



Interactions between iron mineral-humic complexes and hexavalent chromium and the corresponding bio-effects[☆]

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ABSTRACT

The interfacial behaviors of chromium are fundamental for understanding the environmental effects of chromium in contaminated environments. However, complex surfaces can cause chromium to exhibit a variety of behaviors, especially when humic substances are considered. This work illustrated the role of humics (humic acid and fulvic acid) during the adsorption of Cr(VI) onto iron minerals (magnetite and hematite). The interfacial behaviors were investigated through their adsorption kinetics, adsorption isotherms, and thermodynamics. Then, the microbial diversity was monitored to reflect the bio-effects of Cr(VI) adsorbed onto four iron oxide-humic complexes. The differences in the adsorption capacities and mechanisms of Cr(VI) on the surfaces of the iron mineral-humic complexes were observed. Humics obviously decreased the adsorption capacities of Cr(VI) on the hematite complexes and relieved the decline in the microbial diversity; meanwhile, humics imposed relatively insignificant changes to the Cr(VI) adsorption capacity onto the magnetite complexes. Thus, the corresponding microbial diversity might be mainly affected by released micelles formed by Cr(VI) and humics. These results illustrate the complexities of the interfacial behaviors of Cr(VI) on the surfaces of iron mineral-humic complexes and broaden the current understanding of chromium migration and transportation.

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1. Introduction

Chromium-contaminated soils have long been considered as an environmental problem (Kazakis et al., 2018; Brose and James, 2013). Moreover, based on a sampling survey, the ratio of contaminated soil is still increasing (MLR, 2014). The migration, transformation, and bioavailability behaviors of chromium are dominated by interactions at the solid-fluid interface, especially along the interfaces of iron oxides (Zachara et al., 1987). Although the interfacial reactions would be decided by multiple reasons including environmental conditions (pH, ionic strength, and temperature, etc.) and interfacial properties. This work only focuses on

interfaces of iron mineral-humic complexes by controlling environmental parameters. The changes of interfacial reactions can alter the pathways and kinetics, and consequently result in chromium exhibiting distinct bio-effects. For example, Cr(VI) is mainly reduced to Cr(III) and chelated by hydroxy groups on the surface of Fe(II) (Kendelewicz et al., 2000; Grossl et al., 1997), while the adsorption of Cr(VI) by Fe(III) is mainly achieved by ion exchange between hydroxy and Cr(VI) (Cao et al., 2012). Although some studies have been reported on this topic, more complex mineral interfaces are expected to be critical and predominant in different environments (Batchelli et al., 2010; Hiraide, 1992; Tipping et al., 2002).

Humic substances are heterogeneous and functional group-rich organic molecules (Lovley et al., 1996) that account for 60% of the overall dissolved organic carbon in aquatic systems (Stevenson, 1994). When humics interact with minerals, negatively charged humics are likely to be retained on positively charged mineral surfaces. Thus, the interactions between humics and minerals could

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alter the original properties of either substance and generate complex humic minerals (Hu et al., 2010). For example, magnetite that is coated with humic acid could prevent the transformation of the mineral core during an interaction with Cr(VI) (Jiang et al., 2014). Nevertheless, it is worth mentioning that complicated humics include both soluble humic acid and fulvic acid (Hiraide, 1992). Meanwhile, the minerals that can interact with humics encompass various structures with different properties. Hence, it is necessary to systematically study the performances of chromium on the interfaces of various humic minerals with different properties rather than focus on only one model interface.

Shifts in microbial communities are mainly influenced by environmental pollution within contaminated soils (Nannipieri et al., 2003). Microbial processes link the fluxes of cyclic elements and drive the cycles of multiple nutrients. Therefore, the microbial diversity, which represents one of the key parameters of microbial communities, could be used to reflect the bio-effects of heavy metal pollution (Brookes, 1995). Meanwhile, the bio-effects of Cr(VI) are determined by multiple factors, including interfacial adsorption and released micelles. Humics may favor the toxic persistence of Cr(VI) relative to microbial communities because humics can form micelles with Cr(VI) (Leita et al., 2009). In this work, we focus on the interactions between humics and Cr(VI) and address the role of interfacial adsorption on the bio-effects of chromium.

In this study, the interactions between various iron mineral-humic complexes and Cr(VI) were systematically studied by investigating two minerals, namely, magnetite and hematite, and two humics, namely, humic acid and fulvic acid. Four complexes, including magnetite-humic acid (Mag-HA), magnetite-fulvic acid (Mag-FA), hematite-humic acid (Hem-HA) and hematite-fulvic acid (Hem-FA), were applied to explore their interactions with Cr(VI), each of which was deeply explored with regard to their adsorption kinetics, isotherms, and thermodynamics. From the perspective of bio-effects, the four complexes were added into soil after being coated with Cr(VI) to investigate the shifts in microbial diversity. This work could provide comprehensive insight into how humics change the interfacial behaviors of Cr(VI) and the resulting bio-effects.

2. Experimental methods

Synthesis of iron minerals. Magnetite (Mag) was synthesized using a modified hydrothermal method (Liu et al., 2008). In brief, 3.66 g of FeCl₃ and 4.20 g of FeSO₄ were dissolved in 100 mL MilliQ water (Millipore Corporation, Billerica, MA, USA), after which the solution was heated to 90 °C before the addition of 10 mL of NH₄OH (25%). The mixture was kept at 90 °C, stirred for half an hour, and cooled to the ambient temperature. Subsequently, the black precipitates were gathered and washed until the pH of the supernatant was neutral. Hematite (Hem) was also synthesized using the hydrothermal method. In brief, 50 mL of FeCl₃ solution (1 M) was added one drop at a time into 450 mL of boiling MilliQ water, following which the solution turned from golden brown to dark red. After adding the final drop, the solution was heated for 5 min. Then, the solution was cooled to the ambient temperature and dialyzed for approximately 48 h in a solution of HClO₄ (pH 3.5) (Mulvaney et al., 1988). The methods employed for the structural characterization are described in the Supporting Information.

Preparation of the iron mineral-humic complexes. The iron mineral-humic complexes were obtained by absorbing excess humic acid or fulvic acid onto magnetite or hematite (Iglesias et al., 2010). In brief, humic acid was dissolved in a 20 mM NaCl solution before its pH value was adjusted to 7 using a 5% (w/w) HCl or NaOH solution, thereby forming a 600 mg L⁻¹ humic acid solution. Then, 200 mg of either magnetite or hematite was added to a 1 L

flask containing a 250 mL humic acid solution. The flask was shaken at 150 rpm at a temperature of 298 K in the dark for 24 h. The mixture was then centrifuged at a speed of 7800 rpm for 10 min, after which the precipitates were collected and washed three times. The Mag-HA or Hem-HA complexes were obtained after the precipitates were freeze-dried. Except for the replacement of humic acid with fulvic acid, the Mag-FA and Hem-FA complexes were prepared similarly.

Procedure of Cr(VI) adsorption. All of the Cr(VI) adsorption batch experiments were accomplished in 50 mL flasks within temperature-controlled shaking incubator at a speed of 150 rpm. The Cr(VI) solution was obtained by dissolving K₂Cr₂O₇ into 20 mM of NaCl, and the pH value of the solution was altered to neutral using a 5% (w/w) HCl or NaOH solution. After cultivation, the samples were taken from the flasks using syringes and were subsequently filtered using 0.22 μm filters.

To derive their kinetic curves, 15 mg of each mineral complex (i.e., Mag, Mag-HA, Mag-FA, Hem, Hem-HA, and Hem-FA) was added to a 10 mL Cr(VI) solution with concentrations of 5, 8 or 10 mg L⁻¹, after which the mixtures were sampled at fixed time intervals. The adsorption isotherms were carried out at 298 K, 308 K, and 318 K. In all, 20 mg of Mag, 20 mg of the Mag-HA, Mag-FA, Hem-HA, and Hem-FA complexes, and 10 mg of Hem were added to 10 mL Cr(VI) solutions with concentrations varying from 2 to 26 mg L⁻¹ (2–30 mg L⁻¹ for Mag-FA), after which samples were taken after 24-h cultures. The Cr(VI) complexes obtained under 298 K were collected for biological experiments. The initial and residual Cr(VI) were both analyzed at 540 nm using an ultraviolet–visible (UV–Vis) spectrophotometer (UV-1200, Mapada, China) (Yang et al., 2014). The quantities of Cr(VI) adsorbed onto the iron oxides or iron oxide complexes were calculated using the following equation:

$$q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

where q_e is the Cr(VI) adsorption capacity at adsorption equilibrium (mg g⁻¹), C_0 and C_e are the initial concentration and equilibrium concentration of Cr(VI) in the solution (mg L⁻¹), respectively, V is the volume of the Cr(VI) solution (L) and m is the weight of the iron oxide or iron oxide complex (mg).

Soil microcosms of iron oxides and iron oxide-humic complexes. Soil samples (at depths of 5–20 cm) were collected from a paddy field located in Xiamen (Fujian, China, 24°37'18"N, 118°2'34"E). To minimize spatial disparities, approximately 4 kg of soil was mixed to form homogeneous samples prior to the experiments. Twelve soil microcosms with volumes of 60 mL were mixed with different mineral complexes (i.e., Mag, Mag-HA, Mag-FA, Hem, Hem-HA, and Hem-FA) either with or without Cr(VI) in sealed bottles. The ratio of soil was regulated at 18% to maximize microbe activity (Ge et al., 2011), and the exposure dosage of each mineral complex was 1‰. The microcosms were incubated at 25 °C in the dark, and samples were taken after 10 and 20 days. The batch experimental design engendered 72 microcosms with 3 duplicates per exposure dosage.

Soil DNA extraction and bacterial community analysis. Each soil sample was entirely mixed, and the extraction and purification of genomic DNA were conducted following a previous report (Yang et al., 2007). The methods employed for the quantification and sequencing of the purified genomic DNA were described in a previous paper (Zheng et al., 2014a). In brief, the genomic DNA was polymerase chain reaction (PCR) amplified to obtain the V4-V5 region, after which the PCR products were purified before constructing libraries for Illumina MiSeq sequencing. The sequenced data were processed using the Quantitative Insights Into Microbial

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