Examination of effects of Cu(II) and Cr(III) on Al(III) binding by dissolved organic matter using absorbance spectroscopy

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Effects of Cu(II) and Cr(III) ions on the binding of Al(III) onto Dissolved Organic Matter (DOM) exemplified by Suwannee River Humic Acid (SRHA) at pH 6.0 were quantified in this study using linear and log-transformed SRHA absorbance spectra acquired at varying Al\(^{3+}\) concentrations and Cu\(^{2+}\) or Cr\(^{3+}\) levels. The competition between Al\(^{3+}\) and Cu\(^{2+}/Cr^{3+}\) for the binding sites in DOM was ascertained by examining the intensity and shapes of the metal-specific differential spectra of DOM. The results indicated that the binding of Al\(^{3+}\) onto SRHA is little influenced in the cases of in presence of 1.0 and 10.0 \(\mu M\) background Cr\(^{3+}\) and in presence of 1.0 \(\mu M\) background Cu\(^{2+}\), but it is significantly depressed in presence of 10.0 \(\mu M\) Cu\(^{2+}\). Changes of the spectral slope of the log-transformed absorbance spectra in the 350–400 nm wavelength range (S\(_{350-400}\)) were unambiguously correlated with the total amount of DOM-bound metals. The concentrations of Me-DOM complexes were determined using the NICA-Donnan Model. The results demonstrate that differential absorbance measurements provide quantitatively interpretable information concerning the nature and mechanisms of metal-DOM interactions and effects of metal cations competition on these processes.

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1. Introduction

Aluminum is the third most abundant element in the earth’s crust and it plays important roles in a variety of geochemical and engineered processes (Nordstrom and Ball, 1986; Furrer et al., 2002; Palmer and Driscoll, 2002; Tipping et al., 2002). Al has strong affinity to dissolved organic matter (DOM) (Tipping and Hurley, 1992; Kinniburgh et al., 1999; Milne et al., 2003) and Al\(^{3+}\)-DOM interactions affect the mobility and toxicity of other metals because Al\(^{3+}\) is a strong competitor for cations-DOM binding (Mota et al., 1996; Norden et al., 1997; Tipping et al., 2002; Marsac et al., 2012; Chappaz and Curtis, 2013).

The competition between Al\(^{3+}\) and other metals for binding sites in DOM has been a subject of extensive prior research (Tipping et al., 2002). These studies have demonstrated that Al\(^{3+}\) affects the binding of Cu\(^{2+}\) (Alberts et al., 1992; Cabaniss, 1992; Town and Powell, 1993; Tipping, 1998; Chappaz and Curtis, 2013), Pb\(^{2+}\) (Mota et al., 1996; Pinheiro et al., 2000), Cd\(^{2+}\) (Pinheiro et al., 2000), Cr\(^{3+}\) (Gustafsson et al., 2014) and rare earth metals such as Eu\(^{3+}\) (Susetyo et al., 1990; Bidoglio et al., 1991; Norden et al., 1997; Lead et al., 1998; Peters et al., 2001; Marsac et al., 2012). Metal binding data used in these and other pertinent studies have been obtained using ion-selective electrodes (ISE), voltammetry, Donnan membrane separations and other techniques that allow measuring concentrations of free ions of interest and their changes induced by varying levels of DOM and competing cations such as Al\(^{3+}\) (Town and Powell, 1993; Mota et al., 1996; Norden et al., 1997; Pinheiro et al., 2000; Tipping et al., 2002; Marsac et al., 2012). These data have been interpreted using geochemical approaches such as NICA-Donnan Model, Model V/VII (or SHM) and others (Mota et al., 1996; Lead et al., 1998; Tipping, 1998; Pinheiro et al., 2000; Tipping et al., 2002; Chappaz and Curtis, 2013; Gustafsson et al., 2014). The existing models allow achieving good fits between the experimental free metal data and predictions made based on...
empirical insights into the nature of metal binding by DOM (Lu and Allen, 2002) yet per se these approaches do not yield information about the microscopic nature of the functional groups involved in metal-DOM interactions (Mota et al., 1996; Norden et al., 1997; Pinheiro et al., 2000; Tipping et al., 2002; Marsac et al., 2012).

The microscopic nature of metal cation-DOM interactions can be examined based on the behavior of DOM fluorophores and chromophores that represent the entire ensemble of metal-binding DOM functionalities. The quenching of DOM fluorescence observed in the presence of many metals, notably Cu$^{2+}$, has been successfully used to probe metal-DOM interactions (Stedmon et al., 2003; Ohno et al., 2008; Wu et al., 2011) but the intensity of DOM fluorescence has been observed to increase rather than decrease in the presence of Al(III) (Cabaniss, 1992; Zhao and Nelson, 2005). The existence of different trends (both quenching and enhancement) in the changes of the intensity of DOM fluorescence in the presence of dissimilar metals as well as a relatively small fraction of the organic carbon associated with DOM fluorophores interferes with the characterization in metal-Al-DOM systems.

The absorbance of DOM is also sensitive to pH and metal concentrations (Yan et al., 2014; Gao et al., 2015a, 2015b), and the fraction of the organic carbon associated with DOM fluorophores is orders of magnitude higher than that of DOM chromophores. Prior research has shown that interactions between DOM and proton and/or metal cations can be quantified based the concept of differential absorbance (Yan et al., 2014; Gao et al., 2015a, 2015b). This concept allows ascertaining general types of the involved functional groups and extent of proton/metal-DOM complexation. In our recent publication, the spectral slope $S_{350-400}$ which is a measure of the rate of changes of log-transformed absorption of DOM vs. wavelength in the 350–400 nm region has been successfully used to quantify the competition between Ca$^{2+}$ and Cu$^{2+}$ for the binding sites in DOM (Gao et al., 2015a).

In this study, we employed this approach to track the competition between Al$^{3+}$ and Cu$^{2+}$ or Cr$^{3+}$ for binding sites in DOM exemplified in this study by standard Suwannee River humic acid (SRHA). The examined systems represent a combination of metal ions and Al$^{3+}$ that is frequently found in wastewater effluents in natural aquatic systems. The differential spectra generated for the Al–Cu–Cr-SRHA system were further deconvoluted to provide interpretable information concerning the nature of Al$^{3+}$ binding by DOM, and effects of the selected metals on these interactions (Gao et al., 2015a). The experimental data were combined with results of NICA-Donnan Model calculations to elucidate the nature of the observed changes and their relationships with overall amounts of the bound metals.

2. Materials and methods

2.1. Reagents and chemicals

Unless noted otherwise, all chemicals were of reagent grade. All solutions were prepared using Milli-Q water (18.2 MΩ cm, Millipore Corp., MA, USA). Suwannee River humic acid (SRHA) (standard number 25101H) was from the International Humic Substances Society (IHSS). The concentration of SRHA was 5.0 mg L$^{-1}$ as dissolved organic carbon (DOC). DOC measurements were done with a Shimadzu TOC-VcsH carbon analyzer. Concentrations of residual metal cations present in the SRHA sample used in this study have been shown to be negligible (Gao et al., 2015a). Ionic strength of SRHA solutions (0.01 M) was controlled by adding requisite amounts of NaClO$_4$ background electrolyte. Stock Al$^{3+}$, Cu$^{2+}$, and Cr$^{3+}$ solutions were prepared using Al(ClO$_4$)$_3$, Cu(ClO$_4$)$_2$ and Cr(ClO$_4$)$_3$ salts purchased from Aldrich Chemical Company (Milwaukee, WI).

2.2. Titrations

Al$^{3+}$ titrations were carried out as described in prior publications (Yan et al., 2013b; Yan and Korshin, 2014; Gao et al., 2015a). Aliquots of stock Al$^{3+}$ solution were added by requisite volumes into a series of 100 mL-jars in presence or absence of 1.0 and 10.0 μM Cu$^{2+}$ or Cr$^{3+}$. Total Al$^{3+}$ concentrations were varied from zero to 23.9 μM, which is below its precipitation level determined using Visual MINTEQ at ionic strength 0.01 M, pH 6.0 and a 5.0 mg L$^{-1}$ DOC concentration. DOM-metal complexation was modeled using the NICA-Donnan Model (Benedetti et al., 1996; Kimmigh et al., 1999; Milne et al., 2003). Complexation constants used in the calculations from Visual MINTEQ database are shown in Table S1. The solutions was controlled by adding small 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 and then the corresponding absorbance spectra were recorded by a Perkin–Elmer Lambda 950 UV/Vis spectrophotometer at wavelength from 200 to 600 nm.

2.3. Absorbance data processing

Numeric processing of DOM absorbance spectra was done as described in previous studies (Yan et al., 2013b; Yan and Korshin, 2014; Gao et al., 2015a). The linear differential and differential log-transformed absorbance spectra were calculated using the equations (1) and (2), respectively:

$$\Delta A_i = A_i - A_{i, ref}$$  \hspace{1cm} (1)

$$\Delta \ln A_i = \ln A_{i, ref} - \ln A_i$$  \hspace{1cm} (2)

In these equations, $A_{i, ref}$ and $A_i$ are, respectively, DOM absorbance measured at the wavelength $\lambda$ for any selected condition (i) and an applicable reference (ref, e.g., zero total metal or Al$^{3+}$ concentration). The slopes and differential slopes of the log-transformed absorbance spectra of DOM were calculated and as defined below:

$$S_{350-400} = \frac{d \ln A(\lambda)}{d \lambda} \text{ at } 350 \text{ to } 400 \text{ nm}$$  \hspace{1cm} (3)

$$\Delta S_{350-400} = S_{350-400,i} - S_{350-400,ref}$$  \hspace{1cm} (4)

In these equations, $S_{350-400}$ is the slope of the linear correlation that fits the log-transformed DOM absorbance spectra in the range between 350 and 400 nm $S_{350-400,i}$ and $S_{350-400,ref}$ are the spectral slopes determined for any selected experimental condition and applicable reference (ref, e.g., zero total metal or Al$^{3+}$ concentration), respectively. The prefix $\Delta$ denotes the differential between any selected experimental condition and the applicable reference against which that differential is calculated.

When dissimilar metal ions were present, the differential spectra ($\Delta A$) generated were deconvoluted using equation (5):

$$\Delta A = \alpha \Delta A_{Cu} + \beta \Delta A_{Al}$$  \hspace{1cm} (5)

In the above equations, $\Delta A_{Cu}$ and $\Delta A_{Al}$ are the differential spectra recorded at corresponding concentration of Al$^{3+}$ and Cu$^{2+}$ without competitive cations, respectively. Coefficients $\alpha$ and $\beta$ were determined via PIKAIA optimization (http://www.hao.ucar.edu/)
modeling/pikaia/pikaia.php) to achieve the best fit between the measured and modeled differential spectra.

3. Results and discussion

3.1. Effect of Al$^{3+}$ binding on SRHA chromophores in presence of Cu$^{2+}$/Cr$^{3+}$

Consistent with the results in prior studies (Yan et al., 2013b; Yan and Korshin, 2014; Gao et al., 2015a), the intensity of SRHA absorbance decreased near-exponentially with wavelength. Changes of SRHA absorbance induced by increasing concentrations of Al$^{3+}$/Cu$^{2+}$/Cr$^{3+}$ were inconspicuous in the zero-order spectra, while they were well discernible in the differential spectra calculated using eq (1) (Fig. 1).

The differential spectra associated with incremental additions of Al$^{3+}$ exhibited a prominent peak at 380 nm and three less intense peaks at 250, 280 and 320 nm, respectively (Fig. 1(a)). The peaks at 250 and 280 nm had negative signs that corresponded to decreases rather than increases of absorbance of DOM in the presence of Al$^{3+}$ ions. Similar albeit more intense and less resolved negative bands were observed in the case of interactions of SRFA with La$^{3+}$, Tb$^{3+}$ and Eu$^{3+}$ (Chen et al., 2015). Their existence was postulated to be a result of a bathochromic shift of absorbance bands of some DOM chromophores interacting with these ions (Chen et al., 2015).

The shape and intensity of the differential spectra obtained for

Fig. 1. Differential spectra of the Al$^{3+}$/Cu$^{2+}$/Cr$^{3+}$-SRHA system generated at varying total Al$^{3+}$ concentrations. (a) in the absence of Cu$^{2+}$ and Cr$^{3+}$ and in the presence of (b) 1.0 mM Cu$^{2+}$; (c) 10.0 mM Cu$^{2+}$; (d) 1.0 mM Cr$^{3+}$; (e) 10.0 mM Cr$^{3+}$. SRHA absorbance spectra recorded in the absence of Al$^{3+}$, Cu$^{2+}$ and Cr$^{3+}$ was used as the reference. Ionic strength 0.01 M, pH 6.0 and DOC concentration 5.0 mg L$^{-1}$.
varying Al³⁺ concentrations in the presence of Cu²⁺ and Cr³⁺ were affected by these metals, especially when their concentrations were at a 10.0 μM levels (Fig. 1(b–e)). At these conditions, besides the intense bands with the maximum at 380 nm, relatively strong bands located at wavelengths <280 nm could be found, especially in the case of Cu²⁺.

To compare the changes of DOM absorbance caused by the addition of Al³⁺ (Al-differential spectra) in the absence and presence of Cu²⁺ or Cr³⁺, the Al-differential spectra were calculated using the absorbance spectra of SRHA measured after the addition of corresponding concentration of Cu²⁺ or Cr³⁺ as the reference (Fig. 2) rather than using the SRHA spectra without any added metals as the reference (Fig. 1). It demonstrates that in the region of wavelengths >300 nm, the intensity of the Al-differential spectra changed only slightly in the presence of 1.0 and 10.0 μM background Cr³⁺ concentrations (Fig. 2(a) and (b)). In the presence of a 1.0 μM Cr³⁺ concentration (Fig. 2(c)), the bands located at wavelengths <300 nm were largely the same as those in the absence of Cr³⁺ but in the presence of a 10 μM Cr³⁺ level their sign reversed (Fig. 2(d)).

Fairly distinct phenomena were observed in the presence of competing Cu²⁺ ions. As was the case for Cr³⁺, 1.0 μM Cu²⁺ concentration did not cause significant changes of the shape and intensity of the Al-differential spectra. In contrast, the presence of 10.0 μM Cu²⁺ resulted in a pronounced decrease of the intensity of Al-differential spectra at wavelengths >300 nm, while the negative bands at λ < 300 nm became more intense than in the absence of Cu²⁺ ions. These may be results of two possible reasons. One of them is that the presence of a competing metal changes the ensemble of the binding sites available to Al³⁺ due to the unavailability of the sites already occupied by the Cu²⁺ ions, resulting in changes of the shape of differential spectra caused by Al³⁺-SRHA binding. Another possible reason is that the addition of gradually increasing Al³⁺ concentrations causes some of the SRHA-bound Cu²⁺ ions to be replaced thus resulting in the decrease of the intensity of the differential spectra caused by Cu²⁺-SRHA binding. While the occurrence and contributions of these alternative mechanisms remains to be elucidated, the discussion that follows addresses some of these issues.

3.2. Quantitation of the competition based on spectral parameters and NICA-Donan model

Previous studies have demonstrated that the slopes of log-transformed absorption of DOM vs. the wavelength in a selected region (e.g., 350–400 nm, S₃₅₀₋₄₀₀) are consistently affected by DOM protonation and formation of metal-DOM complexes (Yan et al., 2014; Gao et al., 2015a, 2015b). Results of similar data processing for SRHA spectra in the presence of incrementally increasing Al³⁺ concentrations and either Cu²⁺ or Cr³⁺ are shown in Figs. S1 and S2.

Fig. S2 shows that the differential log-transformed spectra are especially sensitive to the presence of Al³⁺, Cu²⁺ and Cr³⁺ in the 350–400 nm wavelength region where the intensity of the differential log-transformed spectra changes quasi-linearly vs. the observation wavelength. This result is similar to that observed for a
number of other metals (Yan et al., 2013a; Gao et al., 2015a). Accordingly, the slopes of the log-transformed absorbance spectra in the range of wavelengths 350–400 nm and their changes (denoted as S_{350-400} and DS_{350-400}, respectively) were used to estimate metal-DOM binding at varying system conditions.

The absolute S_{350-400} values increased with total Al^{3+} concentrations in all cases (Fig. 3) although the absolute values of S_{350-400} were notably higher in the presence of 10.0 μM Cu^{2+}. This was because the addition of 10.0 μM Cu^{2+} increased the S_{350-400} value from −0.01547 to −0.01343 nm^{-1} even in the absence of Al^{3+}.

To demonstrate the effect of the presence of Cu^{2+} and Cr^{3+} on the Al^{3+} binding more clearly, the DS_{350-400} values were calculated using as the reference the S_{350-400} values determined in the presence of equivalent amounts of Cu^{2+} or Cr^{3+}. The results are presented in Fig. S3. The DS_{350-400} values were compared with the concentrations of Al^{3+} ions estimated to be bound by SRHA at various total Al^{3+} levels in absence of Cu^{2+} or Cr^{3+} (Fig. 4). These calculations were done using the complexation constants included in the Visual MINTEQ database (Milne et al., 2003). The relevant data demonstrate that DS_{350-400} values measured in presence of 1.0 and 10.0 μM Cr^{3+} and 1.0 μM Cu^{2+} concentrations are strongly correlated with the concentration of DOM-bound Al^{3+} ions. The correlations are nearly linear and have similar slopes in absence and presence of competing cations. The slope determined in these experiments was ca. 0.0054 mol L^{-1} nm which is very close to the slope of a similar correlation determined for Cu^{2+} bound by SRHA (0.0054 mol L^{-1} nm), as reported in Gao et al. (2015a).

However, the correlations obtained between DS_{350-400} and Al^{3+}-DOM complexes in the presence of 10.0 μM Cu^{2+} clearly deviated from this pattern. The results are consistent with those of previous studies that have demonstrated the existence of strong competition of Cu^{2+} and Al^{3+} for binding by phenolic-like high-affinity DOM sites at high Cu^{2+} concentration (Tipping et al., 2002). These studies have also shown that Cr^{3+} exerts less influence on Al^{3+} binding by DOM. This was hypothesized to be a result of their preferential binding by carboxylic-like relatively low-affinity DOM sites (Gustafsson et al., 2014) albeit the conjecture that Cr^{3+} is preferentially bound by carboxylic rather than phenolic groups has not been proven.

The changes of S_{350-400} in presence of Cu^{2+} were interpreted taking into the consideration the binding of Cu^{2+} and the competition between Al^{3+} and Cu^{2+}. The concentrations of Al^{3+} and Cu^{2+} ions bound by SRHA were determined using applicable complexation parameters included in the Visual MINTEQ database (Benedetti et al., 1995; Milne et al., 2003; Cabaniss, 2009, 2011).

Relationships between the MINTEQ-based estimates of the concentrations of Al^{3+} and Cu^{2+} bound by DOM and corresponding changes of the S_{350-400} values are shown in Fig. 5. The sum of the concentration of these metals bound by SRHA formed a strong linear correlation with the S_{350-400} values and the slope is 0.0057 mol L^{-1} nm. This slope is very close to that determined for the binding of Al^{3+} and Cu^{2+} by SRHA. It demonstrates that the spectral parameter S_{350-400} is powerful to quantify the amount of metal bound onto SRHA.

3.3. Deconvolution of the differential spectra and determination of contributions of competing metal cations

The data presented above and those published in prior research demonstrate that differential spectra of DOM associated with its interactions with different metals have metal-specific features (Yan et al., 2013a, 2013b; Yan and Korshin, 2014). The existence of differences in the shapes of the differential spectra associated with SRHA binding of competing metal ions can be used to discern the contributions of these ions. This approach was applied to examine the competition between Al^{3+} and Cu^{2+} in the presence of a 10.0 μM concentration of the latter metal.

Main features of the differential spectra associated with the
binding of Al$^{3+}$ and Cu$^{2+}$ are shown in Fig. S4. It demonstrates that while at wavelengths $>300$ nm the differential spectra for both metals have a prominent peak located at 380 nm, the bands located at $\lambda < 320$ nm have different signs and locations of the constituting sub-bands. Assuming the applicability of the hypothesis that the competition does not change the shape of the metal-specific differential spectra, the competition between Al$^{3+}$ and Cu$^{2+}$ could be modeled by the deconvolution of the spectra based on eq (5).

The sum of the contributions of the differential spectra characteristic for each metal in the absence of competition were compared with the differential spectra generated for the actual Al$^{3+}$-Cu$^{2+}$-SRHA system (Fig. S4). The linear combination of the contributions of the dissimilar metals results in a good fitting for low concentrations of Al$^{3+}$ (<1.0 $\mu$M). However, the quality of the fitting decreases with the increase of Al$^{3+}$ concentration.

To account for this deviation, the relative contributions of the SRHA-bound Cu$^{2+}$ and Al$^{3+}$ ions can be determined via numeric deconvolution. For instance, in the case of 10.0 $\mu$M Cu$^{2+}$ and 10.0 $\mu$M Al$^{3+}$ (Fig. 6), the competition causes the intensity of the contributions of the differential spectra associated with the binding of Al$^{3+}$ and Cu$^{2+}$ per se to be depressed at different degrees, due to the competition between Cu$^{2+}$ and Al$^{3+}$. This approach allowed fitting the experimental data obtained for the Al$^{3+}$-Cu$^{2+}$-SRHA system quite well although some deviations in the wavelength range 280–320 nm were still observed. Their existence may be a result of either small experimental errors, or be reflective of the presence of more complex interactions (Chappaz and Curtis, 2013) that are not accounted for in the hypothesis presented above.

These processes can be quantified via the changes of the coefficients $\alpha$ and $\beta$ in eq. (5) as function of the total Al$^{3+}$ concentration. Decreases of these coefficients compared with the values (strictly one in the absence of Al$^{3+}$/Cu$^{2+}$ competition) would indicate the suppression of the binding of Al$^{3+}$ by Cu$^{2+}$ as well as, on the other hand, a partial replacement of the pre-bound Cu$^{2+}$. These effects are demonstrated in Fig. 7 that presents the behavior of $\alpha$ and $\beta$ coefficients as a function of total Al$^{3+}$ concentration in the presence of 10.0 $\mu$M background Cu$^{2+}$ level. The values of $\alpha$ and $\beta$ decreases to 0.85 and 0.58, respectively with the increase of Al$^{3+}$ concentration up to 23.9 $\mu$M. This indicates that the amount of SRHA-bound copper decreases by 15% compared with the amount of copper bound in the absence of Al$^{3+}$ while the amount of Al$^{3+}$ bound by SRHA in the presence of 10 $\mu$M Cu$^{2+}$ is 42% less than that bound by SRHA in the absence of copper. The fact that the value of $\beta$ decreases more significantly than $\alpha$ shows that Cu$^{2+}$ is only fractionally displaced by increasing concentration of Al$^{3+}$.

This study demonstrated that the effects of competitive binding of Al$^{3+}$ ion, one of the most ubiquitous and environmentally important ions, and Cu$^{2+}$ and Cr$^{3+}$ by DOM could be elucidated by the method of differential spectroscopy. The data confirm the strong performance of the NICA-Donnan Model for the examination of the Al-, Cu- and Al–Cu–SRHA systems. In contrast, there is a significant difference between NICA-Donnan model calculations and experimental data for the Al–Cr-SRHA system. Specifically, the model calculations show a strong competition between Al$^{3+}$ and Cr$^{3+}$, especially at the highest Cr$^{3+}$ concentration of 10 $\mu$mol L$^{-1}$. This prediction is not supported by the experimental data for this system. These data indicate a lack of a significant competition between Cr$^{3+}$ and Al$^{3+}$ for binding to SRHA. This difference may be because the NICA-Donnan model parameters for Cr$^{3+}$ are insufficiently precise. This is not entirely surprising as the complexation data for Cr$^{3+}$-DOM system were not ascertained based on experimental data but rather via examination of linear free energy correlations that relating metal binding constants for HA with the first hydrolysis constant of the metal (Milne et al., 2003). The poor quality of the NICA-Donnan model parameters for Cr$^{3+}$ was observed in previous studies also (Koopmans and Groenenberg, 2011). This clearly indicates that equilibria and mechanisms of interactions in the Cr$^{3+}$-DOM system need to be studied in more detail. On the other hand, the presented approach due its inherent sensitivity to DOM interactions with any metal cation, notably including Cr$^{3+}$ can be employed to ascertain complexation parameters for any combination of competing ions interacting with DOM irrespective of whether data of ISE measurements or related methods are available for such systems.

4. Conclusions

The results presented above support the following conclusions:

1. The differential spectra of DOM caused by metal binding exhibit metal-specific features, and the competition between Al$^{3+}$ and Cu$^{2+}$/Cr$^{3+}$ for the binding sites on DOM could be elucidated by examining the intensity and shapes of the differential spectra of DOM. The differential spectra generated in the Al$^{3+}$-Cu$^{2+}$-SRHA system could be interpreted via spectra deconvolution that provides unambiguous information about the extent of Al$^{3+}$ binding by DOM, and how that...
binding affects these interactions in the presence of competing Cu$^{2+}$ ions.

(2) The binding of Al$^{3+}$ onto SRHA is not significantly affected by the presence of 1.0 and 10.0 μM background Cr$^{3+}$ and 1.0 μM background Cu$^{2+}$. In contrast, it is substantially depressed in the presence of 10.0 μM of Cu$^{2+}$ at pH 6.0.

(3) The prominent differences in the effects of Al$^{3+}$ and Cu$^{2+}$ ions on DOM chromophores allowed quantitating the competition between Al$^{3+}$ and Cu$^{2+}$ for the binding sites in DOM in the mixed Al$^{3+}$/Cu$^{2+}$/DOM system, which was very well described by the NICA-Donnan model. In contrast, significant differences were observed between the experimental data for Al$^{3+}$/Cr$^{3+}$/SRHA system and NICA-Donnan model calculations. It indicates that NICA-Donnan model parameters for Cr$^{3+}$/DOM need to be explored further and quantified with higher precision.

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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.2016.02.017.

References


