The effects of Fe-bearing smectite clays on ·OH formation and diethyl phthalate degradation with polyphenols and H_2O_2

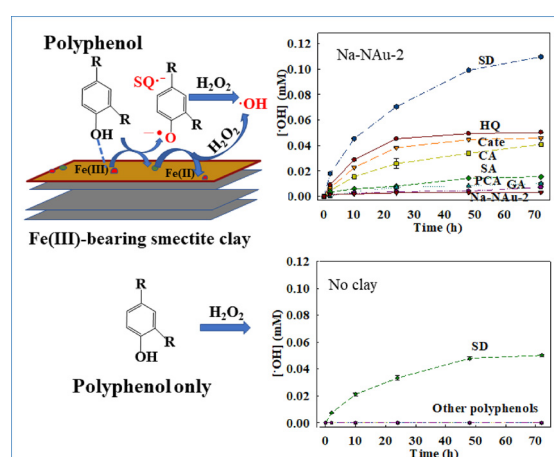Ning Chen[a,b], Guodong Fang[a], Guangxia Liu[a,b], Dongmei Zhou[a], Juan Gao[a,*], Cheng Gu[c,**]

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GRAPHICAL ABSTRACT

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The natural formation of hydroxyl radicals (·OH) is important for the attenuation of organic contaminants. In this study, seven model polyphenols were selected to react with four types of smectite clays with varied Fe contents in the presence of H_2O_2. Diethyl phthalate (DEP) was selected as a model organic contaminant due to its wide distribution in environment. The results show the appearance of Fe-bearing smectite clays can significantly promote ·OH formation with polyphenols and H_2O_2 under anoxic conditions; clay particle size, the content and location of lattice Fe in smectite clays greatly affect ·OH formation. Hydrogen bond between phenolic group and smectite surfaces, and cation assisted hydrogen bond between carboxylic group and clay surfaces are important types of complexation. Electrons can be transferred from coordinated polyphenols to structural Fe(III) atoms in tetrahedral layers or at broken edges to form structural Fe(II) and/or semiquinone radicals, both of which can induce H_2O_2 decomposition to ·OH. DEP can be degraded by ·OH attack, and the main products are proposed as phthalic acid, monomethyl phthalate, hydroxyl-diethyl phthalates. Our findings suggest that Fe(III)-bearing

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smectite clay can be reduced by polyphenol and produce ·OH in anoxic environments, which can induce organic contaminants transformation.

1. Introduction

Dissolved organic matter (DOM) is ubiquitous in waters, runoff and filtration from agricultural fields [1], which is generally composed of a heterogeneous mixture of many small or macro-organic compounds containing aromatic rings with active functional groups, such as hydroxyl, carboxyl, ketone, amine groups [2]. Polyphenolic moieties are widely presenting in DOM, which are active in shuttling electrons from bulk electron donors to the terminal acceptors, and participating in redox cycles of transition metals and organic compounds [3].

Polyphenols, model compounds of DOM, are mainly derived from the decomposition of terrestrial plant and animal residues [4]. They can complex with Fe^{3+} or other transition metals to form semiquinone radicals ($SQ\cdot^-$) and reduced transition metals [5–12], which can further decompose H_2O_2 to form hydroxyl radicals ($\cdot OH$, E_H^0: 2.8 V) [13]. The formed ·OH is of high activity to oxidize contaminants, such as alachlor, tetracycline and As(III) [6,14,15]. Polyphenols and H_2O_2 are co-existing in the subsurface environments [16–19].

Clay minerals are important components of soil, and they are widely distributed in subsurface soils. In the past few decades, lots of works have been devoted to apply the clay mineral-based materials for organic contaminants degradation and pollution control [20–22]. These modified clays (e.g. Fe or Al pillared clays) have higher ability in removing organic contaminants in soils and groundwater [23,24]. However, the reactivity of natural clay minerals (without modification) has rarely been referred, especially in the subsurface environments. At the same time, the interactions between clays and polyphenols have also not been thoroughly investigated [3].

Smectite clays belong to the group of 2:1 type phyllosilicates with high specific surface area (SSA) [25]. They can adsorb large amounts of hydrophobic and planar organic compounds, including polycyclic aromatic hydrocarbons [26], polychlorinated benzenes [27], phthalate esters [28] and indoles [29]. In clay structures, Si or Al in tetrahedral or octahedral layers can be isomorphous-substituted by Fe or Mn, which can act as electron acceptor or donor in redox reactions depending on their redox statuses [30,31]. Prior studies have reported that nitroaromatic compounds [32–34], chlorinated solvents [35] and heavy metals [36,37] can be efficiently removed or immobilized by Fe(II)-bearing smectite clays. At the same time, structural Fe(III) in smectite clays can be reduced to structural Fe(II) by *Shewanella oneidensis* MR-1 in extracellular respiration [38], in which polyphenols act as electron shuttles [38–40]. Polyphenols can form complexes with adsorbed Fe^{3+} on clay surfaces and reduce Fe^{3+} to Fe^{2+} under anoxic conditions [3,40–42], which can induce the decomposition of H_2O_2 to produce ·OH [14–16,43]. Recent published papers (Table A1) have also proven that polyphenols can interact with pyrite and birnessite, and the structure of polyphenols affect their activity [44,45]. Thus, it is reasonable to hypothesize that Fe-bearing minerals may be interacted with polyphenols and produce ·OH in the presence of H_2O_2.

The objectives of this study were to investigate: (i) the effects of Fe-bearing clays on ·OH formation and contaminant degradation in the presence of polyphenols and H_2O_2; (ii) the effects of lattice Fe content and reactive sites on ·OH formation; and (iii) the coordination interactions between Fe-bearing clays and polyphenols. Diethyl phthalate ester (DEP, Table A2) was selected as the model organic contaminant in this study, which is one of widely used plasticizers and frequently occurring in subsurface environments [28,46,47]. The study can help us understand the natural attenuation of organic contaminants in subsurface environments.

2. Materials and methods

2.1. Chemicals and materials

Detailed information of all the chemicals used in this study is included in Appendix A (Text A1). The physicochemical properties of four selected smectite clays are listed in Table 1, including two nontronites (NAu-1 and NAu-2) and two montmorillonites (SMF and FZ-10). Seven polyphenols with different functional groups (Table 2), including caffeic acid (CA), catechol (Cate), gentisuric acid (GA), hydroquinone (HQ), protocatechuic acid (PCA), syringic acid (SA) and syringaldehyde (SD), were selected as DOM model compounds [5,6,48].

2.2. Preparation of clay minerals and particle fractionation

Detailed information about the preparation of Na^+-saturated clay particles at sizes < 0.5 μm and 0.5–2 μm was provided in Appendix A (Text A2).

2.3. Reactor setup

To get rid of oxygen influence, all solutions were purged with 99.99% Ar for more than 1 h before transferred into an AW400SG anaerobic workstation (Electrotek, UK). Batch experiments were conducted under anoxic conditions in dark (25 °C). The total volume of the reaction system was 20 mL, and the background solution was 10 mM phosphate buffer at pH 7.0. The initial concentrations of polyphenol, benzoic acid (BA), H_2O_2 and smectite clay (< 0.5 μm) were 0.1 mM, 2.0 mM, 2.0 mM and 5.0 g L^{-1}, respectively. At predetermined time intervals (0, 2, 10, 24, 48, and 72 h), 0.9 mL aliquots were withdrawn and filtered through 0.22 μm syringe filters into 2 mL brown vials. In each brown vial, 0.1 mL methanol was pre-added to quench the reactions. Control experiments without polyphenol or clay particles were conducted in parallel under the same conditions.

Table 1
Properties of the clay minerals selected in this study.

Clay minerals[a]	A_s[b] $m^2 g^{-1}$	CEC[c] $cmol_c kg^{-1}$	Fe %
SMF $M_{0.68}^+Si_{8.00}Al_{0.55}Fe_{0.05}Mg_{0.5}O_{20}(OH)_4$	231 ± 40	64.7 ± 0.1	1.76
FZ-10 $M_{0.79}^+Si_{8.00}Al_{0.53}Fe_{0.21}Mg_{0.4}O_{20}(OH)_4$	295 ± 1	77.2 ± 0.2	4.91
NAu-1 $M_{1.0}^+(Si_{7.00}Al_{1.00})(Al_{0.58}Fe_{3.38}Mg_{0.5})O_{20}(OH)_4$	779 ± 22[63]	116 ± 7.0[63]	21.2[63]
NAu-2 $M_{0.72}^+(Si_{7.57}Al_{0.01}Fe_{0.42})(Al_{0.52}Fe_{3.32}Mg_{0.7})O_{20}(OH)_4$	703 ± 38[80]	69.7 ± 7.3[80]	19.2[63]

[a] In the unit formulas of the selected clays, M represents the interlayer cations, such as Na^+, Ca^{2+} or K^+ [79]; The structure Fe content of SMF and FZ-10 were examined with X-ray fluorescence (XRF) spectroscopy and calculated based on *the Data Handbook for Clay Minerals and Other Non-metallic Minerals* [80]; The structures of NAu-1 and NAu-2 were obtained from the research of Gorski et al. [63].
[b] The total specific surface areas of the clays were determined from the method of ethylene glycol monoethyl ether [80], The total surface area (A_s) of NAu-1 and NAu-2 were obtained from the research of Gorski et al. [63].
[c] The cation exchange capacity was determined from compulsive exchange with Ba^{2+}.