JOURNAL OF ENVIRONMENTAL SCIENCES XX (2017) XXX–XXX

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Two-dimensional correlation spectroscopic analysis on the interaction between humic acids and aluminum coagulant

Pengkang Jin[1,*], *Jina Song*[1,2], *Xiaochang C. Wang*[1], *Xin Jin*[1]

1. *School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China*
2. *College of Energy and Environmental Engineering, Hebei University of Engineering, Handan 056038, China*

ARTICLE INFO

Article history:
Received 15 March 2017
Revised 15 June 2017
Accepted 16 June 2017
Available online xxxx

Keywords:
Two-dimensional correlation spectroscopy
Al-HA complex
Surface complexation
Interaction sequence

ABSTRACT

In this study, two-dimensional correlation spectroscopy integrated with synchronous fluorescence and infrared absorption spectroscopy was employed to investigate the interaction between humic acids and aluminum coagulant at slightly acidic and neutral pH. Higher fluorescence quenching was produced for fulvic-like and humic-like fractions at pH 5. At pH 5, the humic-like fractions originating from the carboxylic acid, carboxyl and polysaccharide compounds were bound to aluminum first, followed by the fulvic-like fractions originating from the carboxyl and polysaccharide compounds. This finding also demonstrated that the activated functional groups of HA were involved in forming the Al-HA complex, which was accompanied by the removal of other groups by co-precipitation. Meanwhile, at pH 7, almost no fluorescence quenching occurred, and surface complexation was observed to occur, in which the activated functional groups were absorbed on the amorphous $Al(OH)_3$. Two-dimensional FT-IR correlation spectroscopy indicated the sequence of HA structural change during coagulation with aluminum, with IR bands affected in the order of COOH>COO^->NH deformation of amide II>aliphatic hydroxyl C–OH at pH 5, and COO^->aliphatic hydroxyl C–OH at pH 7. This study provides a promising pathway for analysis and insight into the priority of functional groups in the interaction between organic matters and metal coagulants.

Introduction

Humic acid (HA) is the major component of natural organic matter (NOM) and is responsible for the formation of harmful disinfection by-products (DBPs). Currently, the removal of HA from natural waters is primarily achieved using chemical coagulation/flocculation followed by sedimentation or flotation (Wang et al., 2014). Aluminum salts have been extensively used as coagulants because of the strong ability of the cationic hydrolytic species to remove small particles and HA moieties (Zhou and Meng, 2016).

The ability of HA to interact with aluminum salts is attributed to its high content of oxygen-containing functional groups, such as carboxyl, hydroxyl, and carbonyl (Provenzano et al., 2004). A number of analytical techniques are available to study the interaction mechanisms between HA and aluminum coagulants, which include fluorescence quenching, fluorescence excitation-emission matrix spectroscopy (EEMs), X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) and high-performance size-exclusion chromatography (HPSEC) (Cheng and Chi, 2002; Hussain et al., 2013; Lin et al., 2014; Lu et al., 1999; Zhu et al.,

* *Corresponding author*. E-mail: pkjin@xauat.edu.cn (Pengkang Jin).

http://dx.doi.org/10.1016/j.jes.2017.06.018
1001-0742/

2014). These methods have provided insight into the interaction mechanisms between HA and aluminum coagulants based on distinct fluorescence quenching behavior, Al species in the Al-HA flocs, the structures and functionalities of complexes, *etc.* However, it is well known that HA is a macromolecular organic substance with a complex and difficult-to-identify structure. The coagulation effect is attributed to its high content of oxygen-containing functional groups (Cheng and Chi, 2002). Moreover, the coagulation characteristics of the coagulant and various functional groups of HA are distinctive because of the distinct polarity, dissociation and reaction rates of the functional groups. Accordingly, it is necessary to describe the priority of functional groups in the interaction between humic acids and aluminum coagulants. However, it is difficult to identify the sequence of functional groups in HA reacting with the Al coagulant through these methods.

In 1986, Noda proposed the use of the two-dimensional correlation spectroscopy (2D-COS) method to analyze a set of spectral data from a system under the influence of an external perturbation (Noda, 1986), which introduced a new method in the investigation of binding ability between metal ions and organic ligands. Soon afterward, 2D-COS was increasingly applied in various studies. Recent research has explored the binding of natural organic matter (NOM) with metal cations such as Cu^{2+}, Pb^{2+} and Zn^{2+} (Chen et al., 2015; Hur and Lee, 2011; Nakashima et al., 2008; Xu et al., 2013), or the binding of organic ligands in dissolved organic matter from soil with Al^{3+} to understand soil organic carbon storage (Yu et al., 2012) by using 2D-COS. These studies have revealed distinct binding behaviors and the distribution of the binding sites with different metal and organic matter fractions. However, compared with other metal ions, aluminum not only can act as a coagulant that forms a complex with HA followed by the formation of flocs, but also is capable of absorbing HA on the surface of $Al(OH)_{3(s)}$. Therefore, although 2D-COS has been used for the characterization of metal–organic complexes, the characteristics of coagulation of humic acids by aluminum coagulants are quite different from the previous studies on metal–organic complexes, and the distinctive removal rules of functional groups during the coagulation of HA still remain poorly understood.

In principle, two-dimensional correlation spectroscopy could resolve the overlapped peaks and enhance the spectral resolution by extending the spectral intensity within the data, collected as a function of an external perturbation (*e.g.*, time, temperature and concentration), along the second dimension. More importantly, the specific sequential orders of the spectral intensity changes, *i.e.*, structural variations, can be probed through synchronous and asynchronous spectral analysis (Yu et al., 2012), which may be useful to investigate the sequence in which the functional groups in HA react with Al. Moreover, 2D heterospectral correlation spectroscopy could investigate the covariation of two different spectra, such as FT-IR and synchronous fluorescence (He et al., 2014). This approach may be used to identify the functional groups that are responsible for the peaks in the synchronous fluorescence spectra. Therefore, aiming to probe the characteristics and the sequential order of the corresponding functional groups of HA removed by coagulation, the structural changes of HA as a function of aluminum coagulant concentration were examined using synchronous fluorescence and FT-IR spectroscopy coupled with 2D-COS analysis. Thus, this study provides a promising pathway to analyze the priority of functional groups in the interaction between HA and aluminum coagulants.

1. Materials and methods

1.1. Materials and reagents

Humic acid was obtained from Sigma-Aldrich. The stock HA solution was prepared by adding 1 g of HA into 1 L of 0.1 mol/L NaOH solution. After stirring for 12 hr, the samples were filtered through a 0.45-μm membrane to remove the suspended materials and then passed through H^+-saturated AG-MP 50 cation exchange resin (Bio-Rad) in the hydrogen-saturated form. The resin was packed in 20 mm ID × 300 mm L glass columns and rinsed with 0.1 mol/L NaOH, 0.1 mol/L HCl and deionized water just prior to the extraction. Finally, the hydrogen-saturated acids were adjusted to different pH levels and then lyophilized for the FT-IR analyses.

1.2. Jar test procedure

Coagulation studies were performed in a conventional jar-test apparatus, equipped with six 1-L beakers. The stock HA solution was diluted with ionized water to reach the designated concentration (DOC = 10 mg/L). In addition, $NaNO_3$ was added to adjust the ionic strength of the solution to 0.1 mmol/L. Aluminum chloride (41.4 mmol/L Al^{3+}) was used in the study. The calculated volume of coagulation stock solution (to achieve the required dosage) and NaOH solution (to achieve the required pH) was added to the HA (DOC = 10 mg/L) solution. The coagulation procedure involved rapid mixing at 200 r/min for 1 min, followed by slow stirring at 20 r/min for 30 min. Approximately 20 mL of the solution was taken to determine the fluorescence intensity of the coagulating suspension within 1 min after flocculation. A 60-min settling period followed. The precipitate was then separated from the solution by centrifugation at 6000 r/min for 10 min and later lyophilized for FT-IR analyses.

1.3. Synchronous fluorescence spectra

Synchronous fluorescence spectra were recorded using an FP-6500 fluorescence spectrophotometer (Jasco, Japan). The excitation and emission slits were both adjusted to 5 nm, and the excitation wavelengths ranging from 250 to 550 nm were used with a constant offset ($\Delta\lambda$ = 30 nm).

1.4. FT-IR analysis

A mixture of 0.5 mg sample and 50 mg of KBr was ground and then compressed. The pellets were analyzed using a Fourier transform infrared (FT-IR) spectrometer (Model Nicolet 6700, Thermo Fisher Scientific) covering a frequency range of 4000–500 cm^{-1}.

1.5. Two-dimensional correlation spectroscopy

The 2D correlation spectra were produced according to the method of Noda and Ozaki (2004). Fig. 1 shows the general

Please cite this article as: Jin, P., et al., Two-dimensional correlation spectroscopic analysis on the interaction between humic acids and aluminum coagulant, J. Environ. Sci. (2017), http://dx.doi.org/10.1016/j.jes.2017.06.018