



Characterization of humins from different natural sources and the effect on microbial reductive dechlorination of pentachlorophenol



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HIGHLIGHTS

- Chemical, spectroscopic, and electrochemical analyses were conducted on humins.
- Humins were extracted from seven types of soil and from a river sediment.
- All humins facilitated microbial reductive dechlorination of pentachlorophenol.
- Cyclic voltammetry analysis confirmed the presence of redox-active moieties.
- Estimated redox potential of humins ranged from -0.30 to -0.13 V.

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ABSTRACT

Humins have been reported to function as an electron mediator for microbial reducing reactions. However, the physicochemical properties and the functional moieties of humins from different natural sources have been poorly characterized. In this study, humins extracted from seven types of soil and from a river sediment were examined on the effect on microbial reductive dechlorination of pentachlorophenol (PCP) and characterized polyphasically. All humins facilitated microbial reductive dechlorination of PCP as electron mediators using formate as carbon source, with different dechlorination rates ranging from 0.99 to 7.63 ($\mu\text{mol Cl}^-$) $\text{L}^{-1} \text{d}^{-1}$. The highest rates were observed in humins with high carbon contents, extracted from Andisols containing allophone as major clay. Yields of the humins and the elemental compositions varied among sources. Fourier transform infrared analysis showed that all the humins exhibited similar spectra with different absorbance intensity; these data are indicative of their similar structures and identical classes of functional groups. The electron spin resonance spectra of humins prepared at different pH showed typical changes for the semiquinone-type radicals, suggestive of quinone moieties for the redox activity of the humins. Cyclic voltammetry analysis confirmed the presence of redox-active moieties in all the humins, with the estimated redox potentials in the range of -0.30 to -0.13 V (versus a standard hydrogen electrode), falling into the range of standard redox potential between the oxidation of formate as electron donor and the initial dechlorination of PCP as electron acceptor.

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1. Introduction

Humic substances (HSs) are redox-active natural organic matter ubiquitous in the environment and can be extracted from nearly all types of soil, sediments, peatlands, and bogs (Stevenson, 1994;

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Lovley et al., 1996, 1999). In all environments, HSs contain plant, animal, and microbial residues at all stages of decay and a variety of heterogeneous organic substances that are often intimately associated with inorganic components of a soil or sediment (Mikutta et al., 2006; Miltner et al., 2012; Semenov et al., 2013).

Although HSs are considered inert refractory organic material, accumulating evidence shows that they function as electron mediators that facilitate anaerobic bioremediation processes (Bradley et al., 1998; Van der Zee and Cervantes, 2009). The function of HSs as electron mediators has been studied extensively during the past two decades with the focus on dissolved HSs and their

quinoid analogues (Workman et al., 1997; van der Zee et al., 2001; Van der Zee and Cervantes, 2009). Recently, we reported that solid-phase humin, a fraction of HSs that is water insoluble at any pH (Rice, 2001), works as an electron mediator for microbial reductive dechlorination of pentachlorophenol (PCP) (Zhang and Katayama, 2012; Zhang et al., 2014b), reductive debromination of tetrabromobisphenol A (Zhang et al., 2013), Fe(III) oxide reduction (Zhang and Katayama, 2012), and nitrate reduction (Zhang et al., 2015).

Humin contains a high amount of organo-mineral complexes, in contrast to the mostly organic fulvic acids and humic acids, and the solid-phase humin, being an all-natural substance, is attractive for the use as an electron mediator in *in situ* remediation because its own pollution potential is minimal and it will not be flushed away during treatment like soluble electron mediators. In our laboratory, we have maintained an anaerobic humin-dependent PCP-to-phenol dechlorinating culture. This culture was enriched from an uncontaminated paddy soil (Kim et al., 2004), and the PCP dechlorination pathway as well as the microbial community structure in the soil culture was analyzed (Yoshida et al., 2007). However, soil was requisite for the dechlorination activity in the culture (Yang et al., 2009). Finally we found that humin in the soil served as electron mediator for the microbial reductive PCP dechlorination (Zhang and Katayama, 2012). Loss of the electron mediating function by substantial removal of organic matter suggested that the function was attributable to the organic fraction of humin (Zhang and Katayama, 2012). Nevertheless, how the differences in humins in relation with their natural sources such as different geographical locations and land types influence their role as a solid-phase electron mediator has not been explored.

Therefore, in this study, the anaerobic humin-dependent PCP-to-phenol dechlorinating culture (Zhang and Katayama, 2012) was used as an inoculum source for examining the activity of humins from different natural origins. The humins were characterized: we analyzed their chemical, spectroscopic, and electrochemical properties to gain insight into the electron-mediating characteristics of humins.

2. Materials and methods

2.1. Soil and sediment samples

Soil samples used in this study include soils with different land use (upland and paddy soils) as shown in Table 1. Kamajima and Yatomi paddy soils were classified as Aquepts with kaolinite as major clay. Nagano paddy and upland soils were Aquepts predominated with smectite. Ibaraki paddy and upland soils were Udands containing allophane as major clay (volcanic Andisols), while Nagakute upland soil was Ustand containing vermiculite

(non-volcanic Andisol). These samples were air dried, sieved (<2 mm) and stored at room temperature until use.

2.2. Extraction and purification of humins

Humin samples were prepared as described previously (Zhang and Katayama, 2012). Briefly, 250 g of air-dried soil was extracted with 150 mL of 2% hydrofluoric acid (HF) exhaustively to remove the clay minerals and silicate (Schmidt et al., 1997) by shaking for 16 h (once), 24 h (three times), 48 h (twice), and 64 h (once). The HF-treated residue was then further extracted with 150 mL of 0.1 M NaOH by shaking for 24 h at least 10 times until the dark color in the extract was not noticeable (Schnitzer and Khan, 1978). The soil residue after NaOH extraction was shaken with 200 mL of 2% HF for 24 h (three times) to remove mineral impurities. Thereafter, the residue was neutralized, thoroughly rinsed with distilled water and freeze-dried as the humin sample. All the solutions and distilled water used were purged with N₂, and all the centrifugation steps was carried out at 8000 g for 10 min.

The humins extracted from the soils in Kamajima, Yatomi, Nagano (both paddy and upland field soils), Ibaraki (both paddy and upland field soils), Nagakute and from Arako River sediment were designated as KM-HM, YA-HM, NGP-HM, NGU-HM, IRP-HM, IRU-HM, NT-HM, and AR-HM, respectively.

2.3. Influence of humin on the microbial reductive PCP dechlorination

An anaerobic humin-dependent PCP-to-phenol dechlorinating culture was used as the inoculum source in this study (Zhang and Katayama, 2012). This humin culture had been maintained through serial transfers of 5% (v/v) of the inoculum to serum bottles, containing 20 mL of a mineral medium, 10 mM formate as a sole source of carbon and energy, 5 g L⁻¹ humin (KM-HM), and 20 μM PCP. The cultures were incubated statically at 30 °C in the dark. In this culture, no PCP dechlorination takes place without the presence of either humin or inoculum (Zhang and Katayama, 2012). Also, chemically-reduced (by NaBH₄) humin could not abiotically reduce PCP by chemical reaction, but needed the involvement of microorganisms. The microbial community composition has been provided previously (Zhang and Katayama, 2012). The mineral medium consisted of (per liter) 1.0 g NH₄Cl, 0.05 g CaCl₂·2H₂O, 0.1 g MgCl₂·6H₂O, 0.4 g K₂HPO₄, 1 mL of trace element SL-10 solution (Widdel et al., 1983), 1 mL of Se/W solution (Widdel et al., 1983), and 15 mM MOPS buffer (pH 7.2).

The influence of the humins of different origins on the microbial PCP-to-phenol dechlorination activity was examined by an incubation experiment conducted in the same way as the culture maintenance. Humins of different origins were added at a concentration of 2.5 g L⁻¹ and autoclaved with the medium. After the incubation, PCP and its metabolites in the culture were analyzed using a

Table 1
Sampling sites and physicochemical characteristics of the soils and river sediment used in this study.

Soil/sediment samples	Sampling site	Soil Taxonomy ^a	Description	Texture	Major clay type ^b	C (%)	N (%)	H (%)
Kamajima	Kamajima, Yatomi City, Aichi Prefecture	Endoaquept	Paddy soil	Silt loam	Kaolinite	1.30	0.09	0.56
Yatomi	Yatomi City, Aichi Prefecture	Endoaquept	Paddy soil	Silt loam	Kaolinite	0.95	0.05	0.39
Nagano-P	Nagano City, Nagano Prefecture	Endoaquept	Paddy soil	Silt loam	Smectite	1.54	0.10	0.55
Nagano-U	Nagano City, Nagano Prefecture	Fluvaquept	Upland soil	Silt loam	Smectite	1.53	0.04	0.59
Ibaraki-P	Tsukuba City, Ibaraki Prefecture	Hapludand	Paddy soil	Light clay	Allophane	2.55	0.25	0.98
Ibaraki-U	Tsukuba City, Ibaraki Prefecture	Melanudand	Upland soil	Light clay	Allophane	2.13	0.15	1.18
Nagakute	Nagakute City, Aichi Prefecture	Haplustand	Upland soil	Sandy loam	Vermiculite	0.73	0.03	0.31
Arako	Arako river, Nagoya City, Aichi Prefecture	–	River sediment	Silt loam	–	1.68	0.13	0.36

^a United States Department of Agriculture (2014). Keys to soil taxonomy, 12th edition, 360 pp.

^b Based on the references Adachi and Kuwahara (1980), Saitou et al. (1999) and Kato (1962).

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