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Structural response of humic acid upon binding with lead: A spectroscopic insight

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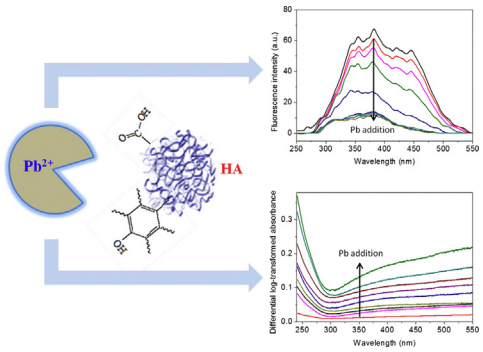
HIGHLIGHTS

- The binding characteristic of Pb onto HA was explored.
- The carboxylic and phenolic groups in HA were the binding sites to Pb.
- The Pb-HA interaction process was highly dependent on solution pH.
- Pb binding with carboxylic groups in HA was superior over phenolic groups.

GRAPHICAL ABSTRACT



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ABSTRACT

Lead (Pb) is a widespread heavy metal that can cause damage to the ecosystem, and the ubiquitously existing dissolved organic matter (DOM) can significantly affect the environmental behavior of Pb. The present work explores the interaction process of Pb with humic acid (HA) through integration of synchronous fluorescence and log-transformed UV–vis absorption spectroscopy coupled with spectral slope calculation and two-dimensional correlation analyses. The spectral slope calculation results show that the carboxylic and phenolic groups in HA were the predominant binding sites to Pb, and the interaction process was highly dependent on solution pH. Correlation analyses confirmed a superior binding affinity of carboxylic groups in HA over phenolic groups. Integration of spectral slope calculation with two-dimensional correlation spectroscopy is a promising tool for better understanding the molecular structure of Pb-DOM complexes and the characteristics of Pb binding to DOM, which may provide new insights into the prevention, control, and remediation of Pb contamination in environment.

1. Introduction

Lead (Pb) is a widespread heavy metal pollutant in water and soil, which possesses high potential toxicity to plants, animals, and humans (Li et al., 2016; Wang et al., 2018). Uptake and accumulation of Pb could cause vital damage to the metabolic systems of organisms and humans (Dai et al., 2015; Huang et al., 2015). Thus, Pb pollution control and treatment have always been hot topics in the area of environmental science (Y.N. Liu et al., 2017; Zhang et al., 2014). The treatment and remediation of Pb polluted water or soil requires a comprehensive understanding of the chemical state, migration, and physicochemical properties of Pb species in the environment

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(Gan et al., 2015; Leng et al., 2015; Yang et al., 2016). Dissolved organic matter (DOM) exists ubiquitously in aquatic and soil environments, and contains various chemical groups such as hydroxyl, carboxyl, and phenolic groups (Kellerman et al., 2015; Park, 2009). The interaction of DOM with Pb could strongly affect the distribution, toxicity, bioavailability, migration, and ultimate fate of Pb in the environment. On the one hand, DOM may interact with Pb ions to form soluble coordination complexes, thus inhibiting the adsorption and precipitation of Pb. On the other hand, Pb may also be extracted from the soil or mineral surfaces by DOM, facilitating the mobility of Pb (Zhang et al., 2017). Therefore, investigation of the interaction between Pb and DOM is significantly important for the control and governance of Pb contamination in environment.

Various techniques have been applied for the exploration of the impact of DOM on the environmental behavior of Pb. Molecular spectroscopy is a powerful tool for the study of DOM related interactions, because the structural changes of DOM during interaction can be revealed by the spectra of specific functional groups (Hur and Lee, 2011; Xu et al., 2013; Yan et al., 2013b). UV–vis, fluorescence, and infrared spectroscopic techniques have been widely applied in DOM studies. Xiong et al. used NICA-Donnan modeling and XAFS spectroscopy to investigate the binding of Pb to humic substances, and found that Pb was bound in bidentate complexes of one carboxylic and one phenolic group (salicylate-type) or two phenolic groups (catechol-type) in ortho position (Xiong et al., 2013). Using differential UV–vis absorption spectra, Yin et al. demonstrated that a dosage of Pb^{2+} ions could increase the molecular weight or size of extracellular polymeric substances (Yin et al., 2016). It is also reported that the oxygen containing functional groups and negatively charged humic acid (HA) could increase Pb^{2+} sorption on carbon nanotubes (Lin et al., 2012).

It should be noted, however, that DOM is a complicated organic mixture with high heterogenity (Akagi et al., 2007; Nebbioso and Piccolo, 2013), thus its spectra consist of highly overlapping bands. Only partial information on DOM structural change induced by heavy metal interaction can be revealed by conventional spectroscopic techniques. Further spectral data processing methods, such as differential and log-transformed absorption spectra, the calculation of spectral slopes and absorption ratios, can be applied to extract more useful information from the conventional UV–vis spectroscopy (Zhou and Meng, 2015). Two-dimensional correlation spectroscopy (2DCOS) is an emerging analytical method that has been recently introduced in the study of environmental interaction (Abdulla et al., 2010; Chen et al., 2018; Yu et al., 2012). 2DCOS analyzes a series of dynamic spectra obtained under an external perturbation, and provides better spectral resolution as well as the change sequences of spectral bands by generating two two-dimensional maps, i.e., synchronous and asynchronous maps (Noda, 2012). The perturbation can be temperature, pressure, concentration, etc. Specifically, hetero-2DCOS integrating two different spectral probes can give complementary relationships on the structural variation induced by the perturbation (Chen et al., 2015). Therefore, 2DCOS techniques could be promising to offer a better understanding of the molecular structure of Pb-DOM complexes and the characteristics of Pb binding to DOM. To the best of our knowledge, there are very few reports on the investigation of interaction between Pb heavy metal and DOM using the integration of log-transformed UV–vis/fluorescence spectroscopy with 2DCOS.

The present work is therefore aimed at exploring the interaction process of Pb with DOM through combining molecular spectroscopy with correlation analyses. Synchronous fluorescence and UV–vis spectra were used as two probes to detect the structural change of DOM during Pb binding, and spectral slope calculation, 2DCOS and hetero-2DCOS analyses were employed as complementary tools to extract the binding information hiding behind the conventional spectra. HA was used as the representative for DOM.

2. Experimental section

2.1. Sample preparation

HA was purchased from Sigma-Aldrich Co., USA, and was purified before use following a previous study (X.-Y. Liu et al., 2017). The purified HA contains 49.8% carbon. Analytical reagent grade $Pb(ClO_4)_2$, NaOH, and HCl were purchased from Sinopharm Chemical Reagent Co., China, and were used as received.

The purified HA and $Pb(ClO_4)_2$ were dissolved and diluted with deionized water to concentrations of 25.0 mg/L and 1.0 mM, respectively,

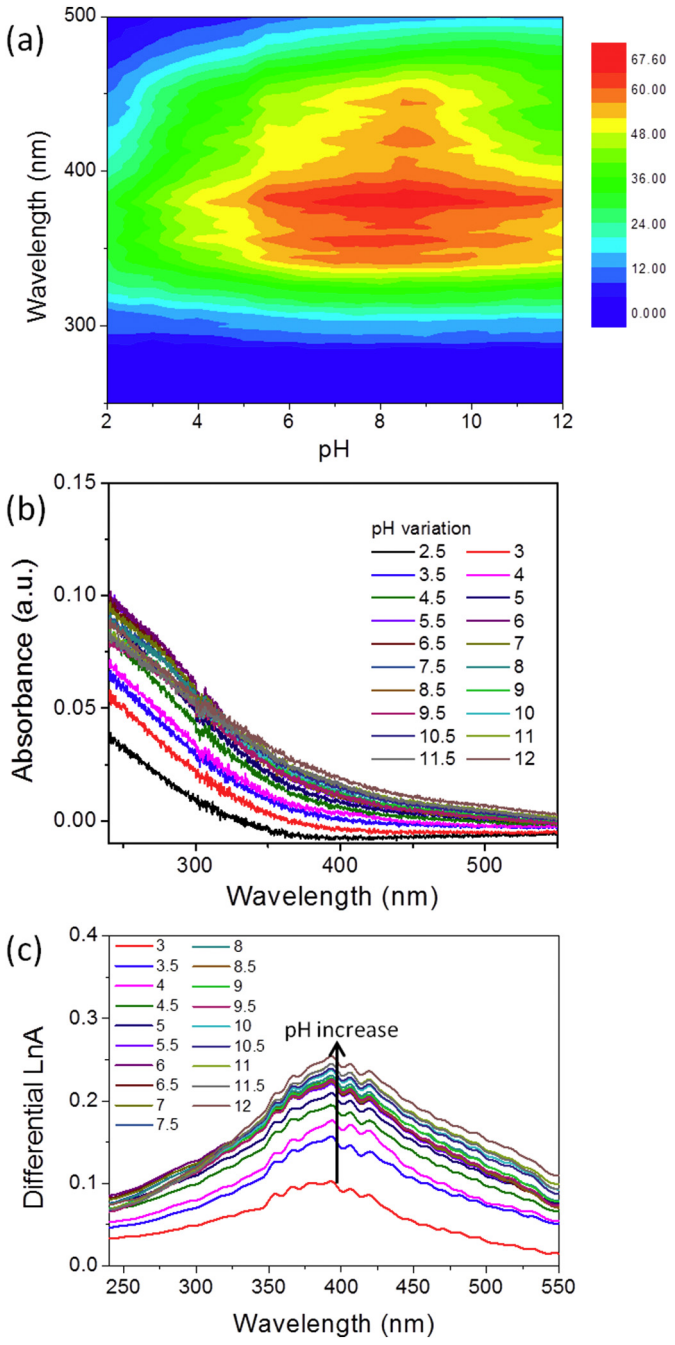

Fig. 1. (a) Synchronous fluorescence spectra of HA with solution pH variation. offset: 60 nm. (b) UV–vis absorption spectra of HA with increasing pH values. (c) Differential log-transformed absorption spectra of HA at different pH values.