The role of major functional groups: Multi-evidence from the binding experiments of heavy metals on natural fulvic acids extracted from lake sediments

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ABSTRACT

Fulvic acid (FA) plays a key role in governing the environmental geochemistry behavior of heavy metals. In this work, the roles of major functional groups were investigated based on binding experiments of heavy metals on natural FA extracted from lake sediments. The results showed that the adsorption capacities were ranked as $Cu^{2+} > Pb^{2+} > Cd^{2+}$. The differences of peak area at 3412, 1713, 617 and 2430 cm^{-1} pre- and post-binding reactions in FTIR spectra suggested that phenolic, carboxyl and nitrogen-containing groups were the major functional groups providing sites binding heavy metals. Moreover, the results of bi-Langmuir model and the ionic strength effects jointly indicated that electrostatic attraction was the key mechanism during the adsorption process. The fitted results of Ligand-binding model suggested that the major functional groups in FA were classified into two types binding sites: weak (i.e. phenolic and carboxyl groups) and strong binding sites (i.e. nitrogen-containing groups). Additionally, there might be p-benzoquinone-like formed in FA which were then reduced to hydroquinone during the adsorption process, corresponding to the changing of peak area at 1614 and 830 cm^{-1} in FTIR spectra, the occurrence of Peak C in Fluorescence excitation-emission matrix (EEM) spectra and the ratios of H/C (< 1) and O/C (≈ 1). The organic matter in sediments from Lake Wuliangsuhai presented similar characteristics with terrestrial plants due to the lake characterized by *Phragmites australis* and *Potamogeton pectinatus* L. being the dominant species, which shared large proportions of woody tissues as well as waxy hydrocarbons resembling that of terrestrial plants. This work is useful to insight the environmental effects of FA on heavy metals in environment.

1. Introduction

Humic substances (HS), as an ubiquitous complexant and important components in soils and aquatic environments, play a key role in governing the geochemistry behavior and process of heavy metals (Gondar et al., 2006), especially its fractions of humic acid (HA) and fulvic acid (FA). Comparatively, the adsorption capacity of FA was 2–20 times higher than HA (Boruvka and Drabek, 2004; Donisa et al., 2003) due to its great amount of chemical functional groups such as carboxyl, phenolic and carbonyl groups associating with the aliphatic or aromatic carbons in its macromolecules (Alberts and Filip, 1998; Rey-Castro et al., 2009).

Phenolic and carboxyl groups in FA have been proved to present the major functional groups for binding heavy metals during the adsorption process (Boguta et al., 2016; Janowska, 2013; Spark et al., 1997), meanwhile nitrogen-containing groups in FA also show important roles in this process (Chen et al., 2015; Zhang et al., 2018). Models such as Ligand-binding model were developed or employed to explain the adsorption mechanism between HS and heavy metals (Fakour and Lin, 2014; Liu and Cai, 2010), in which the chemical functional groups were classified as two types: (1) strong binding sites such as nitrogen-containing groups and (2) weak binding sites such as carboxylic and

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phenolic groups (Chakraborty et al., 2014; Fakour and Lin, 2014). These studies provided useful knowledge of binding mechanism between the functional groups and heavy metals.

Therefore, the models and the characterization methods were jointly applied to illustrate the role of different functional groups during the binding process of heavy metals onto FA. The objects of this work were to (1) compare the amount and affinity of different functional groups in FA by Ligand-binding models and the FTIR spectra and (2) understand the binding mechanisms and possible material transformation during the adsorption process using FTIR, Fluorescence excitation-emission matrix (EEM) spectra and elemental compositions. This work is hopeful to understand the binding mechanisms between FA and heavy metals in depth, which is of great significance for aquatic environment quality and safety (Gezici et al., 2007).

2. Materials and methods

2.1. Materials

Lake Wuliangsuhai (WLSH) is located in Bayan Nur, Inner Mongolia, China. WLSH is a typical macrophyte-dominated lake covered by the flourishing emergent vegetation (*Phragmites australis*) and submerged macrophyte (*Potamogeton pectinatus* and *Myriophyllum spicatum L*), resulting in the accumulation of plant residuals at a rate of 9–13 mm/a in the lake bottom. According to our previous work, the total organic carbon (TOC) was about 3.6 wt% in the surface sediment from WLSH (Wang et al., 2016).

Seven surface sediment samples (0–20 cm) were collected from WLSH in August 2012. FA was extracted with 0.1 mol/L NaOH from the sediment samples. Briefly, 0.5 kg of air-dried and sieved (0.2 mm) sediments were extracted using 5 L of 0.1 mol/L NaOH under N_2 condition. After 24 h of mechanical shaking in darkness at 25 °C, the suspension was centrifuged at 3000 rpm for 15 min and the supernatant was collected for further FA fractionation. The supernatant was poured through a column filled with XAD-8 resin, on which FA was retained and then eluted with 0.2 mol/L NaOH. The yellow solution containing FA in the form of sodium fulvate converted to the protonated form using a column of Dowex 50 strong acid cation exchange resin (H^+) to remove Na^+. The protonated final product (FA) was freeze-dried under vacuum and was kept in a vacuum desiccator over P_2O_5 in the dark (Wang et al., 2016). The elemental compositions and acidic functional groups contents of FAs were provided in Table S1. Total acidity of FA was measured by the $Ba(OH)_2$ titration method, the carboxyl group was determined by the calcium acetate method, and the phenolic group content was calculated by subtracting the carboxyl contents from the total acidity (Schnitzer and Gupta, 1965).

2.2. Binding experiments

The condition settings of binding experiments were shown in Table S2. The metal ions concentrations in the system before binding with FA were prepared using $Cu(NO_3)_2$, $Pb(NO_3)_2$ and $Cd(NO_3)_2$ (Guaranteed reagent GR, purchased from China Standards Material Network), respectively. All experiments were performed under N_2 condition. In all cases, blank samples and 3 replicate samples were performed to ensure the data quality, in which the SD (Standard deviation) ranged from 0% to 11%. The binding experiments were carried out in centrifuge tubes (50 ml) which were shaken for 2 h at 180 rpm, room temperature and dark condition and then balanced for 12 h. The concentrations of Cu^{2+}, Pb^{2+}, Cd^{2+} in solutions were measured by ion-selective electrode. To investigate the effects of FA concentrations on Cu^{2+} adsorption, FA concentrations were set as 25, 50, 100, 200, 250, 400 and 500 mg/L under the conditions of 0.01 mol/L ionic strength, 0.8 mmol/L Cu^{2+} and pH = 5. In the experiments of pH effects on Cu^{2+} adsorption, the solution pH was set as 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5 and 7 under conditions of 250 mg/L FA, 0.01 mol/L ionic strength and 0.8 mmol/L

Cu^{2+} respectively. In the experiments of ionic strength effects on Cu^{2+} adsorption, the concentrations of KNO_3 were 0, 0.0005, 0.001, 0.005, 0.01, 0.05, 0.1, 0.5 and 1 mol/L under the conditions of 250 mg/L FA, 0.8 mmol/L Cu^{2+} and pH = 5. The conditions for Pb^{2+}, Cd^{2+} binding experiments were the same as Cu^{2+}. To investigate metals speciation distribution, Visual MINTEQ was employed to calculate the speciation of Cu^{2+}, Pb^{2+}, Cd^{2+} under the experimental conditions of FA concentration = 250 mg/L, ionic strength = 0.01 mol/L, metal ion concentration = 0.8 mmol/L.

2.3. Characterization

The contents of C, H, and N in the extracted FA were determined by elemental analyzer (Elementar, Vario EL cube, Germany); O content was calculated by the mass difference, which was detailed by Lu et al. (2000). The functional groups presenting in the FA and FA-Metal complexes which obtained by freeze-drying were characterized by Fourier transform infrared spectrometer (FTIR, BRUKER, TENSOR 27, Germany) using the KBr method. The FTIR spectrum was obtained in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. EEM spectra was measured by fluorescence spectrometer (Edinburgh instruments, FSL920, UK). The Ex = 230–500 nm and the Em = 240–700 nm (Response time: automatic; Scanning speed: 1200 nm/min). Data analysis and statistics was performed using SPSS 21.0 and Origin 8.5.

3. Results and discussion

3.1. Impact factors

The adsorption capacity of Cu^{2+}, Pb^{2+}, Cd^{2+} onto FA increased with increasing equilibrium concentration and ranked as $Cu^{2+} > Pb^{2+} > Cd^{2+}$ (Fig. S1).

3.1.1. Effect of pH

FA is highly pH-dependent (Deng and Bai, 2003) which influences not only FA nature characteristics but also its biding capacity for heavy metals. In Fig. 1, the adsorption capacity of Cu^{2+}, Pb^{2+} and Cd^{2+} on FA gradually increased along with increasing pH (3–6). This trend could be explained by the following reasons: (1) the increase of pH weakened the competitive adsorption of H^+ against Cu^{2+}, Pb^{2+} and Cd^{2+}; (2) the increasing pH could promote the deprotonation of the acid functional groups on FA surface and then provided more opportunities for electrostatically attracting Cu^{2+}, Pb^{2+} and Cd^{2+} as a result of the dissociation of carboxyl and phenolic groups (Bigalke et al., 2010) or generated surface complexes with Cu^{2+}, Pb^{2+}, Cd^{2+} through the specific adsorption; (3) the increasing pH would increase the Donnan Volume of the FA, thus providing more space for metal to diffuse in the fulvic matrix and a better access to the binding sites; (4) there was a reaction in the solution:

$$M_mA_n + 2mH^+ \leftrightarrow H_{2m}A_n + mM^{2+}$$
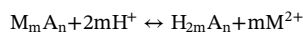
When the concentration of H^+ gradually decreases with increasing pH, the reaction will shift toward left. Accordingly, the arising M_mA_n (For example, $Pb(NO_3)_3^-$) induced the increase of measuring adsorption capacity.

When pH > 6, the adsorption capacity of Cu^{2+} and Pb^{2+} onto FA showed a downward trend due to the hydrolysis of Cu^{2+} and Pb^{2+}. For Cd^{2+}, its adsorption capacity did not show a decreasing trend due to that Cd^{2+} hydrolysis was weak in the range of pH 6–8 (FA concentration = 250 mg/L, ionic strength = 0.01 mol/L, metal ion concentration = 0.8 mmol/L) (Fig. S2).

3.1.2. Effect of FA concentration

As can be seen from Fig. 2(a, b, c), the adsorption capacity of Pb^{2+}, Cu^{2+}, Cd^{2+} onto FA decreased as the concentration of FA increased which is attributed to the concentrations effects. However, the binding