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Nature differences of fulvic acid fractions induced by extracted sequence as explanatory factors for binding characteristics of Cu^{2+}

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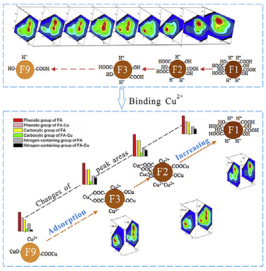
HIGHLIGHTS

- Nine extracted FA fractions presented differences in nature.
- The earlier of FA fractions the higher abundance of carboxyl and phenolic groups.
- Binding sites for Cu^{2+} were mainly provided by carboxyl and phenolic groups.
- Nitrogen-containing groups gradually contributed more from F1 to F9.

GRAPHICAL ABSTRACT



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ABSTRACT

The isolation of fulvic acid (FA) fractions with relatively homogeneity is a key to reveal the binding mechanisms between FA and heavy metals. In this work, nine FA fractions were obtained using sequential alkali extraction procedure and nature differences of the extracted FA fractions were considered as explanatory factors for binding characteristics of Cu^{2+}. The results indicate that the contents of carboxyl and phenolic groups decrease with increasing extractions along with an opposite trend for the content of nitrogen-containing groups. The fitted results of ligand binding and bi-Langmuir models indicate that the binding sites for Cu^{2+} were mainly provided by carboxyl and phenolic groups, which explained the higher sorption capacity and binding affinity of earlier extracted FAs due to its higher contents of carboxyl and phenolic groups. Furthermore, the systemic characterization of FA fractions before and after adsorption indicate the nitrogen-containing groups were gradually showing their contribution in binding Cu^{2+} with increasing extractions. This work is very helpful to insight the environmental effects of natural organic matter and the behavior of heavy metals in natural environment.

1. Introduction

Humic substances (HS) are a ubiquitous heterogeneous complexant and important components of soils, sediments and aquatic

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environments, which play a key role in governing the geochemistry behavior and process of heavy metals (Sekaly et al., 1999; Gondar et al., 2006). Traditionally, HS have been classified, based on their solubility in water at different pH, into three separate fractions: FA (fulvic acids, alkali and acid soluble), HA (humic acids, alkali soluble and acid insoluble), and HM (humin, alkali and acid insoluble) (Stevenson, 1994; Sutton and Sposito, 2005; Ikeya et al., 2011). One of the well-documented effects of FA is its influence on concentrations and mobility of metals in the environment (Grant et al., 2004). The extent of FA-metal binding and the nature of FA functionalities engaged in interactions with metal cations are site-specific (Giesy and Alberts, 1982). The diversity of FA sources and generation pathways results in a highly complex nature of FA with various molecular weights, conformations, proton affinities and abundences of carboxyl, phenolic and other metal cation-binding functional groups (Buffel, 1990; Donisa et al., 2003; Borůvka and Drábek, 2004). However, the component and structure of FA is so heterogeneous that it brings significant barriers to investigate the interaction between FA and heavy metal ions (Reemtsma et al., 2006). The previous studies showed that the acquisition of homogeneous FA fraction was a key to reveal the interaction mechanisms of FA binding heavy metals (Silva and Oliveira, 2002). There are two popular methods to obtain FA fractions, including different fractions based on sequentially alkali extraction times or based on molecular weight by high performance size-exclusion chromatography (HPSEC) and ultrafiltration (Ma and Xiao, 2011). In comparison, FA fractions extracted by sequential alkali extraction has the advantage of its behavior similar to that of natural humic substances over HPSEC and ultrafiltration.

FA contains both hydrophobic and hydrophilic moieties as well as many functional groups such as carboxyl, phenolic and carbonyl groups connected with the aliphatic or aromatic carbons in the macromolecules (Alberts and Filip, 1998; Reycastro et al., 2009). The previous study indicates there are different species and portions of functional groups among FA fractions, which leads to changes in affinity for metal ions (Christl et al., 2001). Moreover, most researchers have used only one-step extraction of FA or a mixed FA combined from several extractions, which could not reveal the metal-FA interact mechanism in great detail.

In addition, FA strongly influence the adsorption of Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} onto FA (Kulikowska et al., 2015). A clear understanding of the FA-metal interactions is therefore crucial to fully elucidate fate and transport mechanisms of heavy metals and pollutants in the environment (Kang et al., 2002; Li et al., 2017). Therefore, the procedure of sequential alkali extraction was applied to extract nine FA fractions from natural sediments of Lake Wuliangsuhai (WLSH) in this work. The objectives of this study were (1) to investigate the difference of structure and composition of nine FA fractions from a natural sediment, (2) to reveal the key binding mechanism of heavy metal ions on FA fractions based on the differences of composition and structure before and after binding interaction. It could give a theoretical and practical direction to understand the environmental effect of HS and environmental geochemical behavior of heavy metals in lakes.

2. Materials and methods

2.1. FA fractions extraction

Nine FA fractions (F1-F9) were sequentially extracted from a natural sediment collected from WLSH (Inner Mongolia, China.) in August 2014. The study background (He et al., 2016; Wang et al., 2016) and extraction method (Wang et al., 2016) are described in our previous study and please get more information from the Supplementary Material.

2.2. Characterization

FA fractions were characterized to obtain the results of elemental compositions, ratios of absorbance at 250 nm and 365 nm (E2/E3), 250 nm and 465 nm (E2/E4), 465 nm and 665 nm (E4/E6), specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), acidic group contents, Fourier transform infrared spectra (FTIR spectra), Three-Dimensional Excitation-Emission Matrix (3DEEM) spectra and scanning electron microscopy (SEM) photo, respectively. Please see Supplementary Material for more information.

2.3. Sorption experiments

Under the conditions of temperature at $25.0 \pm 0.5\,^{\circ}C$, $pH = 5.00 \pm 0.10$ and 0.01 mol/L KNO_3, adsorption isotherm experiments were conducted as adding 5 mg of FA and 20 mL solution containing 0.2–12 mg/L Cu^{2+} into 50 mL centrifuge tubes, shaking the tubes for 3 h and then static balancing them for 12 h at $25.0 \pm 0.5\,^{\circ}C$.

For pH-dependent sorption experiments, 20 mL of 4 mg/L Cu^{2+} solutions with 0.01 mol/L KNO_3 were mixed with 5 mg FA fractions in 50 mL centrifuge tube, with the values of pH from 3.00 ± 0.10 to 11.00 ± 0.10.

For ionic strength sorption experiments, 20 mL of 4 mg/L Cu^{2+} solutions were mixed with 5 mg FA fractions in 50 mL centrifuge tube at $pH = 5.00 \pm 0.10$ and $25.0 \pm 0.5\,^{\circ}C$. The ionic strength of KNO_3, $Ca(NO_3)_2$ and $Mg(NO_3)_2$ in solution ranged from 0.005 to 0.5 mol/L, respectively.

The adsorbed amounts of Cu^{2+} on FA fractions in all experiments were calculated by the mass difference between the initial and equilibrium Cu^{2+} concentrations, and Cu^{2+} concentrations in solutions were all measured by ion-selective electrode.

2.4. Data analysis

In this work, ligand binding and bi-Langmuir models were used to fit the data of experiment (He et al., 2016; Wang et al., 2016). Please see Supplementary Material for more information.

3. Results

3.1. Characteristics of extracted FA fractions

Elemental compositions, atomic ratios, and acidic functional group contents of the nine FA fractions (FAs) are listed in Table S1. The results showed that the decrease of O/C and (N + O)/C ratios ranged from 1.18 to 0.90 and from 1.19 to 0.98 with increasing extractions, respectively, which indicated that the latter extracted FA fractions contained weaker polarity and less oxygen-containing functional groups (Jin et al., 2009; Yang et al., 2011). In addition, the H/C ratios increased with increasing extractions, which implied that the latter FA fractions contained more unsaturated hydrocarbons and higher aliphaticity (Rice and Maccarthy, 1991). The contents of phenolic and carboxyl groups declined from 7.46 to 2.81 mmol/g and from 2.58 to 0.24 mmol/g, respectively from F1 to F9, which revealed that there are less carboxyl and phenolic groups in the latter extracted FA fractions.

The absorbance of FA increased with a decreasing wavelength of UV–visible, and the similar trend can be found in each of nine fractions (Fig. S1). The $SUVA_{254}$ values decreased from 5 to 0.2 with increasing extractions (Table S2), which indicated that the latter fractions contained more unsaturated carbon bonds (Yuan et al., 2013). The E2/E3 ratios increased from 3.77 to 15.02, the E2/E4 and the E4/E6 ratios decreased from 27.03 to 4.25 and from 3.25 to 0.27 with increasing extractions (Table S2), respectively, which