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Characterizing the interaction between uranyl ion and fulvic acid using regional integration analysis (RIA) and fluorescence quenching

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ABSTRACT

The development of chemometric methods has substantially improved the quantitative usefulness of the fluorescence excitation-emission matrix (EEM) in the analysis of dissolved organic matter (DOM). In this study, Regional Integration Analysis (RIA) was used to quantitatively interpret EEMs and assess fluorescence quenching behavior in order to study the binding between uranyl ion and fulvic acid. Three fulvic acids including soil fulvic acid (SFA), Oyster River fulvic acid (ORFA) and Suwannee River fulvic acid (SRFA) were used and investigated by the spectroscopic techniques. The EEM spectra obtained were divided into five regions according to fluorescence structural features and two distinct peaks were observed in region III and region V. Fluorescence quenching analysis was conducted for these two regions with the stability constants, ligand concentrations and residual fluorescence values calculated using the Ryan-Weber model. Results indicated a relatively strong binding ability between uranyl ion and fulvic acid samples at low pH (log K value varies from 4.11 to 4.67 at pH 3.50). Fluorophores in region III showed a higher binding ability with fewer binding sites than in region V. Stability constants followed the order, SFA > ORFA > SRFA, while ligand concentrations followed the reverse order, SRFA > ORFA > SFA. A comparison between RIA and Parallel Factor Analysis (PARAFAC) data treatment methods was also performed and good agreement between these two methods (less than 4% difference in log K values) demonstrates the reliability of the RIA method in this study.

1. Introduction

The use of uranium in military and energy applications along with its increased mining and refining activities have caused uranium to become a potential hazard to both environmental and human health (Bleise et al., 2003). Uranium is soluble in water as uranyl ion (UO_2^{2+}) in low pH environments, and uranyl hydroxyl and uranyl carbonate complexes when the pH is higher (Meinrath, 1997; Vandenhove et al., 2010). The migration and sorption of uranyl ion in soil and aquatic systems can be affected by a wide variety of reactions, especially by its interaction with dissolved organic matter (DOM) (Schmeide et al., 2003; Shin et al., 2001). Many approaches have been applied in understanding the structure of DOM (Mopper et al., 2007; Ryan and Zhu, 2013) and the mechanism by which it binds to metals (Mibus et al., 2007; Möser et al., 2012). However, most of these techniques, such as chromatography and mass spectrometry, require specific sample pretreatment procedures that alter the sample or disturb the equilibrium between the metal ion and DOM. Fluorescence spectroscopy, therefore, has become a widely used technique for studying DOM in aquatic samples because it provides a relative rapid analysis requiring little or no sample pretreatment and does not degrade the sample or disturb the equilibrium of interest. The presence of abundant aromatic structures in DOM provides reasonably good fluorescence characteristic and a means to probe various properties of these important molecules (Chen et al., 2003; Hudson et al., 2007).

A fluorescence quenching phenomenon, or a reduction in the fluorescence intensity, has been observed when certain metal ions are bound to DOM and a method was developed to quantitatively monitor the interaction between the DOM and selected metals (Ryan and Weber, 1982a, b; Saar and Weber, 1982). Originally, only excitation and emission wavelengths that produced the maximum signal were used in this analysis, and these wavelengths were obtained by scanning the emission at a fixed excitation wavelength

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and vice versa (Ryan and Weber, 1982a, b). Subsequently, synchronous fluorescence, which scans at a constant offset between excitation and emission wavelengths, was applied revealing more fluorophores in the samples (Esteves da Silva et al., 1998; Hays et al., 2003). In recent years, fluorescence excitation-emission matrix (EEM) fluorescence spectroscopy has been much more widely used in the characterization of aquatic samples (Baker, 2001; Coble, 1996; Henderson et al., 2009). Based on the use of EEMs, parallel factor analysis (PARAFAC) was developed and successfully applied in the fluorescence quenching study of DOM when it is bound with metal (Ohno et al., 2007; Stedmon and Bro, 2008; Wu et al., 2011; Yamashita and Jaffé, 2008; Zhu et al., 2014). A new method called regional integration analysis (RIA) was proposed by Chen (Chen et al., 2003) to help interpret EEM data. They divided an EEM into different regions according to fluorescence spectral features exhibited by DOM and integrated the volume under the peaks in those regions to get quantitative information. The application of the RIA data treatment method to fluorescence EEMs has been used to investigate the composition and transformation of humic and fulvic acid from a land fill and in animal manure (Chai et al., 2012; Yu et al., 2011). Furthermore, this method can be applied in the investigation of complexation between metal ions and DOM with the potential to become a new approach to better understand the mechanism of binding.

This work mainly focused on the interactions between fulvic acid, a major component in DOM, and uranyl ion. The objectives of this study were to (a) use EEMs to explore fluorescence properties of these fulvic acid samples (b) investigate the binding behavior and stability constants for binding between uranyl ion and fulvic acid, and (c) compare the RIA and PARAFAC data treatment methods.

2. Experimental section

2.1. Reagent

Isolated samples of a well-characterized soil fulvic acid (SFA) and Oyster River fulvic acid (ORFA) were obtained from Dr. James Weber, Department of Chemistry, University of New Hampshire, Durham, NH, USA. Commercially available Suwannee River fulvic acid (SRFA) was also used in this study. Fulvic acid solutions were prepared by dissolving fulvic acid in water and stirring for 2 h. These solutions were then filtered through 0.2 μm Whatman (Maidstone, UK) Nylon membrane filters and transferred to volumetric flasks. Uranium atomic absorption standard solution (Ricca Chemical Co., Arlington, TX) was obtained as a 1000 ppm solution. The de-ionized water used throughout these experiments was 18.2 MΩ de-ionized water obtained from an Elga Purelab Option-Q water purification system.

2.2. Apparatus

A Perkin Elmer LS55 spectrofluorometer equipped with a xenon light source was used to obtain fluorescence data. A 10 mm quartz cuvette was used as the sample cell. Solution temperature was maintained at 25 °C using a constant temperature water bath (VWR Scientific, Boston, MA). A WTW InoLab pH Level 2 pH meter was used to measure the pH. A Perkin Elmer Spectrum 100 model FTIR spectrometer was used to conduct infrared analysis and spectra were measured using 2–4 mg of SFA, ORFA and SRFA in KBr pellets. The spectra were collected from 4000 to 400 cm^{-1} averaging 4 scans with a resolution of 4.0 cm^{-1}. A Perkin Elmer Lambda 35 UV–vis spectrometer was used for absorbance measurements.

2.3. Titration experiments

Titration experiments were used to investigate the interaction between uranyl ion and fulvic acid. The SFA solution was placed in a beaker with constant stirring maintained by a magnetic stirrer and a pH meter was used to monitor the pH. Then a series of known quantities of uranyl ion were titrated into the beaker in microliter amounts. EEMs were recorded after each addition of titrant, as well as the EEM of SFA without uranyl addition. The concentration of SFA was remained essentially constant at 20 mg/L and the concentration of uranyl ion increased from 0 to 0.8 mmol/L during the titrations. The same protocol was carried out for the measurement of ORFA and SRFA. All measurements were conducted three times at 25 °C (±1 °C) and at a pH of 3.50 (±0.01). The 20 mg/L concentration of each fulvic acid gave a relatively low absorbance (lower than 0.04 absorbance units for all three fulvic acids) at the emission wavelengths in the vicinity of 450 nm. For this reason the secondary inner filter effect is not significant. Although the absorbance of fulvic acid samples was more significant at typical excitation wavelengths used, studies have been reported that a low concentration of 20 mg/L of fulvic acid has a negligible primary inner filter effect (Hudson et al., 2007). The fluorescence intensity presented a relative linear relation with the concentration of fulvic acid within the range lower that 20 mg/L, this ensures the soil fulvic acid was not too concentrated. It should also be noted that since the experiments were conducted with an essentially constant concentration of soil fulvic acid throughout, any primary inner filter effect that might be present was constant throughout and had no effect on the results. Experiments were conducted at pH 3.50, because most of the uranyl ion is not hydrolyzed at this pH value (Esteves da Silva et al., 1996; Esteves da Silva et al., 1998; Zhu et al., 2014).

2.4. RIA and PARAFAC data treatment

For each EEM obtained, the background Raman scattering from water was removed by subtracting a blank EEM spectrum. The first order Rayleigh scattering was removed by setting the values to zeros, then the second order Rayleigh scattering was removed using an interpolation method. This interpolation method allowed input of new values to replace the data that are in the second order Rayleigh scattering region. Using this method, a smooth surface for an EEM was obtained.

Both RIA and PARAFAC were the methods that were used to provide quantitative peak information. The RIA data treatment was proposed by Chen (Chen et al., 2003). The volume beneath the peak was calculated by integration of the area multiplied by the height (i.e. fluorescence intensity). EEMs were divided into five regions and the volume of each region was calculated separately. Total volume was the sum of the volume for all regions. The volume percentage was calculated by taking the volume of a certain region divided by the total volume. The RIA calculation was conducted by MATLAB (Version 2010b, MathWorks, Natick, MA).

PARAFAC modeling has been described by Bro (Bro, 1997). Briefly, a series of EEM spectra can be considered as a three-dimensional data array, which is composed of excitation wavelength, emission wavelength and sample number. It is modeled as a three-way array $i \times j \times k$, and x_{ijk} represents the fluorescence intensity of sample i, measured at emission wavelength j and excitation wavelength k. PARAFAC analysis decomposes multi-way data and turns it into tri-linear components. Excitation, emission spectra and relative intensities of different fluorophores are calculated as outputs (Stedmon and Bro, 2008). The PARAFAC modeling was conducted by MATLAB (Version 2010b, MathWorks, Natick, MA) with the N-way toolbox (Andersson and Bro, 2000).