WATER RESEARCH 68 (2015) 273–281

Available online at www.sciencedirect.com

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Spectroscopic *in situ* examination of interactions of rare earth ions with humic substances

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ARTICLE INFO

Article history:
Received 25 June 2014
Received in revised form
23 September 2014
Accepted 5 October 2014
Available online 14 October 2014

Keywords:
Rare earth ions (REIs)
Humic substances (HS)
Differential absorbance spectroscopy (DAS)
Fluorescence
MINTEQ
Complexation

ABSTRACT

This study utilized the methods of fluorescence quenching and differential absorbance to probe *in situ* the extent and the nature of the interactions between rare earth ions (REIs) and humic substances. Experiments were conducted with the standard Suwannee river humic acid (SRHA) in the presence of varying amount of lanthanum, europium and terbium. The data of differential absorbance showed that the mechanism of SRHA-metal complexation was largely the same for all the examined REIs. In all cases several discrete bands whose properties were discerned via numerical decomposition of the differential spectra absorbance were observed. Their nature was examined based on the comparison of the experimental data and those of NICA-Donnan modeling carried out for Eu^{3+}. The observed effects suggested that the changes of SRHA absorbance induced by REIs binding are likely to be caused by a bathochromic shift of the absorbance bands associated with such chromophores. The intensity of the Gaussian band with a maximum at 387 nm was observed to be proportional to the total concentration of SRHA-bound REIs. The data obtained in this study demonstrate the existence of complex yet quantifiable changes of the spectroscopic properties of humic species in the presence of REIs and their utility to quantify modes of interactions in such systems.

1. Introduction

The group of rare earth elements (REEs) comprises the fifteen lanthanides as well as scandium and yttrium. REEs are subdivided into the groups of light and heavy REEs based on their atomic masses being lower or higher than 153 Da, respectively. These metals have typically a +3 oxidation state and their chemical properties tend to be similar, with some

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http://dx.doi.org/10.1016/j.watres.2014.10.008
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important element-specific differences. While the presence of REEs in the environment have rarely been associated with pronounced problems, their rapidly increasing mining, refining, use and recycling can lead to significant impacts on the exposed terrestrial and aquatic ecosystems (Ippolito et al., 2010; Mireles et al., 2011). For instance, REE mining activities result in effluents that affect the quality of water used for agricultural purposes contaminating with REEs vegetables grown for human consumption (Li et al., 2013). In general, REEs released as a consequence of various industrial and agricultural practices have been detected in soils, runoff, wastewater and aquatic ecosystems with their concentrations frequently being in nmol/L range (Gaillardet et al., 2003; Johannesson et al., 2004; Censi et al., 2013; Protano and Riccobono, 2002), but the extent of the occurrence of REEs, their accumulation, toxicity and long-term risks are still to be ascertained (Weltje et al., 2002; Liang et al., 2005). Heavy REEs in dissolved fractions are found in soil solutions, surface runoff and river waters (Shiller, 2002), while suspended particles in rivers tend to be enriched in light REEs that originate from soil (Sonke, 2006). Some REEs, for instance Eu, can also be introduced into the environment as a result of contamination from radioactive wastes while Eu(III) itself can be considered as a proxy of the radionuclide Am(III) (Rabung et al., 2000; Reiller, 2005; Rahman et al., 2007).

REEs occur in widely different geochemical systems and their concentrations, speciation and transport are strongly affected by the complexation of rare earth ions (REIs) and their sorption at environmental interfaces. These aspects of REE chemistry have been subject of extensive research (Janot et al., 2013; Xu et al., 2012; Tang and Johannesson, 2010; Wang et al., 2006; Pourret et al., 2007), but some of the characteristic features of the environmental chemistry of REIs, for instance their interactions with humic substances (HS) remain to be explored in more detail.

Humic substances (HS) comprise complex polydisperse molecules formed in soils, sediments and natural waters by biochemical reactions involving the decay and transformations of plant and microbial biomass. HS affect practically all environmental processes, for instance mineral and soil weathering, plant nutrition, buffer capacity of water, trace metal mobility and toxicity, bioavailability, degradation and transport of hydrophobic organic chemicals. The role played by HS in the transport and sorption of REIs in the environment is highly important (Janot et al., 2013; Reiller and Brevet, 2010; Marang et al., 2009; Tan et al., 2008). In HS-REI interactions, functional groups with low and high proton affinities are deemed to affect strongly both the complexation and sorption processes, but a deeper microscopic-level understanding of these interactions is needed to predict the environment fate of REIs.

REIs form complexes with distinct chemical and spectroscopic characteristics defined by the electronic configurations that are unique to these ions. On the other hand, spectroscopic properties of HS themselves are affected by their interactions with metal ions thus providing an opportunity to quantify HS-REI complexation via measurements of the absorbance and emission spectra of HS. Spectroscopic properties of HS of different provenance have been intensively investigated in prior research (Del Vecchio and Blough, 2004; Henderson et al., 2009; Park, 2009; Baker et al., 2008; Fabbricino and Korshin, 2005; Gao and Korshin, 2013; Sharpless and Blough, 2014). Fluorescence (including time-resolved fluorescence of Eu^{3+} ion itself) (Janot et al., 2013; Monsallier et al., 2001; Brevet et al., 2009) and in much lesser extent absorbance spectroscopic methods have been applied to generate information necessary to understand metal-HS binding. Recent research has shown that interactions of HS with metal cations such as Cu^{2+}, Cd^{2+}, Al^{3+} and Fe^{3+} can be quantified using the method of differential absorbance spectroscopy (DAS) (Fabbricino and Korshin, 2005; Janot et al., 2010; Dryer et al., 2008; Yan et al., 2013a). The approach allows obtaining series of evolving differential spectra generated for incrementally increasing total concentrations of the metal of interest. These spectra have multiple distinct features that are absent in the initial (zero order) absorbance spectra. The intensity of these features has been shown to be well correlated with the amount of metal cations bound by HS, but the exact position of these features, their number and emergence at varying metal loads and pHs appear to be dependent on the provenance of any particular HS samples.

In this study, we applied this DAS technique and the method of fluorescence quenching that has been used more widely in prior research to examine the interactions of representative REIs such as Tb^{3+}, Eu^{3+} and La^{3+} with a standard HS from the Suwannee River (2S101H). Lanthanum is fairly abundant in the environment and used in many practical applications, while Eu^{3+} is frequently associated with radioactive wastes, as discussed above. Both Eu^{3+} and Tb^{3+} have fluorescence properties that make them highly attractive for studying the environmental chemistry of REIs in particular and that of heavy metals in general (Kumke et al., 2005; Wu and Horrocks, 1996). Given these and other points presented above, specific goals of the study include i) elucidation of the extent of interactions of the selected REIs and the standard HS, ii) comparison of the effects seen in *in situ* measurements with predictions of REI–HS binding made using the widely accepted NICA-Donnan modeling approach and iii) examination of the microscopic nature of interactions of the selected REIs with standard HS.

2. Material and methods

2.1. *Reagents and chemicals*

A standard humic substance (HS) from the Suwannee River (SRHA, sample 2S101H) was used in this study. The sample was purchased from the International Humic Substances Society (IHSS). This commercially available and widely used HA sample represents humic species present in an organic matter rich river (Suwannee River).

To prepare the solutions SHRA isolate was dissolved in Milli-Q water containing the background sodium perchlorate salt. The prepared solutions were not filtered. The pH was adjusted to 5.0, 6.0 and 7.0 by adding dilute HCl and NaOH. pH was measured using a conventional pH meter (Fisher Scientific Accumet, Model 25) which was periodically calibrated following a three points calibration procedure.

The concentration of SRHA solution was 5.0 mg C L^{-1} as dissolved organic carbon (DOC). DOC concentrations were determined with a Shimadzu TOC-Vcsh (Columbia, MD, USA)