External Electron Mediating Function of Humin Extracted by Different Methods

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The electron mediating function of humin (HM, an insoluble humic substance) was first reported in 2012[1]. However, the redox active components and their stability were still a question. In this research, humins from Kamajima paddy soil (Aichi, Japan) were extracted by five different washing methods, which were: HM-M1 (used 2% HF and 0.1 N NaOH); HM-M2 (used acidic mixture of concentrated HCl/HF 1:9 v/v); HM-M3 (used MIBK and 0.1 N NaOH); HM-M4 (solid residue after DMSO + H_2SO_4 6% v/v wash); and HM-M5 (dark supernatant from DMSO + H_2SO_4 6% v/v wash). These humins mediated the external electron transfer for a pentacholorophenol dechlorinating anaerobic culture, except for HM-M5. Synchrotron radiation based X-ray absorption fine structure measurement of Fe1s confirmed that Fe was not a redox component. In C1s spectra obtained from the synchrotron radiation based X-ray photoelectron spectroscopy (XPS), binding peaks of C=C, C-C/C-H, C-O,C=O, O=C-O, O=COO were determined. Observation of flourinated carbon (CF_X) in HM-M1 and HM-M2 indicated great advancement of XPS compared to other conventional measurements. The carbonyl and carbon-carbon double bond groups in fourier transforms infrared spectroscopic spectra suggested quinone structure which was considered to be a potential redox center. This was then proved by organic radicals (at g = 2.00) in electron spin resonance spectra (no signals in HM-M5).

[1] Zhang and Katayama (2012) *Environ.Sci.Technol.*, **46**, 6575-6583.