Ca^{2+}/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 Ca^{2+}/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+}-Ca^{2+}/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 Ca^{2+}/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+}-Ca^{2+}/Mg^{2+}-SRHA system can be deconvoluted by Eq (4)