



# Oxidative coupling of acetaminophen mediated by $\text{Fe}^{3+}$ -saturated montmorillonite

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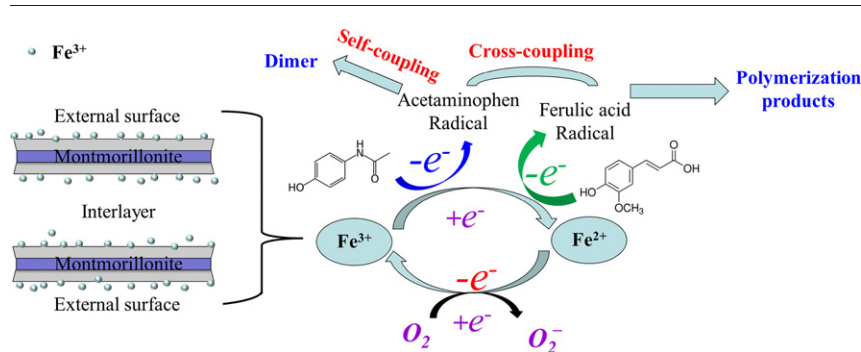
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## HIGHLIGHTS

- $\text{Fe}^{3+}$ -montmorillonite can efficiently catalyze the polymerization of acetaminophen.
- Reduction of adsorbed  $\text{Fe}^{3+}$  coupled with acetaminophen oxidation was main mechanism.
- Ferulic acid suppressed acetaminophen transformation by  $\text{Fe}^{3+}$ -montmorillonite.
- Cross-coupling of ferulic acid and acetaminophen was observed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The wide usage of acetaminophen as human medicine has resulted in its ubiquitous occurrence in various environmental compartments. However, the information for the transformation of acetaminophen in soil is still limited. In this study, oxidative coupling of acetaminophen in bulk solution mediated by  $\text{Fe}^{3+}$ -saturated montmorillonite was observed under different environmental conditions. In the absence of natural phenolic acids, acetaminophen could be fully eliminated from the solution within 72 h at pH 3.5, acetaminophen dimer was identified as the major reaction product. Reduction of montmorillonite associated  $\text{Fe}^{3+}$  coupled with the oxidation of acetaminophen was considered as the main mechanism for acetaminophen transformation on  $\text{Fe}^{3+}$ -saturated montmorillonite. The clay associated  $\text{Fe}^{3+}$  showed higher reactivity than  $\text{Fe}^{3+}$  in solution due to the strong complexation between surface  $\text{Fe}^{3+}$  and acetaminophen. The cross-coupling reaction between acetaminophen and phenolic acids was also observed when phenolic acids were present in the system. While with the increase of phenolic acid concentration, the competition for the reactive sites between acetaminophen and phenolic acids significantly suppressed acetaminophen removal. These results demonstrated the importance of transition metal saturated clay minerals for the abiotic transformation of anthropogenic micropollutants.

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## 1. Introduction

Pharmaceuticals have been widely used not only for human but also for animals. However, due to the abuse of these chemicals, a large amount of pharmaceuticals have been released into the environment

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and caused severe adverse ecological effects (Carlsson et al., 2006). Acetaminophen is an antipyretic and analgesic ingredient used in many over-the-counter and prescription drugs with the global production of >100,000 tons per year (Anderson, 2008; Joncour et al., 2014; Zhao and Pickering, 2011). Moreover, acetaminophen cannot be completely metabolized by human body and has high water solubility (Amidon et al., 1995), which renders a considerable portion of acetaminophen entering into municipal wastewater treatment plant, and finally transporting to various environmental compartments (Kim et al., 2007). As a result, acetaminophen has been frequently detected in surface water, groundwater and soils with the concentrations ranging from ppt to ppm levels (Bedner and MacCrehan, 2006). Some prior studies demonstrated that the environmental residues of acetaminophen might interfere with normal embryonic development, survival and endocrine systems of aquatic organisms (Kim et al., 2007). Once released into the soil, acetaminophen would go through various abiotic/biotic processes which could significantly affect its bioavailability and toxicity (La Farre et al., 2008; Wu et al., 2012).

Clay minerals are important soil components with the unique sequestering and catalytic properties for many organic contaminants (Gao and Pedersen, 2005; Kowalska et al., 1994; Wilson, 1999). Montmorillonite, a 2:1 layered aluminosilicate mineral, is one of the most common clay minerals, which is widely distributed in soils, subsoils, and sediments with strong swelling capacity, large surface area and high cation exchange capacity (CEC) (Beermann and Brockamp, 2005). Prior researches have indicated that when the interlayer cations of montmorillonite are exchanged with some transition metal ions (e.g.,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ ), it can catalyze the degradation or polymerization of aromatic compounds (Gu et al., 2008; Jia et al., 2014; Joseph-Ezra et al., 2014). The mechanism for the reaction catalyzed by transition metal saturated montmorillonite involves a single electron transfer from aromatic compounds to the interlayer cations, resulting in the formation of organic radicals that are highly susceptible to undergo further polymerization or degradation reaction (Boyd and Mortland, 1986). However, only a few studies have investigated the interaction between pharmaceuticals and  $\text{Fe}^{3+}$ -montmorillonite. Liyanapatirana et al. (2009) observed that under relatively dehydrated condition (40% relative humidity),  $\text{Fe}^{3+}$ -montmorillonite can oxidize triclosan to produce several polymers with different molecule weights. So far, most of the prior studies on the transformation or polymerization reactions catalyzed by  $\text{Fe}^{3+}$ -montmorillonite were conducted under relatively low moisture conditions, it is still not clear whether the similar reaction can also occur in aqueous solution with pharmaceuticals. Furthermore, as the ubiquitous substance in the environment, phenolic acids are involved in various oxidative coupling reactions (Haider and Martin, 1967; Weber and Huang, 2003). The polymerization of phenolic compounds to form humic substances catalyzed by clay minerals has been extensively studied (Shindo and Huang, 1982, 1984). Therefore, the presence of phenolic acids might substantially affect the fate of acetaminophen in soil. However, to the best of our knowledge, there were still few studies conducted to investigate the influence of phenolic acids on the transformation of pharmaceuticals on clay mineral surface.

In this study,  $\text{Fe}^{3+}$ -saturated montmorillonite was prepared and mixed with acetaminophen in aqueous solution, the transformation kinetic, degradation mechanism and reaction pathway of acetaminophen in the presence of two representative natural phenolic acids were systematically investigated. Our results indicated that the high catalytic activity of  $\text{Fe}^{3+}$ -montmorillonite for oxidative coupling of acetaminophen was attributed to the associated  $\text{Fe}^{3+}$ . The cross-coupling reaction between acetaminophen and ubiquitous phenolic acids leads to the formation of oligomers, and the competition for the reactive sites between acetaminophen and phenolic acids was also observed. The results from current study demonstrated the importance of clay minerals on the abiotic transformation of anthropogenic micropollutants.

## 2. Materials and method

### 2.1. Chemicals

Acetaminophen, ferulic acid (FA) and *p*-coumaric acid (PCA) were purchased from Sigma-Aldrich with purity > 98%. Selected physicochemical properties of these compounds are provided in the Supporting Information (Table S1). The stock solution of acetaminophen (1.0 mM) and phenolic acids (2.0 mM) were prepared in Milli-Q water and stored at 4 °C for further use. The montmorillonite used to prepare  $\text{Fe}^{3+}$ -saturated clay mineral was obtained from Feng Hong Inc. (Zhejiang Province, China), and the CEC of this montmorillonite was 770 mmol  $\text{kg}^{-1}$  measured by the ammonium acetate method at pH 7.0 (Sparks, 1996). The major chemical compositions of this montmorillonite were analyzed by X-ray fluorescence spectrometer (ARL-9800, Switzerland) and listed in supplementary Table S2.

### 2.2. Preparation of $\text{Fe}^{3+}$ or $\text{Na}^{+}$ -saturated montmorillonite

The  $\text{Fe}^{3+}$  or  $\text{Na}^{+}$ -saturated montmorillonite was prepared following the methods of Arroyo et al. (2005). Briefly, the montmorillonite was initially suspended in Milli-Q water, and the pH of the suspension was adjusted to 6.8 with 0.5 M sodium acetate buffer (pH 5.0) to remove carbonate impurities. Clay-sized particles (<2  $\mu\text{m}$ ) were collected by centrifugation for 15 min at 3295g, and then resuspended in 0.1 M  $\text{FeCl}_3$  or 0.5 M NaCl solution for 8 h to exchange interlayer cations. This step was repeated 6 times to fully saturate the exchangeable sites of montmorillonite by  $\text{Fe}^{3+}$  or  $\text{Na}^{+}$ . The newly obtained clay mineral was repeatedly washed using Milli-Q water until  $\text{Cl}^{-}$  was fully removed as indicated by the negative test with  $\text{AgNO}_3$ , then freeze-dried and grounded to pass a 100-mesh nylon sieve, finally stored in the desiccator for experimental use. The iron contents in the montmorillonite before and after  $\text{Fe}^{3+}$  saturation were measured using an atomic absorption spectrophotometer after digestion with the mixture of HF,  $\text{HNO}_3$  and  $\text{HClO}_4$  at 300 °C for 1.5 h. The measured iron contents in the original montmorillonite and  $\text{Fe}^{3+}$ -montmorillonite were 0.76% and 3.63%, which represented the structural iron and the total iron including structural iron and exchangeable iron, respectively. Hence, the exchangeable iron content can be calculated as ~2.87%. To compare the reactivity of  $\text{Fe}^{3+}$  associated with different clay mineral, another common 2:1 type of non-swelling clay mineral (illite) was also prepared by the same procedure. Different from  $\text{Fe}^{3+}$ -montmorillonite, due to its higher surface charge density than montmorillonite, most of the structural charges originated from isomorphic substitution in illite are compensated by fixed  $\text{K}^{+}$ , which cannot be replaced by the added  $\text{Fe}^{3+}$ , so exchanged  $\text{Fe}^{3+}$  ion on  $\text{Fe}^{3+}$ -illite are mainly located on external surfaces.

### 2.3. Degradation of acetaminophen catalyzed by $\text{Fe}^{3+}$ -montmorillonite

To initiate the degradation reaction, 100  $\mu\text{L}$  of 1.0 mM acetaminophen stock solution was mixed with 1.9 mL clay suspension containing 20 mg montmorillonite in a 8 mL-glass vial with the initial acetaminophen concentration of 50  $\mu\text{M}$ . The pH of the clay suspension was pre-adjusted to 3.5, 5.0, 7.0, and 9.0, respectively using 0.1 M NaOH and HCl. The preliminary experiments showed that the pH variation during the reaction was within  $\pm 0.2$  (Fig. S1), and the greatest acetaminophen transformation was observed at pH 3.5, so all the remaining experiments were conducted at pH 3.5. To investigate the effect of natural phenolic acids on the transformation of acetaminophen, FA or PCA was added into the reaction system to obtain FA concentrations of 5, 50, 100, 500 and 1000  $\mu\text{M}$  and PCA concentration of 100  $\mu\text{M}$ , respectively. Acetaminophen transformations mediated by  $\text{Fe}^{3+}$ -montmorillonite (10.0 g  $\text{L}^{-1}$ ),  $\text{Fe}^{3+}$ -illite (33.3 g  $\text{L}^{-1}$ ), and  $\text{FeCl}_3$  (0.42 g  $\text{L}^{-1}$ ) were also conducted to compare the oxidation efficiency of different iron species, the  $\text{Fe}^{3+}$  amount in three systems was kept the same of 2.57 mM. All the

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