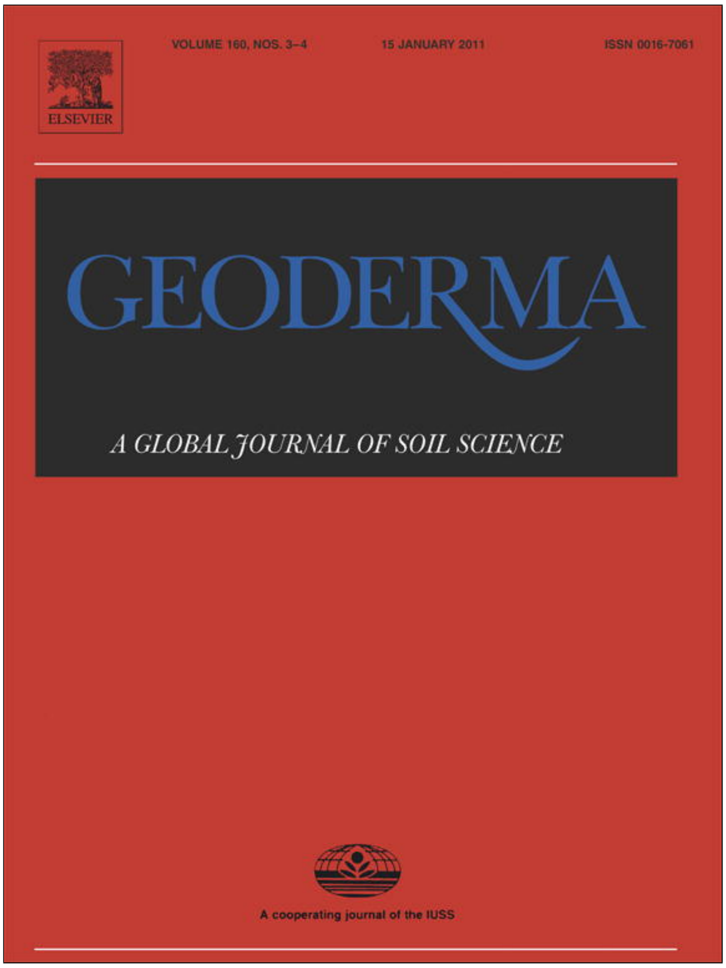
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Interactions of aromatic acids with montmorillonite: Ca^{2+}- and Fe^{3+}-saturated clays versus Fe^{3+}–Ca^{2+}-clay system

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ABSTRACT

Aromatic acids are involved in important soil processes, such as mobilization of microelements by plants and formation of humic components. Interactions of aromatic acids (benzoic, vanillic, *p*-coumaric, syringic and ferulic) with Ca^{2+}- and Fe^{3+}-saturated montmorillonite were studied, and the role of aqueous Ca^{2+} in aromatic acid adsorption to Fe^{3+}-montmorillonite was investigated. Removal of aromatic acids at pH 3 and changes in partial molar free energy of adsorption of benzoic acid were higher for Fe^{3+}-montmorillonite than for Ca^{2+}-montmorillonite. Adsorption of aromatic acids on Ca^{2+}-montmorillonite decreased similarly with increasing pH. The aromatic acids could be divided into two groups according to their behavior on the surface of Fe^{3+}-montmotillonite with increasing pH: *i*) ferulic and syringic and *ii*) benzoic, vanillic, and *p*-coumaric. Adsorption of the studied acids by Fe^{3+}-montmorillonite was affected by their molecular structures. Adsorption of benzoic acid by Fe^{3+}-montmorillonite increased in the presence of 5 mM $CaCl_2$. Adsorption of aqueous Ca^{2+} on Fe^{3+}-montmorillonite was high (0.59 mmo_c/g), and was not influenced by the concentration of benzoic acid. Desorption of benzoic acid from Fe^{3+}–Ca^{2+}-montmorillonite was greater than that from Fe^{3+}-montmorillonite. For the former system, adsorption hysteresis of benzoic acid increased with increasing acid concentration. The current study demonstrates a role of aqueous Ca^{2+}: when adsorbed from the soil solution to iron-containing surfaces, it can change their adsorptive properties towards low-molecular-weight acids.

1. Introduction

Aromatic acids participate in many soil processes, including mobilization of microelements that are required by plants and formation of humic components (Boyer et al., 1989; Dalton et al., 1989; Dec et al., 2003; Lehmann et al., 1987; Stevenson, 1994). Phenolic acids are of concern due to their role as allelopathic agents (Cecchi et al., 2004; Ohno, 2001). Benzoic acid inhibits germination and plant growth when applied exogenously in millimolar concentrations (Baziramakenga et al., 1994). In soils, the fate and potential bioavailability of aromatic acids are mainly controlled by sorption–desorption and oxidation processes (Cecchi et al., 2004; Lehmann et al., 1987). Soil minerals play an important role in soil sorption of aromatic acids via a variety of acid–mineral interactions (Djafer et al., 1991; Keiluweit and Kleber, 2009; Kubicki et al., 1999; McBride, 1987).

Montmorillonite, which belongs to the group of expandable 2:1 layer silicate minerals, is a major component of the clay minerals in soils developed in semiarid regions (Singer, 2003). Calcium is a common exchangeable cation on montmorillonite surfaces, and a dominant cation in the soil solution (Singer, 2003; Wolt, 1994). Soil particles can comprise three sorbents: clay minerals, organic matter and oxides (Johnston and Tombácz, 2002). Hence, large surface areas containing Fe^{3+} or its hydrolyzed forms can also be significant components of the soil system. The Fe^{3+} ions form strong complexes with organic acids (Kubicki et al., 1999; Stevenson, 1994; Stolpe et al., 1993). Interactions of adsorbed organic molecules with Fe^{3+} may result in electron transfer from the organic molecules to the metal cations, and a reduction of metal ions to lower valence (Sparks, 2003). Previously we demonstrated oxidation of phenolic acids on the surface of Fe^{3+}-montmorillonite, accompanied by reduction of Fe^{3+} to Fe^{2+} (Polubesova et al., 2010). In contrast, divalent Ca^{2+} ions do not form strong coordination complexes with organic molecules and are effective only to the extent that a bridge linkage can form. Aqueous Ca^{2+} and organic acids mutually affect their adsorption on iron oxides (Ali and Dzombak, 1996; Tipping, 1981). However, the effect of the presence of alkaline earth metal cations on the sorption of aromatic acids by Fe^{3+}-containing mineral surfaces has not been extensively investigated. The objective of the current study was therefore to evaluate the interactions of aromatic acids with Ca^{2+}- and Fe^{3+}-saturated montmorillonite and to elucidate the role of aqueous Ca^{2+} in adsorption of aromatic acids to Fe^{3+}-montmorillonite.

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2. Materials and methods

Aromatic acids (benzoic, vanillic, *p*-coumaric, syringic and ferulic) were purchased from Sigma (Rehovot, Israel; >98% purity) and used without further purification. Molecular structures of the investigated compounds are presented in Fig. 1.

2.1. 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 $\mathrm{mmol_c/g}$ (Polubesova et al., 1997). The <2 μm fraction of the montmorillonite was collected for the experiments. Homo-ionic Ca^{2+}- and Fe^{3+}-montmorillonite was prepared by sequential washing of the crude montmorillonite with 1 *N* $CaCl_2$ or $FeCl_3$ solution, respectively (Polubesova et al., 2008). Excessive salts were removed by dialyzing the samples against distilled water until the supernatant solution was free of chlorides. Ca^{2+}- and Fe^{3+}-clay samples were freeze-dried and stored in a desiccator.

2.2. Batch sorption experiments

The isotherms of adsorption of the tested organic acids by Ca^{2+}-montmorillonite and Fe^{3+}-montmorillonite were measured at their native pH (7.19 ± 0.1 and 4.02 ± 0.01 for Ca^{2+}– and Fe^{3+}–montmorillonite, respectively), and at pH 3. All experiments were performed with analytes in a concentration range of 0.1 to 8 mM using batch procedure. Sodium azide (100 mg/L) was added to all solutions to inhibit microbial activity (Chefetz et al., 2006). The final concentration of the clay suspensions was 5 g/L. Aromatic acid-clay suspensions and blank solutions (acids without clay) were agitated at 25 °C for 72 h (based on preliminary kinetics measurements). The effect of pH on removal of acids from solution was studied in the pH range of 3 to 6. At the end of the adsorption experiments, samples were centrifuged at 15,000 *g* for 30 min and supernatants were filtered through a 0.2-μm filter. Analyte concentration was measured by HPLC (D7000, Merck-Hitachi, Germany). A C18 RP-amide column (Supelco, 25 cm × 4 mm, 5 μm) was used to determine ferulic, *p*-coumaric, syringic and vanillic acid, and RP-18 (LiChrospher) was used for benzoic acid. The 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.

For benzoic acid, the isotherm of adsorption was measured for Fe^{3+}-montmorillonite in the presence of 5 mM $CaCl_2$, and four sequential desorption steps were performed after adsorption by removing half of the supernatant volume each time using a glass pipette. The removed supernatant was replaced with fresh sodium azide solution and the tubes were agitated for 96 h. At the end of each of the desorption steps, the suspensions were centrifuged, filtered and analyzed as described previously. All experiments were performed in triplicate.

The adsorption isotherms were best fitted with the Langmuir equation. The apparent hysteresis index (AHI) for the desorption of benzoic acid from Fe^{3+}–Ca^{2+}-montmorillonite was calculated as the ratio $N^{\mathbf{D}}/N^{S}$ (Chefetz et al., 2004).

3. Results and discussion

The average pH of the Ca^{2+}-montmorillonite–aromatic acid suspensions was 6.55 ± 0.23. Adsorption of the aromatic acids in this range was negligible, or even negative. Since Ca^{2+}-montmorillonite particles are negatively charged, the concentration of anions near their surface decreases. The latter results in formation of anion-depleted or anion-free water layers near montmorillonite particle surfaces. Thus concentration of anions increases with the increase of a distance from montmorillonite particles. This phenomenon designated “negative adsorption” (Bolt and de Haan, 1982; Sposito, 1984). Negative adsorption of benzoic acid on Na^{+}-montmorillonite has been reported by Bailey et al. (1968). The adsorption isotherms of the studied aromatic acids on Ca^{2+}-montmorillonite at pH 3 are presented in Fig. 2. Parameters of the Langmuir equation are shown in Table 1. Aromatic acids showed a similar decrease in adsorption on Ca^{2+}-montmorillonite with increasing pH (Fig. 3a). At pH 3, less than 10% of the organic acid was ionized (pK_a of acids ranged from 4.2 to 4.6), i.e. acids mostly adsorbed in their molecular form. Adsorption of anionic species of aromatic acids was expected to be low since adsorption decreased with increasing pH (Fig. 3a). The molecules of organic acid are less hydrated than the corresponding anions, which enhances their adsorption at pHs lower than their pK_a. The divalent Ca^{2+} ion does not form strong complexes with organic molecules, and therefore a water-bridging is one of the operating mechanisms of the adsorption of aromatic acid on

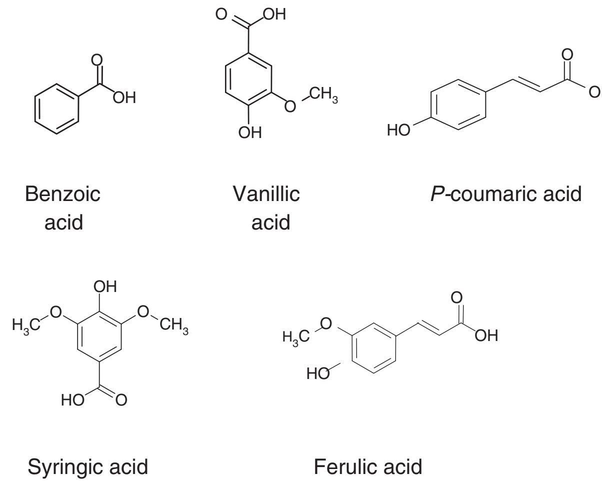

Fig. 1. Molecular structures of aromatic acids used in this study.

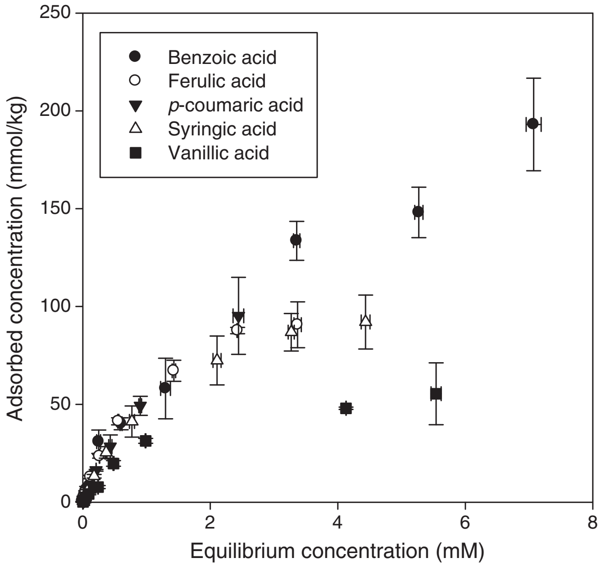

Fig. 2. Adsorption isotherms of aromatic acids on Ca^{2+}-montmorillonite. Experiments were conducted at pH 3.

Table 1
Langmuir parameters fitting the adsorption isotherms of aromatic acids on Ca^{2+}-montmorillonite at pH 3.

Acid	K_L (L/kg)	S_{max} (mmol/kg)	E^a
Benzoic	0.208 ± 0.049	315 ± 37	0.989
Ferulic	0.905 ± 0.066	123 ± 3.4	0.998
p-Coumaric	0.331 ± 0.023	194 ± 8.0	0.999
Syringic	0.686 ± 0.026	124 ± 1.9	0.999
Vanillic	0.833 ± 0.108	65 ± 2.9	0.993

[a] *E* characterizes the model efficiency. A model efficiency of 1 indicates a perfect fit to the data (Bolster and Hornberger, 2007).

Ca^{2+}-montmorillonite. Van der Waals interactions also contribute significantly to the adsorption of aromatic acids on this clay (Sposito, 1984; Stevenson, 1994).

The aromatic acids could be divided into two groups according to their behavior on the surface of Fe^{3+}-montmotillonite with increasing pH (Fig. 3b). Ferulic and syringic acid showed 90 to 100% removal at pH 3–4, and the removed amount decreased abruptly at pH 5–6. Benzoic, vanillic and *p*-coumaric acids showed 30 to 45% removal in the pH range of 3 to 4, with removal gradually decreasing to less than 20% at pH 5.5–6. This difference in the behavior of aromatic acids on the surface of Fe^{3+}-montmorillonite can be explained by the specific interactions of the studied acids with Fe^{3+}-montmorillonite and their different molecular structures. The interactions of aromatic acids with Fe^{3+}-montmorillonite can involve multiple adsorption mechanisms, including: (*i*) inner- and outer-sphere complexation of carboxyl and phenolic groups with the surface of the Fe^{3+}-montmorillonite; (*ii*) hydrogen bonding; (*iii*) non-covalent Fe(III)–π interactions, and (*iv*) interactions of the surface hydroxyl hydrogen with the aromatic π-donor groups (Deiana et al., 1995; Keiluweit and Kleber, 2009; Sparks, 2003; Zhu et al., 2004). Previously we demonstrated that adsorption of aromatic acids on Fe^{3+}-montmorillonite was accompanied by their oxidative transformation, which was dependent on their molecular structure. The following order of transformation intensity was observed: ferulic > syringic > p-coumaric > vanillic > benzoic (Polubesova et al., 2010). The strongest interactions of the studied acids with Fe^{3+}-clay were observed at pH < 4 (Fig. 3b). Similarly, enhanced oxidation of 2,6-dimethylphenol on the surface of Fe^{3+}-montmorillonite at pH < 4 was observed by Yong et al. (1997). At low pH, iron is less hydrolyzed, and it therefore has more vacant coordination sites, enabling stronger interaction with organic acids. At pH 3, Fe^{3+} can be coordinated with oxygen in carboxylic groups (Deiana et al., 1989). Both ferulic and syringic acid contain methoxy and OH groups (Fig. 1), which are considered to be activating groups (Morrison and Boyd, 1981). Moreover, the deactivating carboxylic group of ferulic acid is bound to the aromatic ring through the unsaturated C bond, which decreases its deactivating effect, thereby enhancing the activating effect of the methoxy and OH groups. Furthermore, ferulic acid has conjugated double bonds. The combination of these factors resulted in intense adsorption and oxidation of ferulic and syringic acids at low pH, and removal of the acid molecules from solution. The molecular structures of benzoic, vanillic and *p*-coumaric acid retained their higher stability to oxidation. In the molecules of benzoic and vanillic acid, the deactivating carboxylic group is bound directly to the aromatic ring (even though vanillic acid has methoxy and OH activating groups); *p*-coumaric acid's structure is similar to that of ferulic acid (Fig. 1), but it does not have a methoxy activating group, which probably resulted in its lesser transformation as compared to ferulic acid. Thus adsorption and transformation (removal) of benzoic, vanillic and *p*-coumaric acids were lower than those of ferulic and syringic acids, and the dependence of these processes on pH for vanillic, p-coumaric and benzoic acids was less pronounced.

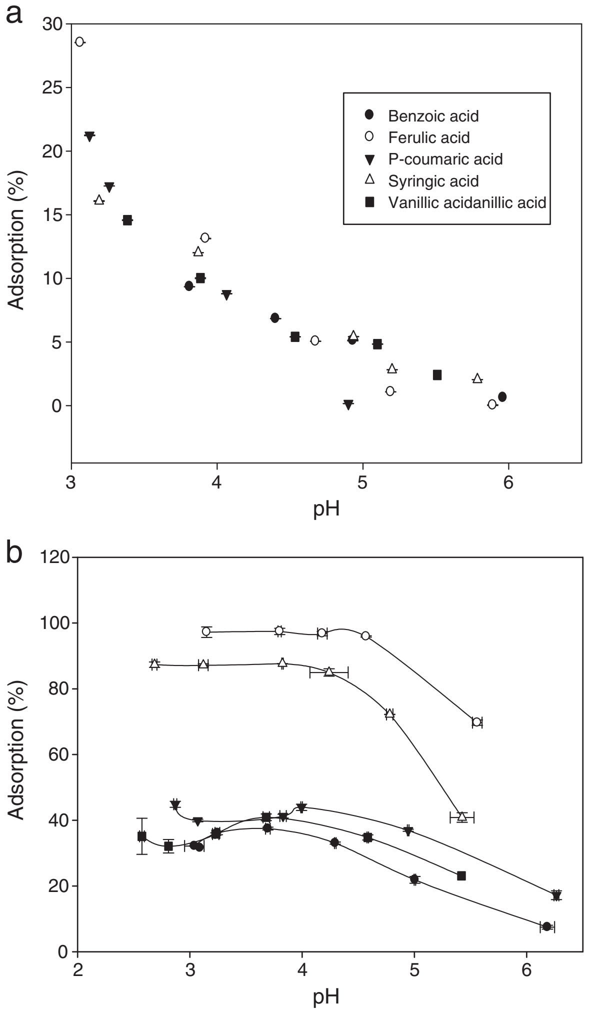

Fig. 3. Effect of pH on adsorption of aromatic acids on a) Ca^{2+}-montmorillonite and b) Fe^{3+}-montmorillonite, at an initial acid concentration of 0.25 mM.

The removal of aromatic acids by Ca^{2+}-montmorillonite at pH 3 was lower than that for Fe^{3+}-montmorillonite at both low and high initial acid concentrations (Table 2). The order of acid removal by Fe^{3+}-montmorillonite corresponded to their order of transformation (Polubesova et al., 2010): ferulic > syringic > p-coumaric > vanillic ≥ benzoic (Table 2).

In contrast to the other acids, benzoic acid does not have any activating group, and the deactivating carboxylic group is bound directly to the aromatic ring. Therefore, the transformation of benzoic acid by Fe^{3+}-montmorillonite was low (1–5%) for the studied range of concentrations (Polubesova et al., 2010). Hence, in this paper, we compare and discuss adsorption of benzoic acid on both systems, i.e. Ca^{2+}- and Fe^{3+}-montmorillonite. To compare the extent of the driving force for benzoic acid adsorption on Ca^{2+}- and Fe^{3+}-montmorillonite, changes in partial molar free energy of adsorption of benzoic acid were calculated according to Bailey et al. (1968):

$$-\overline{F} = RT\, ln(C_e / C_o)$$

Table 2
The fraction of aromatic acids (%) removed from solution by Fe^{3+}- and Ca^{2+}-montmorillonite at pH 3.

Acid	Fe^{3+}-montmorillonite		Ca^{2+}-montmorillonite	
	0.1 mM	1 mM	0.1 mM	1 mM
Benzoic	51 ± 1.2	24 ± 0.9	28 ± 2.2	18 ± 4.9
Ferulic	100 ± 0.1	83 ± 0.1	38 ± 2.3	27 ± 1.2
p-Coumaric	60 ± 0.3	33 ± 1.4	27 ± 1.8	19 ± 1.8
Syringic	77 ± 0.1	44 ± 6.0	29 ± 3.4	21 ± 4.1
Vanillic	51 ± 2.1	28 ± 2.4	18 ± 1.9	14 ± 0.6

where $\overline{F}$ (J/mol) is the change in partial molar free energy, R (J/K mol) is the molar gas constant, T (K) is the absolute temperature, C_e (mM) is the equilibrium concentration, and C_o (mM) is the initial concentration of the solution prior to adsorption. The greater the absolute magnitude of the $\overline{F}$ value, the greater the extent to which the adsorption reaction will take place. Fig. 4 shows that $\overline{F}$ values for Fe^{3+}-montmorillonite were higher than those for Ca^{2+}-montmorillonite, especially at low concentrations, indicating that the driving force for benzoic acid adsorption on Fe^{3+}-clay is higher than that for Ca^{2+}-montmorillonite, which is consistent with the greater removal of benzoic acid by the former clay (Table 2).

Saturation of montmorillonite surface by Fe^{3+} results in similarity of Fe^{3+}-montmorillonite surface reaction to those of goethite due to the changes of montmorillonite surface charge from negative to positive and presence of iron hydroxocomplexes on the surface of Fe^{3+}-montmorillonite (Ali and Dzombak, 1996; Grygar et al., 2007; Polubesova et al., 2008). Thus both goethite and Fe^{3+}-montmorillonite demonstrated preferential uptake of aromatic components of dissolved organic matter (Chorover and Amistadi, 2001; Polubesova et al., 2008). Djafer et al. (1991) suggested that benzoate adsorbs nonspecifically on goethite, whereas Parfitt et al. (1977) reported that benzoate adsorbs as a monodentate species on goethite. Kubicki et al. (1999) related strong complexation of benzoic acid with illite to the availability of iron-reactive sites on the illite surface. Previously, we showed that increasing KCl concentration up to 100 mM does not affect the adsorption of benzoic acid on Fe^{3+}-montmorillonite (Polubesova et al., 2010), which indicated strong inner-sphere complexation of benzoic acid with the Fe^{3+}-montmorillonite surface (Kung and McBride, 1989). The pH of the Fe^{3+}-montmorillonite increased from 4.02 ± 0.01 (clay–water suspension) to 4.5 ± 0.04 (Fe^{3+}-montmorillonite–benzoic acid suspensions) followed by adsorption of benzoic acid, indicating exchange of carboxylate anions for the surface hydroxyls. Surface acidity of montmorillonite increases in the presence of interlayer trivalent cations (Soma and Soma, 1989). Fe^{3+}-montmorillonite has strong BrØnsted and Lewis acidity (Akçay, 2005; Soma and Soma, 1989), which strengthened the adsorption of benzoic acid.

The presence of 5 mM $CaCl_2$ decreased the pH of the Fe^{3+}-montmorillonite–benzoic acid suspension from 4.5 ± 0.04 to 3.7 ± 0.05, and affected the sorption behavior of benzoic acid on Fe^{3+}-montmorillonite. Fig. 5 shows the distribution coefficients (calculated as the ratios of the adsorbed amounts of benzoic acid to the corresponding equilibrium benzoic acid concentrations) for three types of Fe^{3+}-montmorillonite–benzoic acid suspensions: Fe^{3+}-montmorillonite at pH 4.5, Fe^{3+}-montmorillonite at pH 3, and Fe^{3+}-montmorillonite in the presence of 5 mM $CaCl_2$ (pH 3.7). The order of affinity of benzoic acid to the surface of Fe^{3+}-montmorillonite was: Fe^{3+}-clay (pH 3)≈Fe^{3+}-clay in the presence of 5 mM of $CaCl_2$>Fe^{3+}-clay (pH 4.5). Thus the presence of aqueous Ca^{2+} in the system increased the affinity of benzoic acid to Fe^{3+}-montmorillonite.

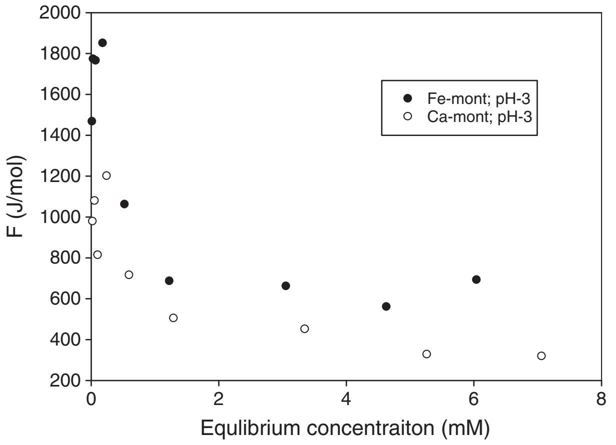

Fig. 4. $\overline{F}$ values for adsorption of benzoic acid on Ca^{2+}-montmorillonite (Ca-mont) and Fe^{3+}-montmorillonite (Fe-mont). Each value is an average of three replicates with standard error lower than 7%.

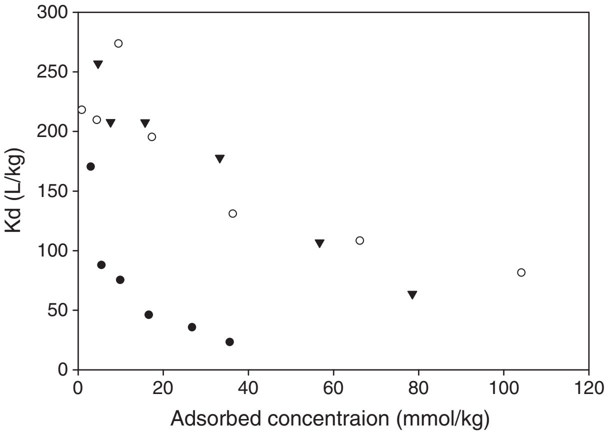

Fig. 5. Adsorption of benzoic acid on Fe^{3+}–montmorillonite at pH 3 (triangles), Fe^{3+}–montmorillonite at pH 4.5 (filled circles) and Fe^{3+}–montmorillonite in the presence of 5 mM $CaCl_2$ at pH 3.7 (open circles).

Tipping (1981) demonstrated an increase in the adsorption capacity of goethite for dissolved humic substances in the presence of Ca^{2+}, and Kinniburgh et al. (1976) observed adsorption of aqueous Ca^{2+} on iron oxides. Ali and Dzombak (1996) studied Ca^{2+} adsorption on goethite in the presence of organic acids. They suggested formation of $[Fe(OH)_2Ca]^{2+}$ and $[FeOCa]^{+}$ complexes on the goethite surface. Gerstl and Banin (1980) and Grygar et al. (2007) suggested that preparation of Fe^{3+}-montmorillonite is accompanied by hydrolysis and formation of monomers or dimers $Fe(OH)_x^{(3-x)+}$ and polymeric structures with edge-shared Fe $(O,OH)_6$. We assumed that the same $[Fe(OH)_2Ca]^{2+}$ and $[FeOCa]^{+}$ complexes form on the surface of Fe^{3+}-montmorillonite, as was previously suggested for goethite (Ali and Dzombak, 1996), i.e. that Ca^{2+} can exchange the surface H^{+}, resulting in a decrease in suspension pH.

Adsorption of Ca^{2+} on the surface of Fe^{3+}-montmorillonite was surprisingly high (0.59 ± 0.0023 $mmol_c$/g) and was not affected by the concentration of benzoic acid in the range of 0.008 to 4 mM. Thus, an Fe^{3+}–Ca^{2+}-montmorillonite system was formed whose surface properties differed from those of Fe^{3+}-montmorillonite.

Joseph (1946) observed weak interactions of Ca^{2+} with benzoic acid in solution (log K of Ca^{2+}–benzoic acid complex was −0.24). Hence, removal of Ca^{2+} and benzoic acid from solution cannot be explained by the adsorption of calcium benzoate formed in solution. The pH is an important factor influencing the adsorption of benzoic acid. The fraction of dissociated benzoic acid was 6% at pH 3, 24% at pH 3.7, and 67% at pH 4.5. Lower pH induced the formation of molecular species of benzoic acid, which are more hydrophobic than anions; in addition, iron is less hydrolyzed at decreasing pH.

Formation of $[Fe(OH)_2Ca]^{2+}$ complexes in addition to $[FeOCa]^{+}$ species can explain adsorption of Ca^{2+}, due to the electrostatic interaction of Ca^{2+} with iron polymers on the Fe^{3+}-clay surface. Though the adsorption of benzoic acid from solution in the form of calcium benzoate is of minor importance (Joseph, 1946), and benzoic acid did not adsorb on the surface of Ca^{2+}-montmorillonite, Fe^{3+}–Ca^{2+}-montmorillonite can enhance the adsorption of benzoic acid due to noncovalent Fe^{3+}–π interactions (Keiluweit and Kleber, 2009). These interactions can result in redistribution of the electron density in the adsorbed molecules of benzoic acid, enhanced dissociation of the molecule's carboxyl group and formation of benzoate anions on the Fe^{3+}-montmorillonite surface. The low dielectric constant of water adsorbed on the surface of Fe^{3+}-montmorillonite can induce electrostatic interactions between the complexes ($[(FeOH)_2Ca]^{2+}$ and $[FeOCa]^+$) and benzoate anions because ion-pairing formation is promoted by a decrease in dielectric constant (Lee and Rao, 1996; Sposito, 1984). Polubesova et al. (2010) demonstrated that transformation of ferulic acid is more intense on the surface of Fe^{3+}-montmorillonite than in $FeCl_3$ solution. Yariv et al. (1966) observed the formation of Ca^{2+}–benzoate complexes on the surface of Ca^{2+}-montmorillonite under anhydrous conditions. Thus, the clay surface can enhance the electrostatic interactions between benzoate and the cations relative to solution. We suggest that Ca^{2+} adsorption on Fe^{3+}-montmorillonite can increase the affinity of benzoic acid to Fe^{3+}-clay due to Ca^{2+}–H^+ exchange followed by a decrease in pH, and electrostatic interactions of benzoate with surface–formed $[(FeOH)_2Ca]^{2+}$ and $[FeOCa]^+$ complexes in the presence of adsorbed water.

Though adsorption of benzoic acid to Fe^{3+}–Ca^{2+}-montmorillonite increased as compared to its adsorption to Fe^{3+}-montmorillonite, desorption of benzoic acid from Fe^{3+}–Ca^{2+}-montmorillonite was facilitated. The cumulative four-step-desorption release of benzoic acid from Fe^{3+}-montmorillonite was insignificant, whereas the cumulative desorption of acid from Fe^{3+}–Ca^{2+}-montmorillonite was significantly higher (Figs. 6 and 7), confirming the stronger inner-sphere complexation of benzoic acid on Fe^{3+}-montmorillonite as compared to the adsorption of molecular species or electrostatic interactions of acid with Fe^{3+}–Ca^{2+}-montmorillonite.

Desorption of benzoic acid from Fe^{3+}–Ca^{2+}-montmorillonite decreased with increasing acid concentration (Fig. 7). The AHI decreased from 0.87 to 0.24 with an increase in benzoic acid concentration from 0.1 to 4 mM. Increased hysteresis at higher concentrations has also been observed by Undabeytia et al. (1999) for adsorption of the pesticide chlordimeform by Ca^{2+}-montmorillonite, and by Chefetz et al. (2004) for the adsorption of triazine herbicides by river sediments. The interactions of $[FeOCa]^+$ complexes with iron polymers can result in aggregation of the Fe^{3+}-montmorillonite plates according to the reaction:

$$FeOCa^+ + HOFe = FeOCaOFe + H^+$$

We suggest that the additional aggregation of Fe^{3+}-montmorillonite due to the presence of Ca^{2+} explains the greater hysteresis of benzoic acid at high acid concentrations. At high benzoic acid concentrations, a concentration gradient forces the sorbate molecule to penetrate deeper into the clay aggregate and form additional bonds with the clay surface, impairing the desorption of sorbate molecules from $Fe^{3+}—Ca^{2+}$-clay.

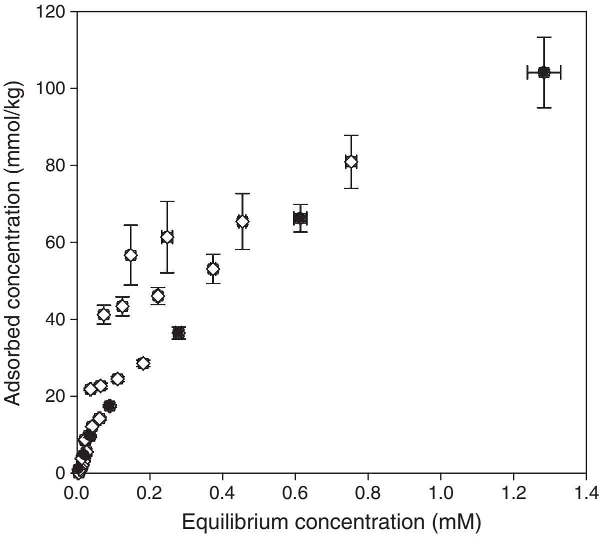

Fig. 6. Adsorption (filled diamonds) and desorption (open diamonds) isotherms of benzoic acid on Fe^{3+}-montmorillonite in the presence of 5 mM $CaCl_2$.

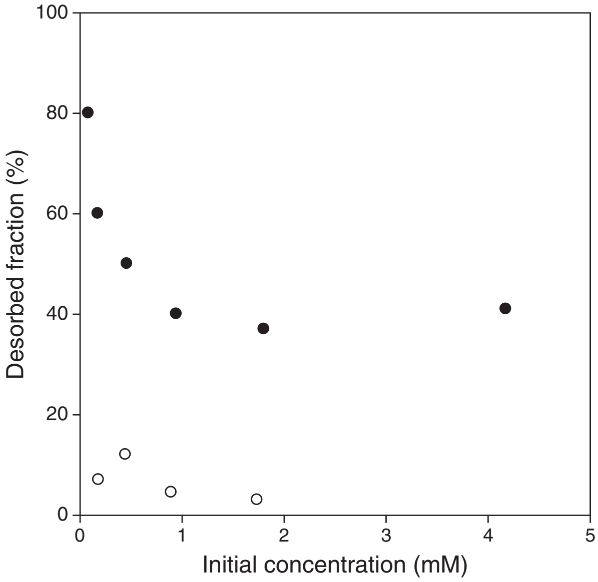

Fig. 7. Cumulative four-step-desorption release of benzoic acid from Fe^{3+}-montmorillonite pH 4.5 (open circles) and Fe^{3+}–Ca^{2+}-montmorillonite (filled circles). Standard errors are 5–7%.

4. Conclusions

The results of the current study demonstrate that adsorption of Ca^{2+} on Fe^{3+}-montmorillonite changes the adsorptive properties of Fe^{3+}-montmorillonite clay towards benzoic acid: acid affinity to $Fe^{2+}—Ca^{2+}$-montmorillonite clay increased as compared to its affinity to Fe^{3+}-montmorillonite. However, desorption of benzoic acid from Fe^{3+}–Ca^{2+}-montmorillonite was facilitated, and greater hysteresis was observed for higher concentrations of benzoic acid. Current research demonstrated a role of aqueous Ca^{2+}: when it is adsorbed from the soil solution on iron-containing surfaces, it can change the latter's adsorptive properties towards low-molecular-weight acids.

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