

Adsorption And Oxidative Transformation Of Phenolic Acids By Fe(III)-Montmorillonite

TAMARA POLUBESOVA, SHAY ELDAD,
AND BENNY CHEFETZ*

Department of Soil and Water Sciences, The Robert H. Smith
Faculty of Agriculture, Food and Environment; The Hebrew
University of Jerusalem, P.O. Box 12, Rehovot 76100, Israel

Received March 9, 2010. Revised manuscript received April
26, 2010. Accepted April 27, 2010.

Phenolic acids participate in various soil processes and are of great concern due to their allelopathic activity. The interactions of phenolic acids (ferulic, *p*-coumaric, syringic, and vanillic) with montmorillonite enriched with Fe(III) was investigated. Adsorption of the phenolic acids on Fe(III)-montmorillonite was accompanied by their oxidative transformation and formation of Fe(II). Oxidative transformation of phenolic acids was affected by their molecular structure. The order of maximal transformation at the initial acid concentration of 20 mg/L on the surface of Fe(III)-montmorillonite was ferulic (94%), syringic (60%), *p*-coumaric (35%), and vanillic (25%). Benzoic acid which was used as a reference aromatic compound exhibited only 5% transformation. Removal of the phenolic acids from solution increased with decreasing pH. LC-MS analysis demonstrated the presence of dimers, trimers, and tetramers of ferulic acid on the surface of Fe(III)-montmorillonite. Oxidation and transformation of ferulic acid were more intense on the surface of Fe(III)-montmorillonite as compared to Fe(III) in solution due to stronger complexation on the clay surface. The results of the current study demonstrate the importance of Fe(III)-clay surfaces for the abiotic formation of humic materials and for the transformation of aromatic (phenolic) pollutants.

Introduction

Phenolic acids participate in soil processes, including mobilization of necessary microelements (such as Fe and Mn) for plants and formation of humic components (1–6). Moreover, phenolic acids are of concern due to their role as allelopathic agents (7, 8). In soils, the fate and potential bioavailability of the phenolic acids are mainly controlled by their sorption–desorption processes and by oxidation which is usually coupled with reduction of soil Fe and Mn oxides (1, 7, 9).

The role of phenolic acids in the formation of humic materials may be enhanced in the presence of clays and Fe- or Mn-oxides due to oxidative coupling. This leads to incorporation of naturally occurring humic acid precursors and phenolic compounds via covalent linkage (10). Wang et al. (11) described the formation of humic substances from phenolic acids and alcohols, followed by their reactions with clay samples. It was suggested that the silicate layer catalyzed the process, and the presence of iron promoted the darkening of the color of the humic materials.

Interactions of adsorbed organic molecules with Fe(III) may result in electron transfer from the organic molecules to the metal cations, and the formation of radical cations and reduction of metal ions to lower valence are therefore observed simultaneously (13). The initial step in this process involves an electron transfer from the adsorbed organic molecule to the cation, which may be followed by the oxidative transformations of the molecules. The successive dimerization, oligomerization or even polymerization proceeds through the formed radical cation (13, 14). Fe(III)-saturated smectite induces formation of radical cations from a variety of aromatic compounds through electron transfer from the aromatic molecule to Fe(III), followed by transformation and polymerization of the formed aromatic products (15–17). Environmental importance of Fe(III)-smectite was demonstrated by adsorptive transformation of the widely applied contaminant triclosan on the surface of Fe(III)-montmorillonite (18), and clay-catalyzed formation of octachlorodibenzo-*p*-dioxin from pentachlorophenol (17).

In this study, we evaluated the interactions of phenolic acids (ferulic, *p*-coumaric, syringic and vanillic) with montmorillonite enriched with Fe(III). Benzoic acid was used as a reference aromatic acid. Montmorillonite is a clay mineral that is common in soils of arid and semiarid regions and known to contribute significantly to the reactions on the surfaces of soil particles (12). Iron(III) is ubiquitous in soils and may play an important role in the oxidation and polymerization of aromatic compounds (13). We elucidated a two-step process: adsorption followed by transformation as affected by the molecular structure of the sorbate and the chemistry of the solution. In addition, the transformation of ferulic acid was compared in Fe(III)-clay suspension versus Fe(III) in solution. We aimed to evaluate the efficiency of Fe(III)-montmorillonite as an oxidative adsorbent for organic molecules containing electron-rich moieties.

Experimental Section

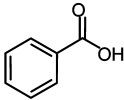
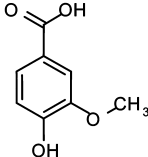
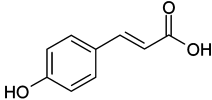
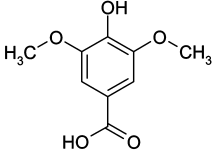
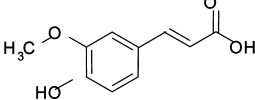
Phenolic acids and benzoic acid were purchased from Sigma (Rehovot, Israel; >98% purity) and used without further purification. Structures and selected properties of the investigated compounds are presented in Table 1.

Preparation of Clay Sorbents. Wyoming Na-montmorillonite SWy-1 was obtained from the Source Clays Repository (Clay Minerals Society). The cation exchange capacity of the clay was 0.8 mmol_c/g (19). The <2 μm fraction of the montmorillonite was collected and used for experiments. Homoionic Fe(III)-montmorillonite was prepared by sequential washing of the crude montmorillonite with concentrated FeCl₃ solution (20). Excessive salts were removed by dialyzing the Fe(III)-montmorillonite samples against distilled water until the supernatant solution was free of chlorides. Fe(III)-clay samples were freeze-dried and stored in a desiccator.

Batch Sorption/Transformation Experiments. The isotherms of removal (adsorption and transformation) of the tested organic acids by Fe(III)-montmorillonite were measured in a concentration range of 1–1000 mg/L of the analytes using batch procedure. Sodium azide (100 mg/L) was added to all solutions to inhibit microbial activity (21). The final concentration of the clay suspensions was 5 g/L. Organic acid-clay suspensions and blank solutions (acids without clay) were agitated at 25 °C for 72 h (based on preliminary kinetic measurements). The effect of pH on removal of acids from solutions was studied by measuring isotherms at pH 3, 4.5, and 5.5. The effect of ionic strength on removal of

* Corresponding author phone: + 972 (8) 948-9384; fax + 972 (8) 947-5181; e-mail: chefetz@agri.huji.ac.il.

TABLE 1. Molecular Structure and Selected Properties of Aromatic Acids Investigated in This Study

Aromatic acid	Molecular formula	Molecular structure	Molecular Weight	Aqueous solubility (mg/L)	p <i>K</i> _a
Benzoic	C ₇ H ₆ O ₂		122.1	3400	4.19
Vanillic	C ₈ H ₈ O ₄		168.2	1500	4.51
<i>p</i> -Coumaric	C ₉ H ₈ O ₃		164.2	740	4.39
Syringic	C ₁₀ H ₁₀ O ₅		198.2	5780	4.34
Ferulic	C ₁₀ H ₁₀ O ₄		194.2	5970	4.58

acids was measured by adding KCl. For benzoic acid four sequential desorption steps were performed after adsorption. For that, half of the supernatant volume was removed using a glass pipet. The removed supernatant was replaced with fresh sodium azide solution (100 mg/L) and the tubes were agitated for 96 h.

At the end of the adsorption experiments and each of the desorption steps (only for benzoic acid), samples were centrifuged at 15 000g for 30 min and supernatants were filtered through a 0.2 μ m filter. The analyte concentration was measured by HPLC (D7000, Merck-Hitachi, Germany). A C18 RP-amide column (Supelco, 25 cm \times 4 mm, 5 μ m) was used to determine ferulic, *p*-coumaric, syringic and vanillic acid, and a RP-18 (LiChrospher) was used for benzoic acid. An isocratic mobile phase contained double-distilled water acidified with 0.1% formic acid and acetonitrile (ACN) or methanol (MeOH). The following water:ACN ratios were used: 40:60 for benzoic acid; 60:40 for ferulic acid and syringic acid; and 30:70 for *p*-coumaric acid. For vanillic acid a 35:65 water:MeOH ratio was used. Analytes were detected at the following wavelengths: benzoic acid, 228 nm; ferulic acid, 310 nm; *p*-coumaric acid, 315 nm; syringic acid, 280 nm, and vanillic acid, 258 nm.

Concentration of Fe(II) in the supernatant was measured using ferrozine (22). Briefly, iron-clay suspensions were mixed using Vortex for 30 s. Then 0.5 mL of suspension was collected and added to 1 mL of ferrozine solution (100 mM), and the volume of the mixture was adjusted to 15 mL. The suspensions were agitated for 2 h and filtered through a 0.45 μ m

filter. Concentration of ferrozine-complexed Fe(II) was measured by 8452A diode array spectrophotometer (Hewlett-Packard Co., Palo Alto, CA) at 562 nm. Concentration of the total iron (Fe(II) and Fe(III)) in solution was also measured by ICP-AES (Arcos Spectro Ltd., Germany).

For organic acids at initial concentrations of 20 and 200 mg/L, the transformed products were also determined. The concentration of dissolved transformed product was calculated as the difference between organic C content in the initial concentration of added acids and the C content in nontransformed acid in equilibrium solution. Carbon content was determined by total organic carbon (TOC) analyzer (Shimadzu Corporation, Kyoto, Japan). The amounts of adsorbed nontransformed acids were measured by HPLC (see above) after extraction of the Fe(III)-clay–acid complex with MeOH containing 0.1 M NaOH. The transformation process was almost simultaneous with adsorption for all phenolic acids, however the transformation of benzoic acid was insignificant. Hence we used benzoic acid to estimate the MeOH extraction efficiency of adsorbed nontransformed acids from Fe(III)-clay. The efficiency of the extraction of benzoic acid from Fe(III)-montmorillonite was 95 and 99% for initial concentration of 20 and 200 mg/L, respectively. The amount of adsorbed transformed product was calculated as the difference between C content in initial acid solution, and that in the supernatant in MeOH extract. All experiments were performed in triplicate.

Oligomerization of the products of ferulic acid transformation in the presence of Fe(III)-clay was assessed by LC-

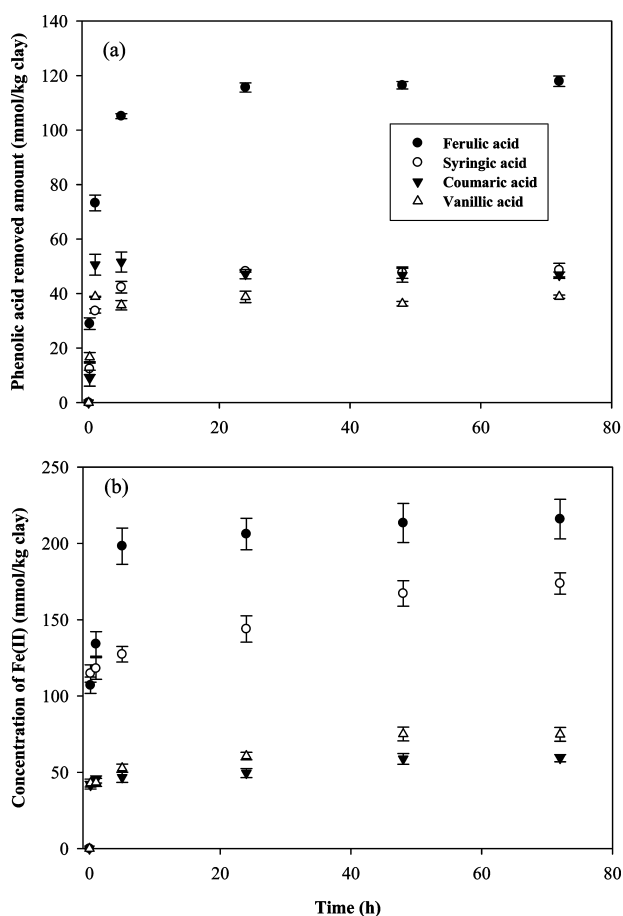


FIGURE 1. Interactions of aromatic acids (200 mg/L) with Fe(III)-montmorillonite (5 g/L) at pH 4.5. Removal of aromatic acids from solution (a) and formation of Fe(II) (b).

MS analysis, which was performed with an Accela High Speed LC system coupled with the LTQ Orbitrap Discovery hybrid FT mass spectrometer (Thermo Fisher Scientific Inc., Germany). HPLC separation was carried out using Agilent Zorbax Eclipse XDB-C8 column (10 cm \times 2.1 mm, 1.8 μ m). The gradient mode elution was performed with a mobile phase containing double-distilled water acidified with 0.05% AcOH (solvent A) and ACN:water at 95:5 (solvent B). The composition of the mobile phase was changed at a constant rate from solvent A:solvent B 90:10 to solvent B 100% over 15 min.

To compare oxidative efficiency of Fe(III)-montmorillonite with Fe(III) in solution, the kinetics of interactions of ferulic

acid with Fe(III)-montmorillonite and with Fe(III) in solution were studied. Solutions of 20 mg/L and 200 mg/L ferulic acid were mixed with Fe(III)-montmorillonite (as above) or with 4 mmol/L solution of FeCl₃. The concentration of FeCl₃ (4 mmol/L or 4 meq/L) was corresponded to the amount of Fe(III), which contained 5 g of Fe(III)-montmorillonite saturated by Fe(III) up to the CEC (0.8 mmol/g), and hypothetically can be transferred from the clay surface to the 1 L of solution. The pH of the FeCl₃-ferulic acid system was adjusted to 4.5, similar to that of the Fe(III)-montmorillonite-ferulic acid suspension. Fe(III)-montmorillonite-ferulic acid suspensions and FeCl₃-ferulic acid solutions were agitated at 25 $^{\circ}$ C for 72 h. Then the concentrations of acids and Fe(II) were measured at the time intervals. At the end of the experiment, 0.1 M NaOH was added to the FeCl₃-ferulic acid system to precipitate the Fe(III)-ferulic acid complex. Then, both Fe(III)-montmorillonite- and precipitated Fe(III)-ferulic acid complexes were centrifuged. The supernatants of both systems were filtered (0.45 μ m) and analyzed for ferulic acid, Fe(II) and dissolved organic carbon. The amounts of adsorbed nontransformed acids were measured in MeOH extracts of Fe(III)-montmorillonite- and Fe(III)-precipitate-ferulic acid complexes, and the amount of adsorbed transformed product was calculated as described above. The recovery of benzoic acid by MeOH from Fe(III)-precipitates at both concentrations was 100%. The oligomerization of the products of ferulic acid transformation on Fe(III)-montmorillonite and Fe(III)-precipitate was determined by LC-MS as described above.

Results and Discussion

Removal and Oxidative Transformation. Removal of phenolic acids from solution is presented in Figure 1a. Ferulic acid exhibited the highest removal. Interactions of phenolic acids with Fe(III)-montmorillonite can involve multiple adsorption mechanisms such as (i) inner- and outer-sphere complexation of carboxyl and phenolic groups with the surface of Fe(III)-montmorillonite; (ii) hydrogen bonding; (iii) noncovalent Fe(III)- π interactions, and (iv) interactions of the surface hydroxyl hydrogen with the aromatic π -donor groups (5, 13, 23, 24). Removal of organic acids was coupled with reduction of Fe(III) to Fe(II) (Figure 1b), due to electron transfer resulting from oxidation of the phenolic acids on the surface of the Fe(III)-montmorillonite. The highest concentration of Fe(II) was recorded for the Fe(III)-montmorillonite-ferulic acid system, followed by the Fe(III)-montmorillonite-syringic acid system. The concentration of Fe(II) in solution measured by ferrozine method coincided with the concentration of iron in solution measured by ICP-AES, that is, no Fe(III) was detected in the solution. This indicates that Fe(III) was not dissolved in the reaction.

TABLE 2. Distribution Coefficients (Removal, K_r ; Adsorption, K_d ; Transformation, K_t) and Percent of Transformed Aromatic Acids on Fe(III)-Montmorillonite

	K_r (L/kg)	K_d (L/kg)	K_t (L/kg)	transformed acid (%)
initial concentration 20 mg/L				
ferulic acid	4891 \pm 244	32 \pm 2.3	4859 \pm 340	94 \pm 4
syringic acid	1834 \pm 147	60 \pm 4.4	1774 \pm 122	60 \pm 5
<i>p</i> -coumaric acid	182 \pm 19	30 \pm 4.2	152 \pm 15.3	35 \pm 3
vanillic acid	155 \pm 12	29 \pm 2.7	126 \pm 11.8	25 \pm 2
benzoic acid	75 \pm 5.14	73 \pm 6.58	2 \pm 0.19	5 \pm 0.5
initial concentration 200 mg/L				
	K_r (L/kg)	K_d (L/kg)	K_t (L/kg)	transformed acid (%)
ferulic acid	357 \pm 29	25 \pm 2.7	332 \pm 38	62 \pm 4
syringic acid	113 \pm 10.8	39 \pm 3.2	74 \pm 6.5	31 \pm 3
<i>p</i> -coumaric acid	88 \pm 6.1	66 \pm 4.8	22 \pm 2.8	15 \pm 2
vanillic acid	39 \pm 3.2	38 \pm 2.9	1 \pm 0.3	11 \pm 2
benzoic acid	35 \pm 2.83	35 \pm 1.94	0 \pm 0.89	1 \pm 0.5

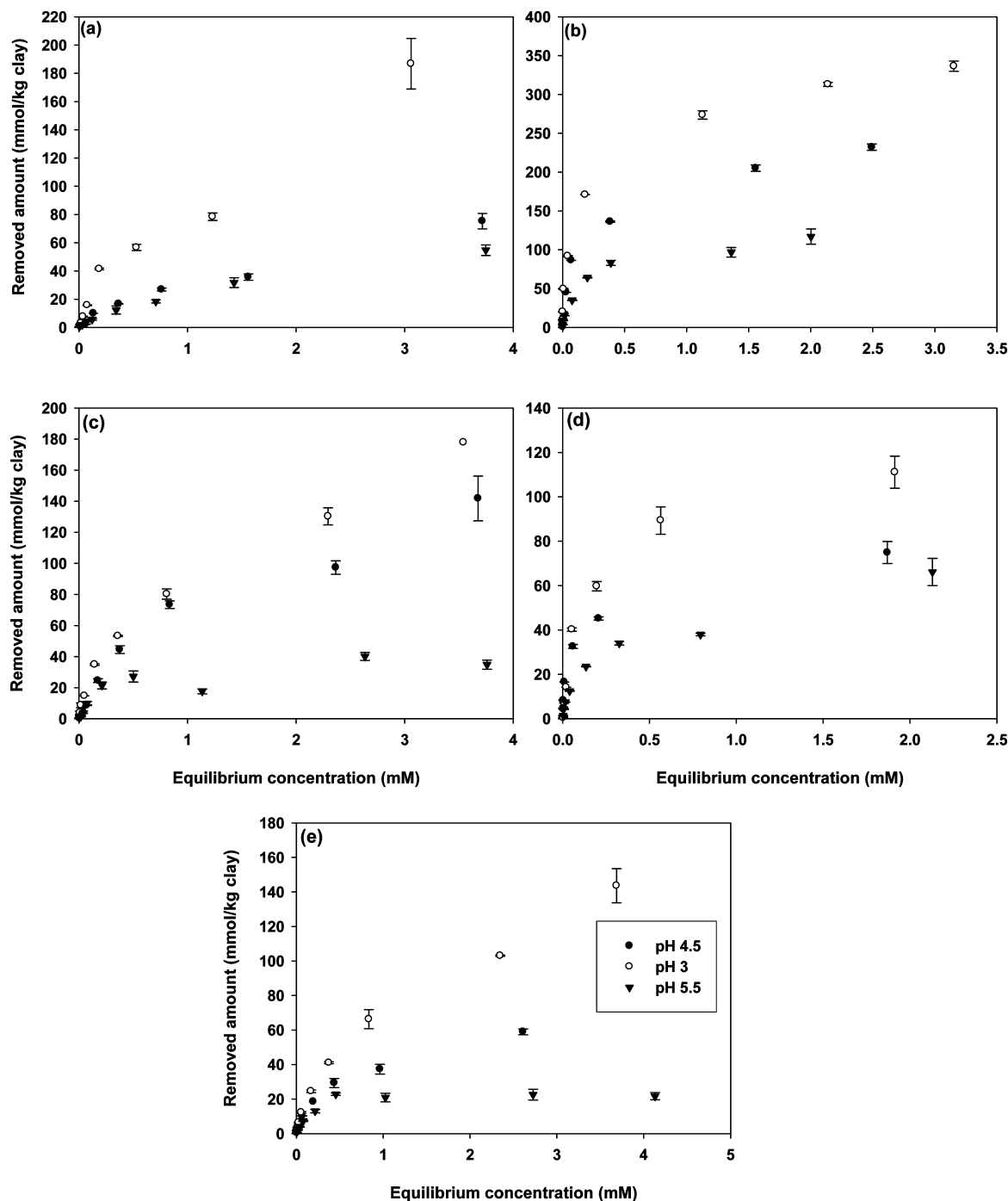


FIGURE 2. Effect of pH on the removal of aromatic acids from solution by Fe(III)-montmorillonite (a, benzoic acid; b, ferulic acid; c, *p*-coumaric acid; d, syringic acid; e, vanillic acid).

Adsorption of phenolic acids by Fe(III)-montmorillonite was followed by oxidative transformation. Distribution coefficients for these processes for initial concentrations of 20 and 200 mg/L of the studied acids at pH 4.5 are presented in Table 2. The removal coefficient (K_r) values (i.e., the overall process, adsorption + transformation) were evaluated using the concentration of acids in supernatants measured by HPLC and calculated removed amounts (Figure 2). The adsorption coefficient (K_d) values were calculated using adsorbed amounts of acids, which were determined by MeOH extraction of Fe(III)-clay-acid complexes after the systems attained apparent equilibrium. The transformation coefficient (K_t) values were calculated as a difference between K_r and K_d .

In most cases, both K_r and K_d decreased with an increase in acid concentration. This suggests that removal and

adsorption are governed by surface reactions with the limited number of reaction sites. The order of the acids affinity to the surface (K_r), which corresponded to the ability of their transformation (K_t and fraction of transformed acids) was ferulic > syringic > *p*-coumaric > vanillic > benzoic. Though K_d values of ferulic and syringic acids decreased with the increasing K_t for both studied concentrations, it is clear that higher adsorption resulted in enhanced transformation, which is generally expressed by K_r . Increased concentration of phenolic acids resulted in a decrease in their transformed fraction (Table 2). The oligomerized products in clay surface can probably prevent contact of additional molecules with the surface iron, thus reducing the fraction of transformed molecules. Benzoic acid at both concentrations and vanillic acid at the high concentration exhibited only limited

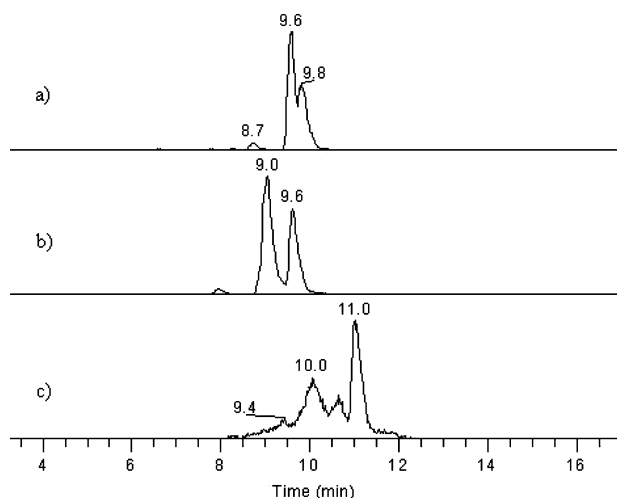


FIGURE 3. LC-MS single-ion chromatograms: (a) dimers ($C_{20}O_8H_{18}$, 386 Da) (b) trimers ($C_{29}O_{10}H_{26}$, 534 Da) and (c) tetramers ($C_{38}O_{12}H_{34}$, 682 Da) of ferulic acid detected in methanol extracts of Fe(III)-montmorillonite-ferulic acid complexes. The numbers above peaks designate retention times.

transformation: their K_f values were nearly equal in magnitude to the corresponding K_d (Table 2).

Effect of Molecular Structure. The molecular structure of organic acids, in particular type and position of functional groups and number of conjugated double bonds, can significantly affect their transformation and determine the stability of intermediate byproduct of the oxidation process (25). Ferulic acid contains methoxy and OH functional groups (Table 1), which are considered to be the activating groups, and a carboxylic functional group that is considered to be a deactivating group (26). The carboxylic functional group of ferulic acid is bound to the aromatic ring through the unsaturated hydrocarbon chain, which decreases its deactivating effect, thus enhances the activating effect of the methoxy and OH groups. Furthermore, ferulic acid has conjugated double bonds. The combination of these factors resulted in intense oxidation and transformation of ferulic acid on the surface of Fe(III)-montmorillonite. Syringic acid has two activating methoxy groups and one activating OH group; however, the carboxylic group is bound directly to the aromatic ring, which enhances its deactivating effect. The molecular structure of vanillic acid also maintained its higher stability to oxidation because it has one activating methoxy and one OH group, and a carboxylic group bound directly to the ring. *p*-coumaric acid structure is similar to that of ferulic acid (Table 1), but it does not have a methoxy activating group, which probably resulted in its lesser transformation as compared to ferulic acid (Table 2). In contrast to all other acids, benzoic acid does not have any activating group, and the deactivating carboxylic group is bound directly to the aromatic ring. Thus, transformation of benzoic acid was significantly lower (only 1–5%) than that of the all other phenolic acids.

Oxidation of aromatic molecules by Fe(III)-montmorillonite results in the formation of aromatic radical cations and reduction of Fe(III) to Fe(II) according to the following suggested reaction (27): $Ar + M^{n+} = [Ar\cdot]^+ + M^{(n-1)+}$, where Ar is aromatic molecule, M^{n+} metal ion, and $[Ar\cdot]^+$ is aromatic radical cation.

Fe(III) can combine with one of the π -electrons of the unsaturated side chain of ferulic acid and produce free radicals, which may subsequently self-interact to form dimers, trimers, or even tetramers (28). Phenoxy radicals, which can also be formed, are highly resonance-stabilized because unpaired electrons can be delocalized across the

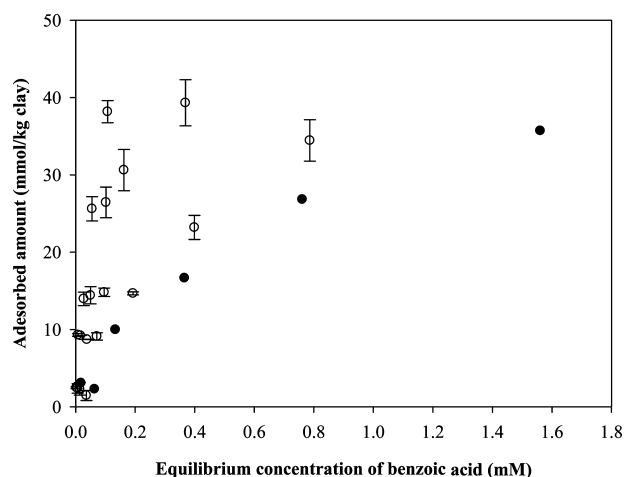


FIGURE 4. Adsorption-desorption interactions of benzoic acid with Fe(III)-montmorillonite (adsorption, filled circles; desorption, open circles; Fe(III)-clay, 5 g/L; contact time for each desorption step 96 h).

entire molecule. Due to this stabilization, phenoxy radicals are unable to initiate and propagate a radical chain reaction: they collide and condense with another radical to yield dimers (25).

In our study, dark color was formed on the Fe(III)-montmorillonite surface after a few days of reaction of ferulic acid, which indicates oxidative oligomerization of ferulic acid on the Fe(III)-clay resulting in the darkening of the clay surface. Darkening of phenolic compounds due to oxidative polymerization in the presence of iron oxide has also been reported by Wang et al. (11) and Shindo and Huang (29). LC-MS analysis of the MeOH extract of Fe(III)-montmorillonite-ferulic acid complexes demonstrated the presence of dimers with molecular formula of $C_{20}O_8H_{18}$ (386 Da), trimers $C_{29}O_{10}H_{26}$ (534 Da) and tetramers $C_{38}O_{12}H_{34}$ (682 Da) (Figure 3). Dimers and trimers of the same molecular masses were observed after peroxidase-catalyzed oxidation of ferulic acid by H_2O_2 (28, 30). Dimers and trimers of phenols have also been observed following their interaction with Fe(III)-smectite (15, 31).

Lehmann et al. (1) suggested that the greater extent of reaction of phenolic acids with soil can be attributed to the higher methoxy substitution. However, our results demonstrated that ferulic acid, containing one methoxy group, is more intensely oxidized by Fe(III)-montmorillonite than syringic acid, with two methoxy activating groups. The molecular weight corresponding to ferulic acid trimers obtained in the current work correspond to the trimers reported by Ward et al. (28). In their case, the trimers were formed following the interactions of oxidant with the electrons of unsaturated chain of ferulic acid. This indicates the importance of the participation of π -electrons of unsaturated bonds in the oxidation and transformation of ferulic acid. Enhanced reactivity of unsaturated carbonyl arrangements in the molecules of phenolic acids toward the Lewis acids (polyvalent metal cations) has been suggested by Dalton et al. (32).

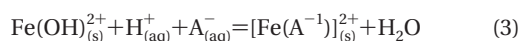
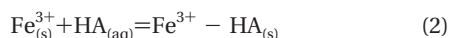
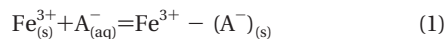
pH effect. Interaction of organic acids with Fe(III)-montmorillonite was influenced by solution pH. A decrease in pH from 5.5 to 3 promoted removal of organic acids from solution (Figure 2). Fe(III) is less hydrolyzed at low pH, and it therefore has more vacant coordination sites enabling stronger interaction with organic acids. Yong et al. (33) demonstrated enhanced oxidation of 2,6-dimethylphenol on the surface of Fe(III)-montmorillonite at pH < 4. Similarly, Deiana et al. (5) reported that a decrease in pH results in an increase in the redox capacity of the Fe(III)-caffeic acid system. At pH 3, Fe(III) can be coordinated with oxygen in

TABLE 3. Transformation of Ferulic Acid in FeCl₃ Solution and by Fe(III)-Montmorillonite Suspension. Standard Errors of the Experiments Were 4–6%.

system	Fe(III)-montmorillonite		FeCl ₃ solution	
initial concentration of ferulic acid (mM)	0.1	1.0	0.1	1.0
equilibrium concentration of ferulic acid (mM)	0.01	0.35	0.08	0.9
concentration of transformation products (mM acid)	0.09	0.65	0.02	0.1
fraction of transformed ferulic acid (%)	90	65	20	10
concentration of Fe(II) (mM)	0.46	1.11	0.06	0.13

carboxylic groups (34). Less than 10% of the organic acid was ionized at pH 3 (see pK_a of acids, Table 1). The molecules of organic acid are less hydrated than corresponding anions, which enhances adsorption of acids, at lower pH. Though the fraction of anions is small at pH 3, ligand exchange of anions on the surface OH-groups adds to the acid removal from the solution. Thus adsorption of both molecules and anions can be suggested for the interaction of Fe(III)-montmorillonite with aromatic acids.

The following Fe(III) species can be observed in the Fe(III)-aromatic acid system in a pH range of 3–5.5 (5): Fe^{3+} , $Fe(OH)^{2+}$, $Fe(OH)_2^+$, and $Fe(OH)_3$. The fraction of these species varied with pH. Hence we can suggest the following reactions on the surface of Fe(III)-montmorillonite (A^- is anion, and HA is undissociated acid):



In addition Fe (III)-induced deprotonated species can be formed in the system (35):



An increase in electrolyte (KCl) concentration up to 100 mM did not affect the removal of acids from solution by Fe(III)-montmorillonite. This suggests that inner-sphere complexation is the major mechanism governing the adsorption of aromatic acids on Fe(III)-montmorillonite (36). Similar to our results, Hanna and Carteret (37) reported insignificant changes in sorption of 1-hydroxy-2-naphthoic acid on iron oxides in the presence of 1.2 M NaCl. Desorption of benzoic acid (which was insignificantly transformed on the Fe(III)-montmorillonite) at pH 4.5 demonstrated pronounced hysteresis (Figure 4). This also supports our hypothesis of strong inner-sphere complexation of tested acids with the clay surface. The irreversibility of phenolic acids sorption of by soils has been previously reported by Cecchi et al. (7).

Transformation of Ferulic Acid: Fe(III)-Clay Surface vs Fe(III) Solution. Transformation intensities of ferulic acid by Fe(III)-montmorillonite and in FeCl₃ solution, containing the same initial amounts of Fe(III), were compared at pH 4.5 (i.e., the initial pH of the prepared Fe(III)-montmorillonite-acid systems). LC-MS analysis showed similar transformation

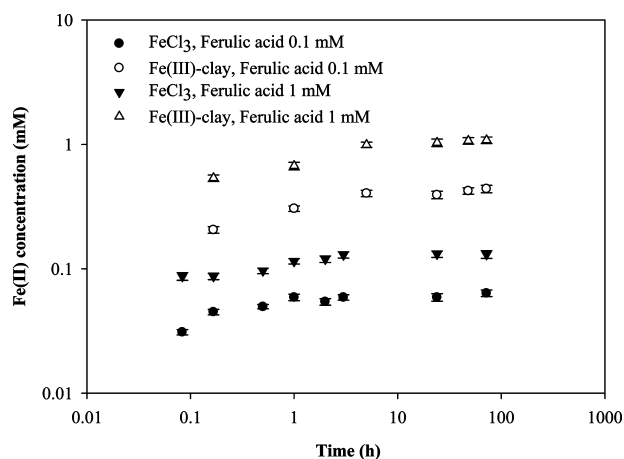


FIGURE 5. Formation of Fe(II) following by interactions of 0.1 and 1 mM ferulic acid with Fe(III)-montmorillonite and FeCl₃ solution at pH 4.5.

products for the two systems. However, the intensity of the ferulic acid transformation by Fe(III)-montmorillonite was much higher than that by the FeCl₃ solution: 90% of the ferulic acid was transformed following by interaction with Fe(III)-montmorillonite at an initial concentration of 0.1 mM, whereas only 20% was transformed in FeCl₃ solution. At a higher concentration (1 mM), 65% of the ferulic acid was transformed in the Fe(III)-montmorillonite versus 10% in the FeCl₃ solution (Table 3). The concentrations of Fe(II) formed in Fe(III)-montmorillonite-ferulic acid suspensions at equilibrium was 0.46 mM (for the 0.1 mM ferulic acid system) and 1.11 mM for the 1 mM system. In the corresponding FeCl₃-ferulic acid system, the concentrations of Fe(II) were 0.06 and 0.13 mM for the two initial concentrations, respectively (Figure 5, Table 3). These differences can be explained by the distinct properties of the water on the clay surface versus bulk water. In solution, electron transfer from ferulic acid to iron has been suggested to occur via outer-spheric mechanism (35). On the clay surface, inner-sphere complexes of organic acid carboxyl groups with the surface Fe(III) can form, and the iron-acid association is stronger due to the reduction in aqueous dielectric permittivity on the clay surface (36). This strong complexation enhances electron transfer, oxidation, transformation and oligomerization of phenolic acids on the surface of Fe(III)-montmorillonite.

Environmental Importance. The results of the current study demonstrate distinction between redox intensity of the reactions proceeding with Fe(III) in solution versus those occurring on Fe(III)-montmorillonite surface. This emphasizes the contribution of surface reactions in the chemical behavior of aromatic compounds in soils. Further studies of the role of Fe(III)-clay surfaces in the abiotic formation of humic materials and in the transformation of aromatic (phenolic) pollutants are needed for the elucidation of these important aspects of the environmental chemistry.

Acknowledgments

This research was supported by grants from the International Arid Land Consortium (IALC) and BARD, the United States-Israel Binational Agricultural Research and Development Fund. We thank Dr. Julius Ben-Ari for the LC-MS analyses.

Literature Cited

- (1) Lehmann, R. G.; Cheng, H. H.; Hersch, J. B. Oxidation of phenolic acids by soil iron and manganese oxides. *Soil Sci. Am. J.* **1987**, *51*, 352–356.
- (2) Boyer, R. F.; Clark, H. M.; La Roche, A. P. Solubilization of ferrihydrite Fe by plant phenolics: A model for rhizosphere processes. *J. Plant Nutr.* **1989**, *12*, 581–592.
- (3) Dalton, B. R.; Blum, U.; Weed, S. B. Plant phenolic acids in soils: sorption of ferulic acid by soil and soil components sterilized by different techniques. *Soil Biol. Biochem.* **1989**, *21*, 1011–1018.
- (4) Stevenson, F. J. *Humus Chemistry: Genesis, Composition, Reactions*; John Wiley and Sons: New York, 1994.
- (5) Deiana, S.; Gessa, C.; Marchetti, M.; Usai, M. Phenolic acid redox properties: pH influence on iron (III) reduction by caffeic acid. *Soil Sci. Am. J.* **1995**, *59*, 1301–1307.
- (6) Dec, J.; Haider, K.; Bollag, J.-M. Release of substituents from phenolic compounds during oxidative coupling reactions. *Chemosphere* **2003**, *52*, 549–556.
- (7) Cecchi, A.; Koskinen, W. C.; Cheng, H. H.; Haider, K. Sorption-desorption of phenolic acids as affected by soil properties. *Biol. Fertil. Soils* **2004**, *39*, 235–242.
- (8) Ohno, T. Oxidation of phenolic acid derivatives by soil and its relevance to allelopathic activity. *J. Environ. Qual.* **2001**, *30*, 1631–1635.
- (9) Schmidt, S. K.; Ley, R. E. Microbial competition and soil structure limit the expression of allelochemicals in nature. In *Principles and Practices in Plant Ecology*; Inderjit, Ed.; CRC Press: Boca Raton, 1999.
- (10) Bollag, J.-M. Decontaminating soil with enzymes. *Environ. Sci. Technol.* **1992**, *26*, 1876–1881.
- (11) Wang, T. S. C.; Li, S. W.; Ferng, Y. L. Catalytic polymerization of phenolic compounds by clay minerals. *Soil Sci.* **1978**, *126*, 15–21.
- (12) Singer, A. *The Soils of Israel*; Springer-Verlag: Berlin-Heidelberg, 2007.
- (13) Sparks, D. *Environmental Soil Chemistry*; Academic Press: Amsterdam, 2003.
- (14) Isaacson, P. J.; Sawney, B. L. Sorption and transformation of phenols on clay surfaces: effect of exchangeable cations. *Clay Miner.* **1983**, *18*, 253–265.
- (15) Sawhney, B. L.; Kozloski, R. K.; Isaacson, P. J.; Gent, M. P. N. Polymerization of 2,6-dimethylphenol on smectite surfaces. *Clay Clay Miner.* **1984**, *32*, 108–114.
- (16) Arroyo, L. J.; Li, H.; Teppen, B. J.; Johnston, C. T.; Boyd, S. A. Oxidation of 1-naphthol coupled to reduction of structural Fe³⁺ in smectite. *Clays Clay Miner.* **2005**, *53* (6), 587–596.
- (17) Gu, C.; Li, H.; Teppen, B. J.; Boyd, S. A. Octachlorodibenzodioxin formation on Fe (III)-montmorillonite clay. *Environ. Sci. Technol.* **2008**, *42*, 4758–4763.
- (18) Liyanapattirana, C.; Gwaltney, S. R.; Xia, K. Transformation of triclosan by Fe(III)-saturated montmorillonite. *Environ. Sci. Technol.* **2010**, *44*, 668–674.
- (19) Polubesova, T.; Rytwo, G.; Nir, S.; Serban, C.; Margulies, L. Adsorption of benzyltrimethylammonium and benzyltriethylammonium on montmorillonite: experimental studies and model calculations. *Clays Clay Miner.* **1997**, *45*, 834–841.
- (20) Polubesova, T.; Chen, Y.; Navon, R.; Chefetz, B. Interactions of hydrophobic fractions of dissolved organic matter with Fe³⁺- and Cu²⁺-montmorillonite. *Environ. Sci. Technol.* **2008**, *42*, 4797–4803.
- (21) Chefetz, B.; Stimler, K.; Shechter, M.; Drori, Y. Interactions of sodium azide with triazine herbicides: effect on sorption to soils. *Chemosphere* **2006**, *65*, 352–357.
- (22) Sørensen, J. Reduction of ferric iron in anaerobic, marine sediment and interaction with reduction of nitrate and sulfate. *Appl. Environ. Microbiol.* **1982**, *43*, 319–324.
- (23) Zhu, D.; Herbert, B. E.; Schlautman, M. A.; Carraway, E. R.; Hur, J. Cation- π bonding: a new perspective on the sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *J. Environ. Qual.* **2004**, *33*, 1322–1330.
- (24) Keiluweit, M.; Kleber, M. Molecular-level interactions in soils and sediments: the role of aromatic π -systems. *Environ. Sci. Technol.* **2009**, *43*, 3421–3429.
- (25) Graf, E. Antioxidant potential of ferulic acid. *Free Radical Biol. Med.* **1992**, *13*, 435–448.
- (26) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon Inc.: Boston, 1981.
- (27) Pinnavaia, T. J.; Hall, S. S.; Cady, S.; Mortland, M. M. Aromatic radical cation formation on the intracrystal surfaces of transition metal layer lattice silicates. *J. Phys. Chem.* **1974**, *78*, 994–999.
- (28) Ward, G.; Hadar, Y.; Bilkis, H.; Konstantinovskiy, L.; Dosoretz, C. G. Initial steps of ferulic acid polymerization by lignin peroxidase. *J. Biol. Chem.* **2001**, *276*, 18734–18741.
- (29) Shindo, H.; Huang, P. M. Catalytic effects of manganese (IV), aluminum and silicon oxides on the formation of phenolic polymers. *Soil Sci. Am. J.* **1984**, *48*, 927–934.
- (30) Ralph, J.; Quideau, S.; Grabber, J. H.; Hatfield, R. D. Identification and synthesis of new ferulic acid dehydromers present in grass cell walls. *J. Chem. Soc.* **1994**, *1*, 3485–3498.
- (31) Mortland, M. M.; Halloran, L. J. Polymerization of aromatic molecules on smectite. *Soil Sci. Am. J.* **1976**, *40*, 367–370.
- (32) Dalton, B. R.; Blum, U.; Weed, S. B. Differential sorption of exogenously applied ferulic, *p*-coumaric, *p*-hydrobenzoic, and vanillic acids in soil. *Soil Sci. Am. J.* **1989**, *53*, 757–762.
- (33) Yong, R. N.; Desjardins, S.; Farant, J. P.; Simon, P. Influence of pH and exchangeable cation on oxidation of methylphenols by a montmorillonite clay. *Appl. Clay Sci.* **1997**, *12*, 93–110.
- (34) Deiana, S.; Gessa, C.; Solinas, V. Analytical study of the interactions of D-galacturonic acid with iron (III) and iron (II) in solution and with iron (III)-bentonite. *Anal. Chim. Acta* **1989**, *226*, 315–322.
- (35) Hynes, M. J.; O'Coinceannainn, M. The kinetics and mechanism of reactions of iron (III) with caffeic acid, chlorogenic acid, sinapic acid, ferulic acid and narigin. *Inorganic Biochem.* **2004**, *98*, 1457–1464.
- (36) Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press: New York, 1984.
- (37) Hanna, K.; Carteret, C. Sorption of 1-hydroxy-2-naphthoic acid to goethite, lepidocrocite and ferrihydrite: Batch experiments and infrared study. *Chemosphere* **2007**, *70*, 178–186.

ES1007593