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Adsorption and desorption of divalent mercury (Hg^{2+}) on humic acids and fulvic acids extracted from typical soils in China

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ABSTRACT

A series of batch equilibration experiments were conducted to assess the adsorption and desorption of divalent mercury (Hg^{2+}) by humic acids (HAs) and fulvic acids (FAs) extracted from black soil and red soil in China. The Fourier transform infrared (FTIR) spectroscopy, cross-polarization (CP) with magic-angle spinning (MAS) ^{13}C nuclear magnetic resonance (NMR) spectroscopy and scanning electron microscopy (SEM) were jointly adopted to characterize the humic substances (HSs) samples and HSs–Hg complexes. The FTIR spectra showed that the adsorption of Hg^{2+} mainly acted on O–H, C–O and C═O groups of HAs and FAs. The NMR spectra indicated that HAs are higher in Paraffin and carbonyl C content compared with corresponding FAs, while FAs exhibit higher methoxy C, O-alkyl C and carboxyl C contents. The SEM images revealed the different surface structures of HAs, FAs and HSs–Hg complexes, which explains Hg^{2+} complexation phenomenon on HSs. The study also showed that HAs have higher adsorption capacity for Hg^{2+} than those of FAs. Hg^{2+} adsorption isotherms could be well fitted with both Langmuir and Freundlich equations. The desorbed percentages of all HSs samples were less than 1%, which indicated their high binding strength for Hg^{2+}. Furthermore, HAs samples have a lower desorption ratio than FAs, HAs can play a more important role in pollution control of Hg^{2+} in environment.

1. Introduction

As one of most harmful global environmental contaminants, mercury has been recognized as a threat to human health [1,2]. Like other trace elements, the behavior and fate of Hg^{2+} in environment are mainly controlled by its adsorption and desorption processes with various adsorbents [3]. Many studies show that organic matter is the most important soil component controlling Hg^{2+} adsorption and desorption processes, affecting its retention and release in environment [2,4–7].

Humic substances (HSs) are the active part of organic matter, which in turn account for 70–80% of all soil organic matter [8]. HSs, among the most widely distributed natural organic macromolecule matters on the earth surface, contain a number of function groups such as carboxylic, carbonylic, phenolic and methoxy groups. Those function groups in HSs may combine with some heavy metals in environment. Therefore, HSs play many significant environmental roles in stabilizing soils and sediments, regulating the levels of water, metals and other components [9]. Both metals and organic contaminants can be adsorbed by HSs in a number of ways such as complexation, ion exchange and reduction [10], forming some hydrosoluble or water-insoluble complex compounds, thus significantly affect the environment. All the three main components of HSs, humic acids (HAs), fulvic acids (FAs) and humin (HU), have similar structures but different in molecular weights, elemental analysis and function group contents [11].

The objectives of this research are to give an in-depth study of the Hg^{2+} adsorption–desorption processes on HAs and FAs extracted from two typical soils (black soil and red soil) in China. The binding capacity of HSs samples was compared to reveal the related complex interactions between Hg^{2+} and HSs. Analysis using multiple methods including FTIR spectroscopy, CP/MAS ^{13}C NMR spectroscopy and SEM revealed structural characteristics and elucidated the mechanism of Hg^{2+} adsorption–desorption on typical HSs.

2. Materials and methods

2.1. Materials

Black soil collected from Gongzhuling of Jilin Province and red soil collected from Yingtan of Jiangxi Province with distinct properties were used as the sources of HAs and FAs. Both soils were

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Table 1
The physical and chemical characteristics of the two typical soils and humic substances extracted from them.

Samples	Soil type[a]	Location	pH (H_2O)	SOM (%)	Particle size distribution (%)[b]			Textural classification	Mercury content (mg kg^{-1})	Humic substances content (%)		Element contents (%)		
					Sand	Silt	Clay					C	H	N
Black soil	Phaeozem	Gongzhuling, Jilin Province	6.30	3.03	17.4	60.3	22.3	Silt loam	0.186	HA	2.47	18.72	2.95	1.44
										FA	10.5	6.94	0.65	0.1
Red soil	Udic Ferrisols	Yingtan, Jiangxi Province	5.03	1.33	24.9	35.4	39.7	Clay loam	0.257	HA	0.39	17.42	3.03	1.75
										FA	0.46	6.32	1.8	0.4

[a] Soil classification according to [47].

[b] Sand (0.05–2 mm), Silt (0.002–0.05 mm), Clay (<0.002 mm).

air-dried and then sieved through a 2 mm sieve for soil particle size distribution, ground to pass through a 1 mm sieve for soil pH, extraction of humic substances, and through a 0.125 mm sieve for soil organic matter and Hg in soil. The physical and chemical properties of the soils and the elemental composition of the purified HAs and FAs extracted from two soil samples were analyzed by the following procedure.

Soil pH value was determined with a pH meter (pHS-3C, Leici, China) in a 1:2.5 suspension in H_2O. Soil organic matter was determined by oxidation with potassium dichromate-titration of $FeSO_4$, which is a standard method recommended by the Chinese Society of Soil Science [12]. Soil particle size distribution was measured by the micro-pipette method [13]. The background Hg in soil was determined by Atomic Fluorescence Spectrometer (AFS 930, Beijing Jitian Instrument Co., China) after digestion in AIM600 Block Digestion System with teardrops using aqua fortis (1:1). Element contents of HSs extracted from soils were measured by Elemental Analyzer (Vario EL III, Elementar Analysensysteme GmbH., Germany). Basic properties of soils and HSs used in this study are listed in Table 1.

2.2. Extraction and purification of humic substances

The extraction and purification of HAs and FAs were performed using a method developed by the International Humic Substances Society (IHSS) [14–16]. Briefly, 100 g of soil sample was weighed and added into a beaker with 1 L 0.05 M HCl, and the solution was intermittently churned for 18 h. Then the soil was separated from supernate by centrifugation at 5000 rpm for 10 min and was washed with deionized water. Then, 1 L 0.1 M NaOH was added to the soil persistently churned for 24 h. The solution was centrifuged at 15,000 rpm for 20 min. This process was repeated at least twice to make sure the supernate was completely separated from the residue. All the supernates were collected into a clean glass beaker. The pH was adjusted to 1–2 using 6 M HCl. HAs do not dissolve in acid while FAs do. Therefore, all HAs precipitates are separated from FAs. The HAs products were obtained by centrifugal precipitation (5000 rpm, 10 min). All experiments were carried out at temperature 25 °C.

The HAs were mixed with 0.5 L HF–HCl acid mixture(0.1 M HCl + 0.3 M HF) and then shaken for 24 h at 25 °C. The silicate in HAs was dissolved in mixture acid and then removed by centrifugation at 5000 rpm for 10 min. This process was repeated three times until little ash left in HAs. Cation exchange resin was filled in dialysis bags and shaken for 24 h in HAs solution to remove ions. At last, the purified HAs were freeze-dried and kept in a refrigerator. The XAD-8 resin (purchased from Sigma Co., USA) was used in FAs purification process. The supernates separated form HAs were flowing through an ion exchange column (length: 20 cm, diameter: 1.0 cm, flow rate: 1.5–2 ml min^{-1}), left the FAs on the resin. After that, the resin was washed with deionized water till pH value at 6–7. Then, 0.1 M NaOH solution was used to elute FAs from the resin. After cation exchange was used in the elute solution, it was concentrated in a rotary evaporator at 45 °C. The purified FAs were freeze-dried and ground to fine powders for characteristic analysis and adsorption/desorption experiments.

2.3. Adsorption and desorption experiments with HAs and FAs

A batch equilibration technique was conducted in this mercury adsorption and desorption experiments. Four kinds of samples were used including two HAs and two FAs extracted from black soil and red soil. An amount of 30 mg HAs (or FAs) was precisely weighed and combined with 25 ml solution in 50 ml plastic centrifuge tubes. The adsorption solutions were prepared in 0.1 M $NaNO_3$ solution [4], with the rising Hg^{2+} concentration gradients of 0, 1.5, 2.5, 3.5