



Formation of environmentally persistent free radicals as the mechanism for reduced catechol degradation on hematite-silica surface under UV irradiation



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ABSTRACT

Iron is rich in soils, and is recently reported to form stable complexes with organic free radicals, generating environmentally persistent free radicals (EPFRs). The observation may challenge the common viewpoint that iron is an effective catalyst to facilitate the degradation of various organic chemicals. But no study was specifically designed to investigate the possible inhibited degradation of organic chemicals because of the formation of EPFRs in dry environment. We observed that catechol degradation under UV irradiation was decreased over 20% in silica particles coated with 1% hematite in comparison to uncoated silica particles. Stabilized semiquinone or quinone and phenol radicals were involved in HMT-silica system. EPFR formation was thus the reason for the reduced catechol degradation on HMT-silica surface under UV irradiation at ambient temperature. EPFRs should be incorporated in the studies of organic contaminant geochemical behavior, and will be a new input in their environmental fate modeling.

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1. Introduction

Degradation is an important process controlling the geochemical behavior of organic contaminants, and thus vital for their risk assessment. However, the method of accurate modeling of degradation is lacking, as suggested by the huge variation of the degradation rate constants for a certain chemical (Cheng et al. 2012). A possible missing link could be the relationship between solid-particle properties and degradation rate constant. For example, it has been well documented that iron is an effective catalyst to facilitate the degradation of various organic contaminants (Pignatello et al. 2006). A parameter on how degradation rate constant is affected by iron content in the terrestrial system for multi-media modeling may improve predictive accuracy. Researchers generally reported that Fe (II) could degrade organic contaminants in aqueous phase with the aid of H₂O₂. This process is called Fenton reaction and demonstrated to be one of the most effective reactions to remove organic contaminants from wastewater (Pignatello et al. 2006). The hydroxyl radicals generated in Fenton reaction played the key role for organic contaminant

degradation, owing to their active chemical reactivity. Although Fe (III) is the major form in the environment (iron oxides), investigators suggested that Fe (III) may be transferred to Fe (II) through chemical reduction and/or biological activities (Li et al. 2008), especially in the presence of low molecular organic acids (Li et al. 2006) or humic substances (Niu et al. 2011), and thus Fenton-like or photo-Fenton reaction play important roles in natural attenuation of organic contaminants in the environment (Pereira et al. 2012). Therefore, modification of degradation rate constant as affected by iron could be easily incorporated in the studies of organic contaminant environmental fate.

However, it should be noted that the above mentioned studies mostly refer to chemical degradation of organic contaminants in aqueous phase or liquid–solid mixture. In dry upland soils, the situation could be completely different. Dellinger's group has systematically reported that transition metals, such as Fe (Vejerano et al. 2011), Cu (Lomnicki et al. 2008; Truong et al. 2010), and Ni (Vejerano et al. 2012), may form complexes with free radicals through electron transfer and subsequently, the free radicals are stabilized. These stabilized free radicals are called environmentally persistent free radicals (EPFRs). The authors generally discussed the formation mechanisms of EPFRs in combustion and high temperature systems, but the EPFRs may be well present in the ambient environments. For example, when

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transition metals are electron acceptors and UV-light is the driving force of electron transfer, the wide occurrence of organic contaminants in high altitude and intensively weathered soils may enable EPFR formation in nature. However, no study was specifically designed to examine the degradation of organic chemicals as affected by the formation of EPFRs. Dellinger's group reported EPFR detection in the environment, but without focusing the interpretation of EPFR generation mechanisms under environmental conditions, nor the potential impacts on organic contaminant behavior (de la Cruz et al. 2011). We propose that in the environment, the surface soil provides abundant transition metals, typically iron, and the UV light is the unique energy source for EPFR formation. Specific study is thus needed to investigate organic contaminant environmental behavior as affected by EPFR formation. This line of work requires firstly the understanding of EPFR generation in natural settings. Therefore, as a part of a systematic study, this current work hypothesizes that EPFRs are universally generated in the ambient environment under UV irradiation, and their property and stability can be comparable to those generated through combustion. EPFR formation may prevent organic contaminants from further degradation and thus increases organic contaminant residence time in the environment.

In order to address the above hypothesis, our experimental design was drastically different from previous work in the following two aspects. 1) Dellinger's group focused on the stabilization of free radicals on solid particles from the air and a gas-phase dosing experiment was used (Lomnicki et al. 2008). Their experimental design could well simulate the combustion system, but could not obtain the recovery of the original organic contaminants. We applied a liquid-phase dosing method, and the recovery of the organic contaminant used was carefully examined to evaluate degradation kinetics and efficiency. 2) In Dellinger's group, the combustion was conducted in a separate chamber and then the obtained samples were transferred to an electron paramagnetic resonance (EPR) spectrometer for free radical analysis. The *in situ* observation was not possible. We used a UV light accessory to an EPR spectrometer and thus *in situ* observation of free radical generation and dissipation was successfully enabled.

Catechol is ubiquitously presented in nature, fulfilling essential and well-defined biochemical roles (Sedo et al. 2013). This chemical was also detected as a common byproduct of organic compounds with aromatic rings (Jaramillo-Sierra et al. 2011). Thus, catechol was used as a model organic molecule. Hematite loaded on silica instead of natural red soil was selected as the model particle to avoid interferences from complex soil components such as humic substances and Mn oxides. The results from this study will shed light on EPFR generation and potential risk in natural settings such as soils. This work is a first step towards quantitative description of EPFR formation to be an important input parameter for multi-media modeling of organic contaminants.

2. Materials and methods

2.1. Preparation of solid particles

Iron was loaded on silica particles by the incipient wetness impregnation method (Vejerano et al. 2011). Briefly, 20 mL of 0.0625 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (iron nitrate nonahydrate, ACS, 98.0–101.0%, Alfa Aesar) solution was introduced into 10 g silica gel (100–200 mesh, Qingdao Haiyang Chemical Co., China) for incipient wetness, adsorption was equilibrated for 24 h at room temperature, and then freeze-dried before calcination at 450 °C in a muffle furnace with air for 5 h. The obtained particles contained 1% Fe_2O_3 (w/w). Bare silica particles were calcined using the same procedure, with the iron nitrate nonahydrate solution replaced by deionized water (Milli-Q water).

The silica particles and those coated with iron were characterized using X-ray diffraction (XRD). XRD patterns were recorded using an X-ray diffractometer (D/Max-2200, Rigaku, Japan), with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15406$ nm) operated at 40 kV and 40 mA.

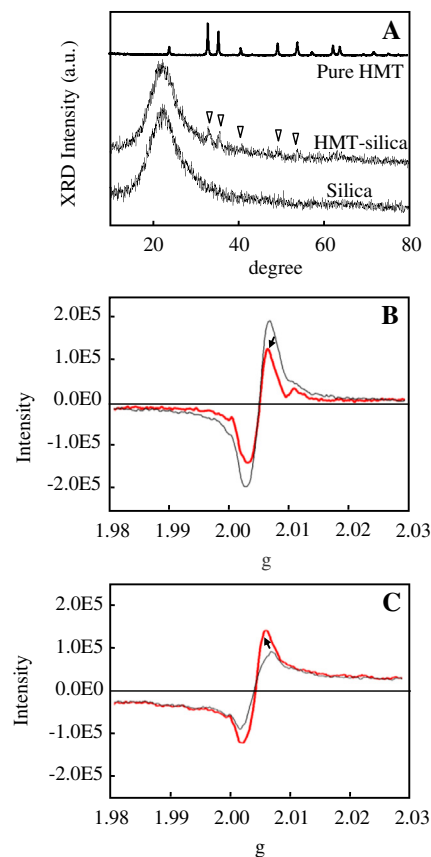


Fig. 1. XRD patterns of silica and HMT-silica particles (A). The symbols of ∇ indicate the typical XRD peaks of HMT. Pure HMT was generated using the same method for HMT-silica. The EPR signals of catechol loaded-silica (B) and HMT-silica particles (C) after 1 h (black thin lines) and 10 h (red bold lines) UV irradiation. The arrows \downarrow indicate the change of EPR signal from 1 h to 10 h. The particles with catechol concentration of 0.15 ± 0.02 mg/g are selectively presented. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Batch sorption experiments

Batch sorption experiments were conducted in 4 mL amber glass vials with Teflon-lined screw caps. The aqueous:solid ratio was 200:1 (w/w). Catechol (AR, 99.0%, Aladdin-reagent Co. Ltd., China) was dissolved in deionized water as stock solutions (50 mg/L). The stock solution was diluted with deionized water to a series of concentrations (0–27.5 mg/L). The same concentration sequence of catechol solution without solid particles was referred to as the initial concentration references. All the vials were kept in the dark and were shaken in an air-bath shaker (80 rpm) at 25 °C for 3 d, then centrifuged at 1000 g for 10 min, the supernatants were sampled for quantification of catechol. No detectable degradation of catechol was observed under our sorption experimental conditions.

Catechol was loaded on solid particles through liquid-phase dosing. Briefly, 1 mL of catechol solution (with different concentrations) was added to 300 mg particles in 8 mL amber glass vials with Teflon-lined screw caps. This liquid–solid mixture was equilibrated for 12 h before freeze-drying. The solid particles were mixed and catechol concentration in these particles was quantified using methanol extraction. According to our preliminary experiments, the two-successive extraction recovered more than 95% of catechol on solid particles. No difference was observed for the extraction efficiencies from silica and pure Fe_2O_3 particles. The degradation efficiency was calculated through the difference between catechol concentrations before and after UV irradiation of the particles.

2.3. UV irradiation and *in situ* EPR measurement

The solid particles (80 mg) were filled into quartz thin-wall EPR tubes (707-SQ-250M, Wilmad, USA) for EPR measurements on a Bruker X-band A300-6/1 EPR spectrometer at room temperature. The EPR spectrometer parameters used for measurements were: modulation frequency of 100 kHz, microwave frequency of 9.86 GHz, microwave power of 10 mW, modulation amplitude of 3 G, receiver gain of 3.17×10^3 , center field of 3520 G, sweep width of 400 G, resolution of 1024 points,

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