

Adsorption Effect on the Degradation of Carbaryl, Mecoprop, and Paraquat by Anodic Fenton Treatment in an SWy-2 Montmorillonite Clay Slurry

PENG YE AND ANN T. LEMLEY*

Graduate Field of Environmental Toxicology, Cornell University, Ithaca, New York 14853

The Fenton reaction-based anodic Fenton treatment (AFT) was applied to three widely used organic agrochemicals, carbaryl, mecoprop, and paraquat, in a clay slurry. The adsorption and degradation behaviors of these neutral (carbaryl), anionic (mecoprop), and cationic (paraquat) agrochemicals were studied in a slurry of SWy-2 Na⁺-montmorillonite clay, and adsorption isotherms were obtained at given experimental conditions. The *d* spacing (*d*₀₀₁) of the clay layer before and after adsorption or degradation was measured by X-ray diffraction (XRD). On the basis of the change of *d* spacing, molecular disposition at the clay interlayer was inferred: both mecoprop and paraquat form a monolayer sitting flat and parallel to the clay siloxane surfaces. Results show that, due to different adsorption mechanisms, the adsorption effect on chemical degradation by AFT varies with pesticide: strong and tight adsorption of paraquat at the clay interlayer protects paraquat from being attacked by hydroxyl radicals; loosely adsorbed carbaryl or mecoprop is readily degraded. XRD analysis clearly indicates that AFT is capable of effectively degrading interlayer noncationic organic chemicals that are not usually available for biodegradation.

KEYWORDS: Carbaryl; mecoprop; paraquat; anodic Fenton treatment; adsorption

INTRODUCTION

The retention time of organic pollutants in soil varies, depending on the nature of the pollutants, the soil types and properties, and the outside environmental parameters, such as rainfall and temperature. Soil organic matter (SOM) and clay are considered two of the most important soil components affecting organic chemical movement in soil. It is well established that nonionic organic chemicals have a strong affinity to SOM (1–3), whereas negatively charged clays, especially 2:1 layered clays, are mainly responsible for the adsorption of cationic organic chemicals, such as paraquat and diaquat, in soil through strong electrostatic attraction (4–6). Adsorption to SOM or clay particles decreases the rates of biodegradation. Studies have found that, compared to controls, biodegradation rates of quinoline (7), citrate (8), parathion (9), naphthalene (10), and benzylamine (11) were slowed dramatically in the presence of clay minerals, either due to the clay protection of chemicals from being directly attacked by microorganisms or due to the inactivation of extracellular enzymes by clay adsorption. Due to the limited accessibility to microorganisms in soils or clay systems, organic compounds that are not strongly adsorbed by soil and should be readily biodegradable, such as fumigant ethylene dibromide (12, 13), can persist in soils for decades, even though the conditions are favorable for microbial growth and biodegradation.

Chemical oxidants are highly aggressive and small in size, making them a good option for degrading specific pollutants in heavily contaminated soils. Fenton reaction-based chemical oxidation is one of the most studied degradation methods in wastewater systems (14–17). Watts and colleagues first used Fenton reagents and Fenton-like processes in degrading organic pollutants, such as pentachlorophenol, trifluralin, hexadecane, dieldrin, and trichloroethylene in contaminated soils (18–23). Degradation of various other contaminants, such as trinitrotoluene, heterocyclic nitramines, 2,4-dichlorophenoxyacetic acid, and metolachlor, and PAHs in soil by Fenton reaction has also been studied recently (24–29). To avoid the highly hygroscopic and readily oxidizable ferrous salt used in classic Fenton treatment and to make the Fenton treatment method more manageable, a more practical Fenton oxidation method, anodic Fenton treatment (AFT), was developed and tested in water systems (30–33). The AFT method has been successfully applied to degrade and detoxify many pesticides, such as ethylene thiourea, 2,4-dichlorophenoxyacetic acid, carbaryl, and carbofuran (30, 31, 33–37), in water systems.

Encouraged by the successful application of AFT in aqueous solution, two preliminary studies were done on the degradation of pesticides in a humic acid (38) or real soil (39) slurry system. Although the effect of sorption on the degradation kinetics was discussed in both studies, this effect was not incorporated in the kinetic model. Also, it is impossible to distinguish the effects of important individual soil properties, such as soil organic matter and soil minerals, in a real soil slurry system. To identify

* Author to whom correspondence should be addressed (e-mail at12@cornell.edu).

the effects of soil components on the degradation of organic agrochemicals in soil slurry by AFT, a synthetic soil composed of kaolin clay, sand, and humic acid was tested in a previous study (40). It was found that kaolin clay, a 1:1 layer clay, has little effect on the degradation kinetics of carbaryl in the slurry due to its limited adsorption capacity and relatively small surface area. However, in real soils there usually is a substantial amount of a 2:1 layer clay, such as smectite clays. It is important to study degradation in slurries with this clay type that has a much higher cation exchange capacity and surface area.

In the present study Na⁺-montmorillonite source clay from the Clay Minerals Society was selected as a testing medium. Widely used agrochemicals, carbaryl, mecoprop (p*K*_a = 3.78), and paraquat, were selected as probes, representing neutral, anionic, and cationic organics, respectively. X-ray diffraction (XRD) analysis was used to measure the *d* spacing of montmorillonite clay. The objectives of this study were (1) to investigate the adsorption effect of layered clay on the degradation of probe chemicals in the AFT system, (2) to explain the effect through adsorption mechanisms and XRD analysis, and (3) to identify whether AFT is able to remove organic chemicals at the clay interlayer.

MATERIALS AND EXPERIMENTS

Chemicals. Source clay Na⁺-montmorillonite (code: Src_eClay_SWy-2) was obtained from the Clay Minerals Society (West Lafayette, IN). Carbaryl (99.5%, CAS Registry No. 63-25-2), mecoprop (99.5%, CAS Registry No. 7085-19-0), and paraquat CL tetrahydrate (99%, CAS Registry No. 1910-42-5) were purchased from ChemService, Inc. (West Chester, PA). Hydrogen peroxide (30%, analytical grade) was from Sigma-Aldrich (St. Louis, MO). Water and acetonitrile, both of HPLC grade, were purchased from Fisher Scientific (Pittsburgh, PA). Methanol (HPLC grade), potassium chloride, sodium chloride, and hydrochloric acid (37%) were purchased from Mallinckrodt Chemicals (Phillipsburg, NJ). Deionized water (electricity resistant, *R* ≥ 18.1 MΩ·cm⁻¹) was produced by an MP-1 Mega-Pure system (Corning, NY).

Purified Clay. The purification process is based on the literature (41). To obtain purified clay (<2 μm), 25 g of SWy-2 was placed in a 2 L beaker with 1.8 L of deionized water and stirred for 8 h using a magnetic stir bar to hydrate the clay. After overnight (~18 h) settling, the supernatant suspension containing the <2 μm clay particles was poured into 50 mL polyethylene centrifuge tubes and then centrifuged for 30 min at 6000 rpm. After the supernatant had been discarded, the purified clay sample was then quick-frozen by liquid nitrogen, freeze-dried, and stored. The cation exchange capacity of the purified clay was determined by BaCl₂ Compulsive Exchange Method (42), and the value was 78.7 mequiv/100 g.

Adsorption Experiments. Adsorption batch experiments were conducted to obtain adsorption isotherms for carbaryl, mecoprop, and paraquat in the clay slurry. One hundred milligrams of original whole clay or purified clay and 10.0 mL of probe chemical solution with or without 0.02 M KCl were placed into 15 mL tubes; the pH was adjusted by 0.01 M HCl if needed. After 24 h of shaking, a 1.0 mL sample was placed in a 1.5 mL centrifuge vial. After 15 min of centrifuging at 10000 rpm in an Eppendorf MiniSpin Personal Microcentrifuge (Westbury, NY), the supernatant was collected for concentration analysis. The amount of adsorbed chemical was calculated on the basis of the difference in aqueous concentration between the initial time and 24 h. A batch experiment for desorption of mecoprop was conducted to obtain clay samples for XRD analysis. After 24 h of mixing to reach adsorption equilibrium, the clay slurry was centrifuged, and the supernatant was decanted as much as possible. Then fresh water was added to the tube, and the clay sample was remixed vigorously for the desorption experiment. A 0.5 mL sample was collected periodically for XRD analysis.

AFT Batch Experiments. All experiments were carried out in two 150 mL beakers; a scheme of the experimental apparatus is documented

elsewhere (31). Typically, 100.0 mL of probe chemical and clay slurry with 0.02 M KCl was added to the anodic half-cell, and the same volume of 0.08 M NaCl solution was added to the cathodic half-cell. These two half-cells were separated by an anion exchange membrane (Electrosynthesis Co., Inc., Lancaster, NY). Each of the half-cells was well stirred by a magnetic stir bar. Ferrous ion was generated by electrolysis in the anodic half-cell from a pure iron anode (0.5 cm × 10 cm × 0.2 cm). A graphite stick [1 cm (i.d.) × 10 cm (length)] was used as the cathode. The electrolysis current was controlled at 0.050 A by a BK Precision DC power supply 1610 (TestPath, Inc., Danvers, MA). Hydrogen peroxide solution (0.311 M) was delivered to the anodic half-cell using a STEPDOS Diaphragm Metering Pump (KNF Neuberger, Inc., Trenton, NJ) at a rate of 0.50 mL min⁻¹. When the first drop of hydrogen peroxide dropped into the anodic half-cell, the electrolysis current was turned on. Clay/solution ratio, molar ratio of H₂O₂ and Fe²⁺, and pH were kept at 1:100 (w/v), 10:1, and pH 3, respectively, unless specified, and all experiments were conducted at room temperature, 22 ± 1 °C. At given time intervals, a 0.7 mL sample was collected and added to a 1.5 mL Microfuge tube containing 0.7 mL of methanol, which was used to quench the hydroxyl radical and to extract probe chemicals (for carbaryl and mecoprop only) from the slurry to get the total concentration. The sample tubes were shaken for 15 min before being centrifuged for 15 min at a rate of 10000 rpm. The supernatant was collected for concentration analysis. The mass recoveries of carbaryl and mecoprop extraction were >98%. For paraquat clay slurry, only the aqueous phase concentrations were measured, and a 1.0 mL sample with the addition of 0.10 mL of methanol was centrifuged right after being collected. The experiments were repeated twice, unless specified.

XRD Analysis. Clay thin film samples for XRD analysis were prepared by air-drying several drops of clay slurry on glass slides. XRD spectra of clay films were obtained using a Scintag X-ray diffractometer equipped with Cu K radiation. The scanning angle (2θ) ranged from 2° to 35° at steps of 3° per minute.

Concentration Measurement. The concentrations of carbaryl, mecoprop, and paraquat were measured by an Agilent 1200 HPLC equipped with a DAD detector and an Agilent 6130 quadrupole mass spectrometer (Agilent Technologies, Inc., Santa Clara, CA). For carbaryl and mecoprop, the mobile phase was composed of 50% acetonitrile and 50% HPLC grade water (pH 3, adjusted by H₃PO₄); for paraquat, the mobile phase was composed of 40% acetonitrile and 60% 0.14 M NaCl water (pH 3, adjusted by HCl). A C₁₈ 5 μm, 150 mm × 4.6 mm (i.d.), Agilent reverse phase column was used. Flow rates were all set to 1.0 mL/min. The chosen UV wavelengths for carbaryl, mecoprop, and paraquat were 220, 200, and 257 nm, respectively.

RESULTS AND DISCUSSION

Adsorption of Carbaryl, Mecoprop, and Paraquat. Adsorption isotherms of carbaryl at pH 6.3, mecoprop at pH 7.8 and 3.0 in whole clay slurry, and mecoprop at pH 7.8 in purified clay slurry are shown in **Figure 1**. All isotherms are fitted with the Freundlich equation, $S = K_F C_e^{1/n}$, in which *S* (mg/g clay) is the mass of the adsorbed probe chemical per gram of clay, *C*_e is the equilibrium concentration of the probe chemical in aqueous solution, and *K*_F and 1/*n* are constants. Fitting parameters, *K*_F, 1/*n*, and *R*², are listed in **Table 1**.

With the same *K*_F (0.0203), but higher 1/*n* (0.95 vs 0.76), the results clearly show that the neutral compound (mecoprop at pH 3.0, whole clay) has a stronger affinity to montmorillonite clay than the anionic compound (mecoprop at pH 7.8, whole clay). Purified clay has a higher adsorption capacity than the whole clay, as indicated by its higher 1/*n* (1.157), due to its smaller size and higher surface area.

The adsorption isotherm of paraquat with purified clay, shown in **Figure 2**, appears to be a Langmuir type and thus different from the mecoprop and carbaryl isotherms, indicating different adsorption mechanisms. Strong electrostatic interaction between the cationic paraquat ions and negatively charged clay surfaces

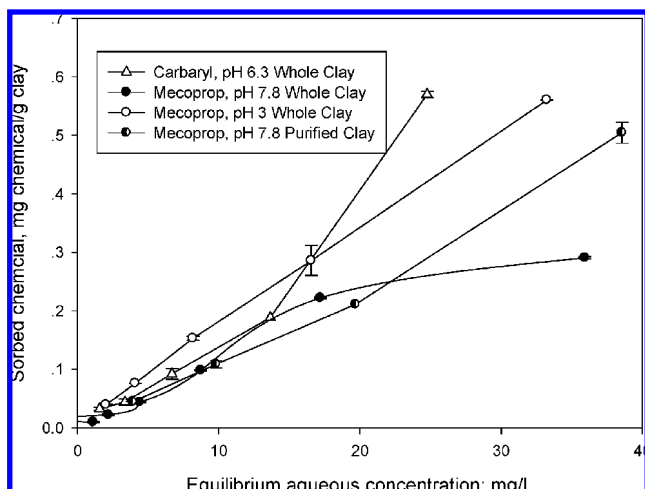


Figure 1. Adsorption isotherms for carbaryl (pH 6.3) and mecoprop (pH 7.8 and 3.0). Clay/solution ratio = 1:100 (w/v), with 0.02 M KCl.

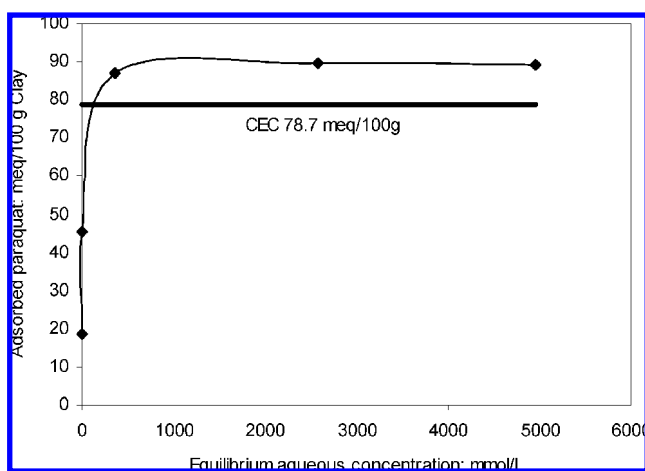


Figure 2. Adsorption isotherm for paraquat in purified montmorillonite clay. Clay/solution ratio = 1:100 (w/v).

Table 1. Freundlich Equation Fitting Parameters for Carbaryl and Mecoprop Adsorption Isotherms

	K_F	$1/n$	R^2
carbaryl, pH 6.3, whole clay	0.00449	1.51	0.990
mecoprop, pH 7.8, whole clay	0.0203	0.76	0.952
mecoprop, pH 3.0, whole clay	0.0203	0.95	0.996
mecoprop, pH 7.8, purified clay	0.00734	1.157	0.994

is the driving force for paraquat sorption, whereas for carbaryl and mecoprop other relatively weak interactions such as van der Waals forces or hydrogen bonding are responsible for the adsorption (43). On the basis of the isotherm, the maximum paraquat adsorption on the purified clay is 147.5 mg/g of clay, or 0.448 mmol/g of clay, equivalent to 89.6 mequiv/100 g of clay, larger than the CEC of the purified clay (78.7 mequiv/100 g), indicating that the purified clay adsorption is oversaturated.

To illustrate the change of clay interlayer distance caused by the adsorption of probe chemicals, the d spacing of clay layers (d_{001}) was obtained by XRD scanning. The results are shown in **Figure 3**, panels **a** and **b**, for mecoprop (0.01 M KCl, pH 7.8) and paraquat (without addition of electrolyte) adsorption on purified clay, respectively.

The initial slurry mecoprop concentrations are 0, 4.36, 43.6, 109, 218, and 436 ppm. For 0–108 ppm, there is no change in the peak or d_{001} (12.05 Å). However, when the concentration

reaches 218 ppm, a small shoulder peak (14.73 Å) appears on the left side of the main peak, and at 436 ppm initial concentration the shoulder peak becomes clearer and stronger, indicating the inclusion of mecoprop molecules at the clay interlayer. On the basis of the d spacing and the dimensions of the interlayer species, the disposition of the interlayer species can be inferred, as illustrated in **Figure 4a** (44). For the used montmorillonite clay, the thickness of its silicate layer is about 9.6 Å (44). Without mecoprop addition, a d_{001} value of 12.05 Å is the sum of the thickness of the silicate layer and two to three layers of water molecules (~2.5 Å) and K^+ (the existence of a small amount of Na^+ is also possible, because the clay is not K^+ saturated). When a small amount of mecoprop is added to the clay slurry, some of the mecoprop molecules may enter the clay interlayer and be adsorbed. However, the adsorbed amount is not high enough to expand the clay interlayer universally in the slurry, and the expansion is not detectable by XRD, but with an increased amount of mecoprop, the expanded layers become more and more universally distributed and are detected as such. The d_{001} is increased to 14.73 Å (new peak), which is about 5.1 Å greater than the silicate layer (9.6 Å); this increase is almost the same as the thickness of a mecoprop molecule, ~5 Å, as estimated by ChemBioOffice (45). This clearly indicates that a monolayer of planar mecoprop molecules (~5.1 Å) is formed at the interlayer, sitting parallel to the clay siloxane surface, which accounts for the appearance of the shoulder peak in **Figure 3**.

For the paraquat case, initial concentrations are 0, 310, 775, 1550, 2324, and 3099 ppm without the addition of KCl. On the basis of the XRD result, without paraquat addition, the value of d_{001} is 15.21 Å. The larger d_{001} here can be compared with the d_{001} of 12.05 Å for mecoprop and is due to the larger hydration radius of Na^+ (1.85 Å) versus K^+ (1.26 Å) (46). A shoulder peak (12.58 Å) appears on the right side of the main peak with the addition of 310 ppm of paraquat. On the basis of the LC-MS measurement, there is no paraquat remaining in the aqueous solution, indicating complete adsorption. With the increase of initial paraquat concentration, the shoulder peak becomes stronger, whereas the left peak becomes weaker until it totally disappears at an initial paraquat concentration of 1550 ppm. Such a reduction in d spacing may indicate water exclusion from the clay interlayer, as reported by other researchers (47). Compared with the left peak, the width of the right peak is much smaller, indicating a very good homogeneity of the clay sample after paraquat adsorption. The disposition of paraquat at the clay interlayer can also be inferred, as illustrated in **Figure 4b**. After adsorption, the d_{001} is decreased to 12.58 Å, which is equivalent to the silicate layer plus ~3 Å, the same as the estimated thickness of a paraquat cation (~3 Å), indicating a flat and tight disposition of planar paraquat cations at the clay interlayer. Due to the presence of paraquat and strong electrostatic forces, the clay layers come closer together, changing the clay's swelling property, as inferred by the occurrence of coagulation and flocculation of the clay particles with paraquat addition.

AFT Treatment of Carbaryl. Montmorillonite clay slurries with different initial carbaryl concentrations were treated by AFT, and the results are shown in **Figure 5**. Carbaryl can be effectively removed from the slurry in 10 min at the tested concentration ranges. The degradation curves were fitted with the classic AFT model (31) with very good correlations. This result is similar to our previous study on kaolinite clay slurry were not affected by the presence of the clay due to the extremely low adsorption of carbaryl.

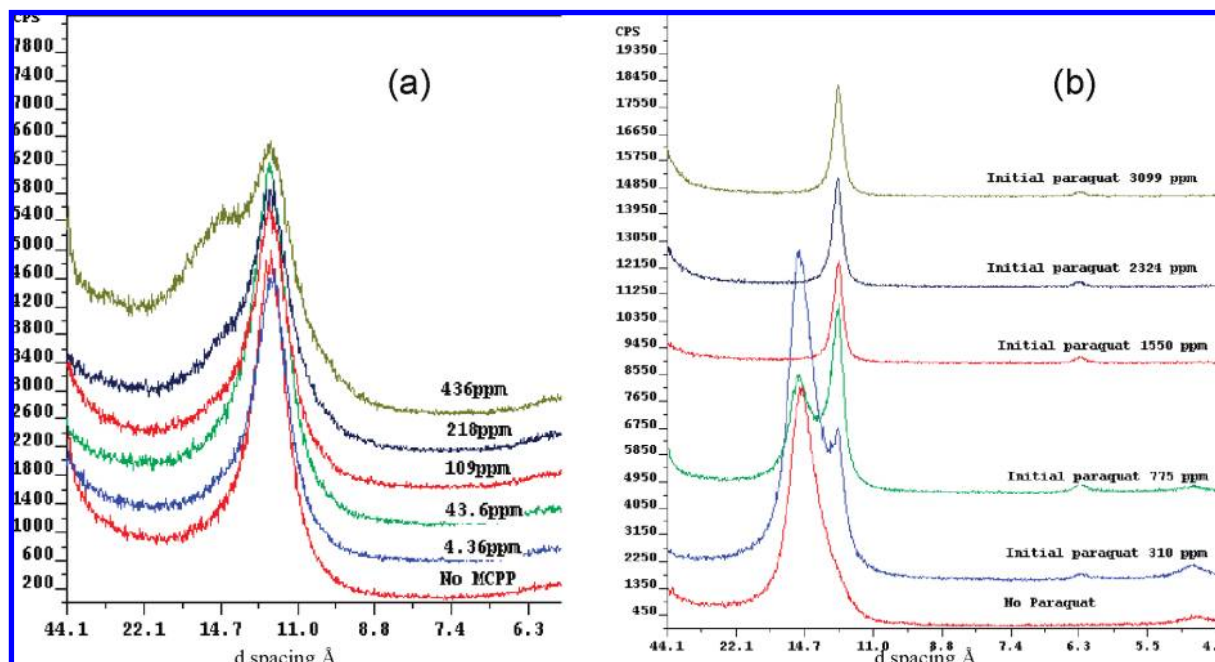


Figure 3. XRD of purified montmorillonite clay with different amounts of sorbed (a) mecoprop and (b) paraquat. Clay/solution ratio = 1:100 (w/v), 0.02 M KCl, pH 7.8; figures shown are initial probe chemical concentrations in the slurry.

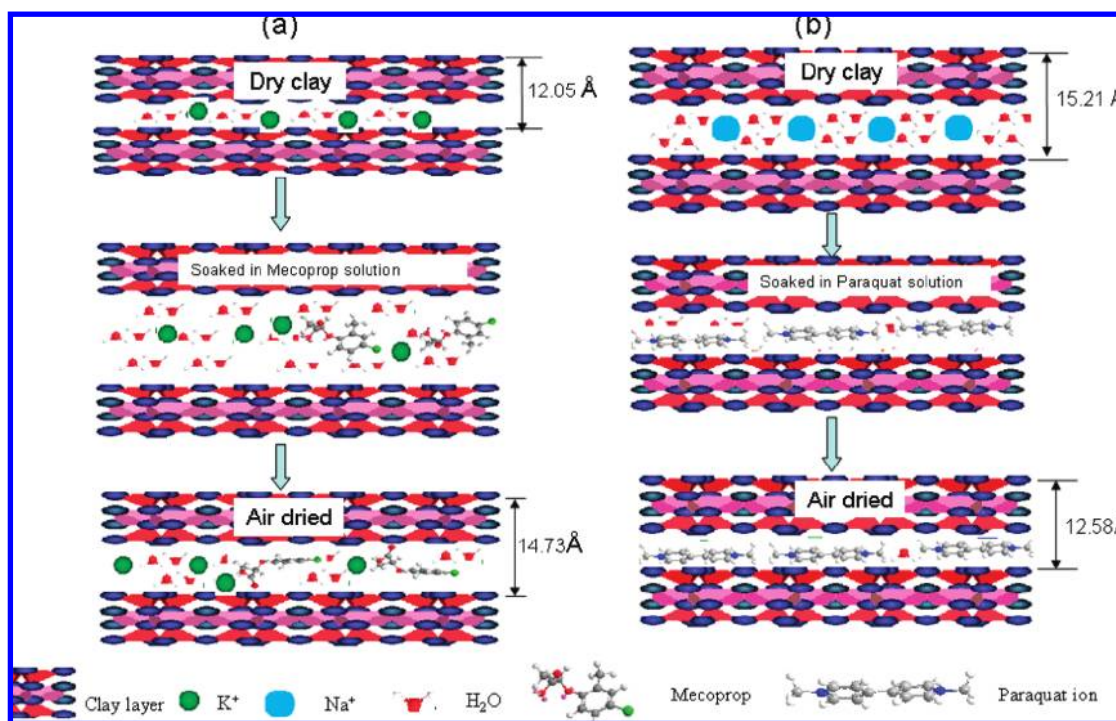


Figure 4. Illustration of mecoprop (a) and paraquat (b) adsorption on montmorillonite clay.

However, in both cases, the carbaryl degradation rates were lower compared with those in a pure aqueous system (data not shown), most likely due to the lower hydroxyl radical generation efficiency in the clay slurry due to the ion exchange process between clay interlayer cations and hydrogen and ferrous ions in the aqueous phase of the slurry. In typical aqueous AFT the solution pH in the anodic half-cell drops quickly after treatment begins (48), a great advantage for the Fenton reaction, which favors an acidic environment. However, in the presence of clay this advantage is diminished by the cation exchange process, with a resulting lower hydroxyl radical generation efficiency.

AFT Treatment of Mecoprop. Degradation of anionic mecoprop (pH 7.8) and neutral mecoprop (pH 3.0) in purified

montmorillonite clay slurry at different initial concentrations was investigated. The results are shown in **Figure 6a**. On the basis of the figure, mecoprop can be completely degraded in the slurries at both pH 7.8 and pH 3.0 in 15 min at the tested concentration ranges. However, at pH 3.0, the degradation rates are much faster because of the higher hydroxyl radical generation efficiency discussed in the previous section. Adsorption of mecoprop was shown to be stronger at the lower pH, but the AFT results indicate that the sorption process is not an influential factor for the degradation rates and that adsorbed mecoprop can be easily removed by AFT.

Experimental data were fitted with the slurry AFT model ($R^2 > 0.99$), and the fitting curves are shown in solid and dotted

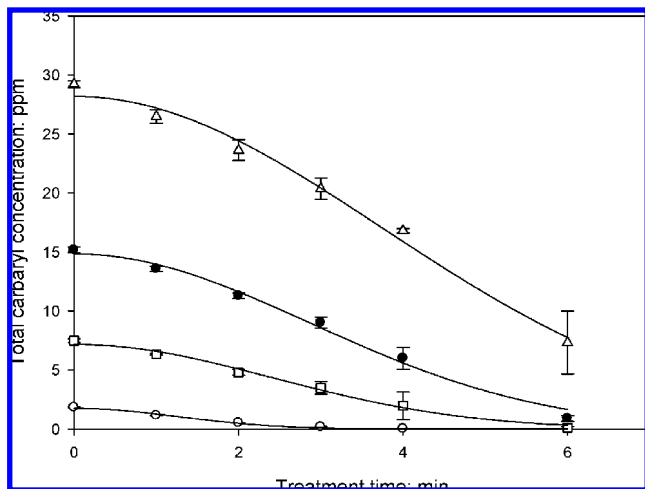


Figure 5. Degradation of carbaryl with different initial concentrations in montmorillonite clay slurry. Dots are experimental data, and lines are fitting curves with AFT model. Clay/solution ratio = 1:100 (w/v), 0.02 M KCl, pH 6.3.

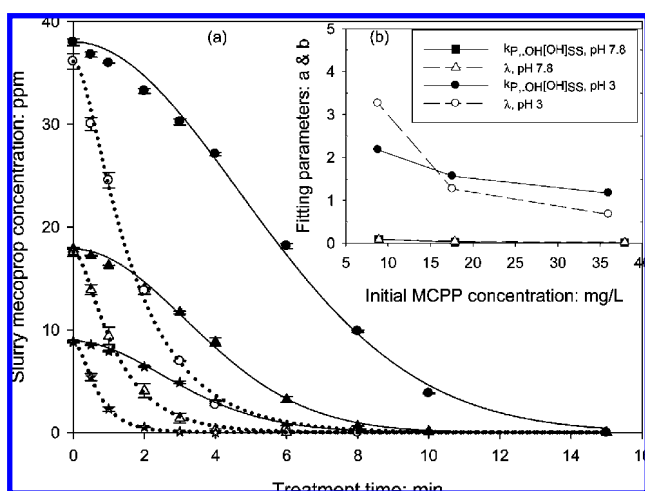


Figure 6. (a) Degradation of mecoprop in montmorillonite clay slurry at pH 7.8 and 3.0. Dots are experimental data, and lines are fitting curves with slurry AFT model. (b) Model fitting parameters. Clay/solution ratio = 1:100 (w/v), 0.02 M KCl.

lines for pH 7.8 and 3.0, respectively. The model equation is shown below; detailed model development was documented elsewhere (40).

$$[P]_t = ([P]_0 - \delta) e^{-k_{p,\text{OH}}[\text{OH}]_{\text{SS}}[t - (1 - e^{-\lambda t})/\lambda]} + \delta \quad (1)$$

$[P]_0$ and $[P]_t$ are mecoprop concentrations (ppm or μM) at $t = 0$ and t , respectively; δ is the residue mecoprop concentration (ppm or μM) that is not available for degradation; $k_{p,\text{OH}}$ is the reaction rate constant between mecoprop and hydroxyl radical ($\text{min}/\mu\text{M}$), $[\text{OH}]_{\text{SS}}$ is the steady state hydroxyl radical concentration (μM), and λ is a coefficient related to the production and consumption of hydroxyl radical (min^{-1}).

There are three fitting parameters for the model, $k_{p,\text{OH}}[\text{OH}]_{\text{SS}}$, δ , and λ . On the basis of the fitting results, δ values are all very small ($<10^{-8}$), in accordance with complete mecoprop removal by the treatment. Values of $k_{p,\text{OH}}[\text{OH}]_{\text{SS}}$, and λ are plotted in **Figure 6b**. At lower pH, values of $k_{p,\text{OH}}[\text{OH}]_{\text{SS}}$, and λ are much higher, indicating higher hydroxyl radical concentration and faster approach to the steady state, resulting in faster degradation.

To further confirm that this treatment process is able to remove chemicals sitting at the clay interlayer, two clay slurry

samples with high mecoprop concentration (436 ppm) were prepared. One clay slurry sample was treated by AFT, and samples were collected on glass slides for XRD analysis, as shown in **Figure 7a**. On the basis of **Figure 7a**, it is clear that, after the treatment begins, the left shoulder peak becomes weaker and weaker, until it totally disappears at 10 min; moreover, the main peak becomes sharper as treatment time increases. This evidence clearly demonstrates that the interlayer mecoprop has been removed during the treatment process. To investigate whether the desorption process is mainly responsible for this removal or not, the other high mecoprop concentration sample underwent a desorption experiment, and samples at different desorbing time intervals were collected for XRD analysis, as shown in **Figure 7b**. On the basis of the XRD results, even after 6 h of desorption, the left shoulder peak is still strong, although it weakens with desorption time, indicating a much lower desorption rate compared with the degradation rate. This fact clearly rules out the desorption effect as the sole removal mechanism of interlayer mecoprop. It can be reasonably inferred that interlayer mecoprop is removed by either direct attack from hydroxyl radicals or accelerated desorption in the AFT system or by a combination of both mechanisms. Collectively, XRD results strongly confirm that AFT is capable of effectively removing interlayer mecoprop.

AFT Treatment of Paraquat. Due to its extremely strong adsorption, it is difficult to establish an effective method to extract paraquat from the clay slurry. In this set of AFT experiments for treatment of paraquat (initial slurry concentration = 1549.5 mg/L) and purified clay slurry (without addition of salt electrolytes), samples were collected for aqueous concentration measurement and XRD analysis, with the objective to investigate whether there is interlayer paraquat removal.

Aqueous paraquat concentration change during AFT is shown in **Figure 8a**, and the data clearly indicate that paraquat can be effectively removed from the aqueous phase. It is interesting to note that there appears to be an increase in aqueous paraquat concentration after the treatment begins, reaching a high point at 3 min, before the concentration starts to decrease quickly. This anomaly in the degradation curve is believed to be due to the desorption of paraquat that is loosely adsorbed on the oversaturated clay surface as shown in the adsorption isotherm. XRD analysis of the clay is shown in **Figure 8b**. If there were significant removal of interlayer paraquat, some of the clay layer might be re-expanded due to the removal of the strong attractive forces between paraquat and the clay layers, and it should be detected by XRD. However, on the basis of the XRD results, even after 1 h of AFT treatment, the d_{001} peak remains sharp and unchanged, indicating no or very limited interlayer paraquat removal.

On the basis of the degradation results of these three widely used agrichemicals, we conclude that the AFT is capable of degrading carbaryl and mecoprop completely from the clay interlayer, whereas interlayer paraquat could not be removed by AFT. This study of the adsorption and degradation behaviors of carbaryl, mecoprop, and paraquat, in an SWy-2 montmorillonite clay slurry, is useful for understanding potential remediation methods. On the basis of their chemical properties the chemicals can be divided into two groups: neutral and anionic (carbaryl and mecoprop) and cationic (paraquat). Carbaryl and mecoprop have a weak affinity to SWy-2 clay. For the highest tested initial concentration of mecoprop in the adsorption experiments, 535.0 ppm, the amounts of sorbed mecoprop on the clay are 8.0 mg/g of clay (pH 7) and 12.6 mg/g of clay (pH 3.0), far less than the maximum amount of sorbed paraquat,

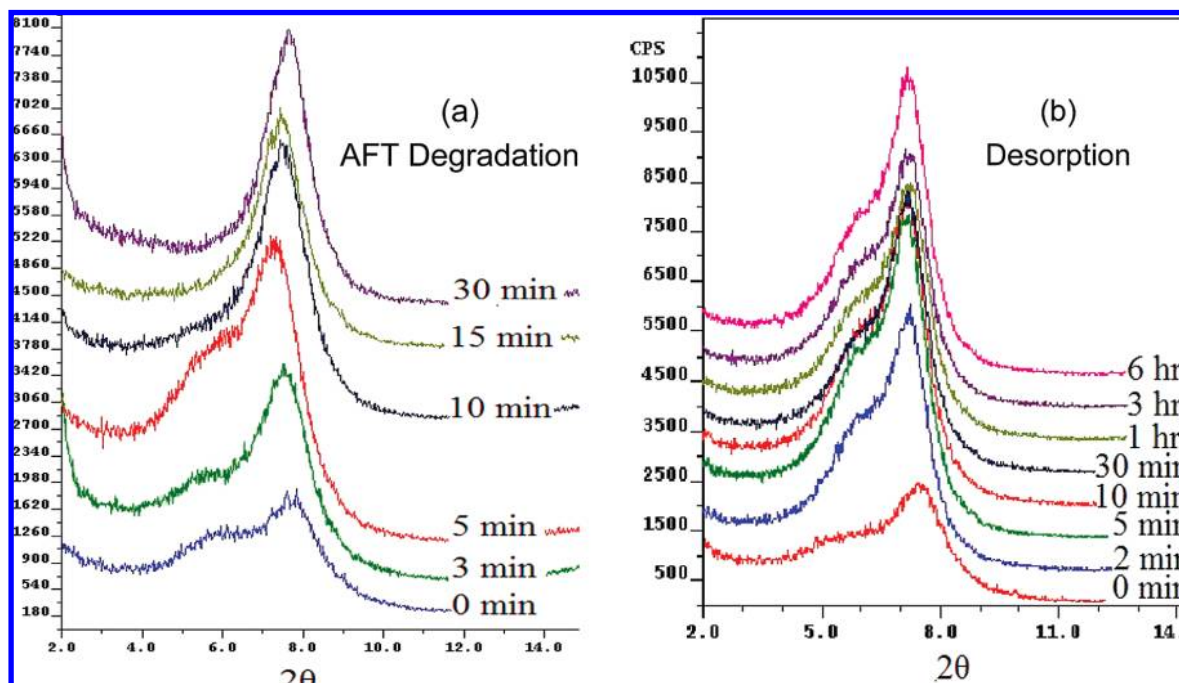


Figure 7. XRD analysis of montmorillonite clay during (a) AFT degradation and (b) mecoprop desorption processes. Clay/solution ratio = 1:100 (w/v), 0.02 M KCl, pH 7.8.

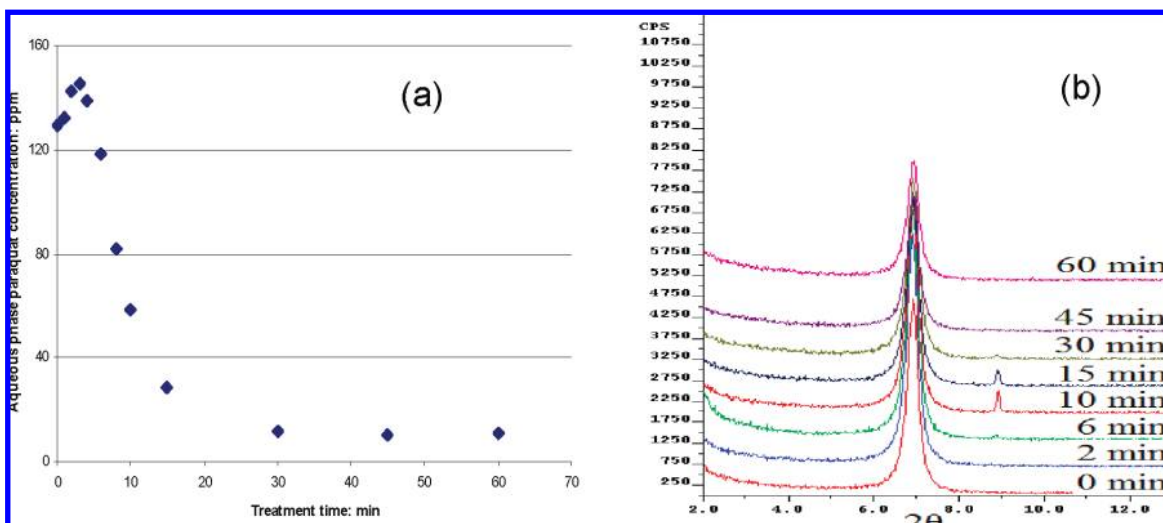


Figure 8. (a) Aqueous paraquat concentration and (b) XRD analysis of montmorillonite clay, during AFT degradation process. Clay/solution ratio = 1:100 (w/v), no KCl addition.

147.5 mg/g of clay. The dipole–dipole force or hydrogen bonding is one of the most important mechanisms believed to be responsible for the adsorption of neutral carbaryl and mecoprop molecules and mecoprop anions on the montmorillonite surface. Through *ab initio* simulation (49), researchers have found that, in the presence of water molecules and due to hydration, formation of complexes (cations as bridges connecting organics and clay surfaces) between counterions and organic anions (2,4-D) is not preferred; however, there are three types of hydrogen bonding formed among species (water and 2,4-D anions) at montmorillonite surfaces. They are hydrogen bonds among water molecules themselves, between water molecules and the 2,4-D anions, and between water molecules and the clay basal siloxane oxygen atoms. Apparently, water molecules act as a bridge between 2,4-D anions and the clay surface. Mecoprop has a structure and functional groups similar to those of 2,4-D, and the carbaryl molecule also has the nitrogen and oxygen atoms necessary for forming hydrogen bonds. Therefore,

hydrogen bonding should be an important adsorption mechanism for these two chemicals.

Through XRD analysis, although it was found that sorbed mecoprop forms a monolayer between montmorillonite clay layers, it should be noted that the XRD sample was air-dried, which was different from the original clay slurry sample. In an air-dried sample, there are limited water molecules between clay layers, whereas in the slurry sample, the clay is soaked with water and the clay is swelling. Through computer simulations (50, 51) it was found that noncationic organic molecules show a tendency to remain completely in the expanded interlayer aqueous phase, if the clay was soaked with water. In the slurry, due to the swelling of layered montmorillonite clay, Fenton reagents are able to actually enter into this interlayer aqueous phase. As a result, hydroxyl radicals can be generated locally at the clay interlayer aqueous phase, and interlayer organic molecules can be attacked by the interlayer-produced hydroxyl radicals. This is believed to be the main reason for the quick

and complete removal of mecoprop from the clay interlayer, as shown in the experimental data.

Paraquat has a completely different scenario. As stated previously, with the addition of paraquat to the montmorillonite clay slurry, the expanded clay began to shrink, squeezing out water molecules from the interlayer, and coagulation, flocculation, and precipitation occurred. Due to the lack of enough water molecules, Fenton reagents are not able to enter into the clay interlayer and there are no interlayer-produced hydroxyl radicals. As a result, the removal of interlayer paraquat is nonexistent or quite limited, as shown by XRD analysis.

These findings may benefit our understanding of the fate, transport, and transformation of organic pollutants in soil and have important implications for selecting soil remediation strategies. Except for nitroaromatic compounds, which have distinct adsorption mechanisms on smectite clay (52), for most other neutral or anionic organic pollutants, their adsorption on SOM generally outweighs their adsorption on clays, and SOM is a more important factor to study the fate and transport of organic pollutants in soil. For cationic organic chemicals, their adsorption on clay will be more important, especially in soils with a large content of layered clays with high CEC because they cannot be removed effectively by AFT at the clay interlayer. The Fenton reaction-based AFT process is capable of removing neutral or anionic organic chemicals adsorbed at the clay interlayer effectively, which is an advantage over bioremediation methods as discussed in the Introduction. The AFT method is an effective and reliable option for treatment, on a small scale, of soils that are highly contaminated by organic pollutants.

LITERATURE CITED

- (1) Sparks, D. L. *Environmental Soil Chemistry*, 2nd ed.; Academic Press: San Diego, CA, 2003; p 111.
- (2) Chiou, C. T.; Peters, L. J.; Freed, V. H. A physical concept of soil-water equilibria for nonionic organic compounds. *Science* **1979**, *206* (4420), 831–832.
- (3) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environ. Sci. Technol.* **1983**, *17*, 227–231.
- (4) Theng, B. K. G.; Greenland, D. J.; Quirk, J. P. Adsorption of alkylammouim cations by montmorillonite. *Clay Minerals* **1967**, *7*, 1–17.
- (5) Tucker, B. V.; Pack, D. E.; Ospenson, J. N. Adsorption of bipyridylum herbicides in soil. *J. Agric. Food Chem.* **1967**, *15*, 1005–1008.
- (6) de Keizer, A. Adsorption of paraquat ions on clay minerals. Electrophoresis of clay particles. *Interfaces Condens. Syst.* **1990**, 118–126.
- (7) Smith, S. C.; Ainsworth, C. C.; Traina, S. J.; Hicks, R. J. Effect of sorption on the biodegradation of quinoline. *Soil Sci. Soc. Am. J.* **1992**, *56* (3), 737–746.
- (8) Jones, D. L.; Edwards, A. C. Influence of sorption on the biological utilization of two simple carbon substrates. *Soil Biol. Biochem.* **1998**, *30* (14), 1895–1902.
- (9) Masaphy, S.; Fahima, T.; Levanon, D.; Henis, Y.; Mingelgrin, U. Parathion degradation by *Xanthomonas* sp. and its crude enzyme extract in clay suspensions. *J. Environ. Qual.* **1996**, *25* (6), 1248–1255.
- (10) Crocker, F. H.; Guerin, W. F.; Boyd, S. A. Bioavailability of naphthalene sorbed to cationic surfactant-modified smectite clay. *Environ. Sci. Technol.* **1995**, *29*, 2953–2958.
- (11) Miller, M. E.; Alexander, M. Kinetics of bacterial degradation of benzylamine in a montmorillonite suspension. *Environ. Sci. Technol.* **1991**, *25*, 240–245.
- (12) Steinberg, S. M.; Pignatello, J. J.; Sawhney, B. L. Persistence of 1,2-dibromoethane in soils: entrapment in intraparticle micropores. *Environ. Sci. Technol.* **1987**, *21*, 1201–1208.
- (13) Pignatello, J. J.; Sawhney, B. L.; Frink, C. R. EDB: persistence in soil. *Science* **1987**, *236*, 898.
- (14) Kwan, W. P.; Voelker, B. M. Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems. *Environ. Sci. Technol.* **2003**, *37*, 1150–1158.
- (15) Chen, F.; Ma, W.; He, J.; Zhao, J. Fenton degradation of malachite green catalyzed by aromatic additives. *J. Phys. Chem. A* **2002**, *106*, 9485–9490.
- (16) Fongsatitkul, P.; Elefsiniotis, P.; Yamasmit, A.; Yamasmit, N. Use of sequencing batch reactors and Fenton's reagent to treat a wastewater from a textile industry. *Biochem. Eng. J.* **2004**, *21*, 213–220.
- (17) Moraes, J. E. F.; Quina, F. H.; Nascimento, C. A. O.; Silva, D. N.; Chiavone-Filho, O. Treatment of saline wastewater contaminated with hydrocarbons by the photo-Fenton process. *Environ. Sci. Technol.* **2004**, *38*, 1183–1187.
- (18) Watts, R. J.; Bottenberg, B. C.; Hess, T. F.; Jensen, M. D.; Teel, A. L. Role of reductants in the enhanced desorption and transformation of chloroaliphatic compounds by modified Fenton's reactions. *Environ. Sci. Technol.* **1999**, *33*, 3432–3437.
- (19) Watts, R. J.; Bottenberg, B. C.; Jensen, M. D.; Hess, T. H.; Teel, A. L. Mechanism of the enhanced treatment of chloroaliphatic compounds by Fenton-like reactions. *Environ. Sci. Technol.* **1999**, *33*, 3432–3437.
- (20) Tyre, B. W.; Watts, R. J.; Miller, G. C. Treatment of four biorefractory contaminants in soils using catalyzed hydrogen peroxide. *J. Environ. Qual.* **1991**, *20*, 832–838.
- (21) Watts, R. J.; Udell, M. D.; Rauch, P. A. Treatment of pentachlorophenol-contaminated soils using Fenton's reagent. *Hazard. Waste Hazard. Mater.* **1990**, *7* (4), 335–345.
- (22) Watts, R. J.; Kong, S.; Dippre, M.; Barnes, W. T. Oxidation of sorbed hexachlorobenzene in soils using catalyzed hydrogen peroxide. *J. Hazard. Mater.* **1994**, *39* (1), 33–47.
- (23) Watts, R. J.; Jones, A. P.; Chen, P. H.; Kenny, A. Mineral catalyzed Fenton-like oxidation of sorbed chlorobenzenes. *Water Environ. Res.* **1997**, *69* (2), 269–275.
- (24) Yang, G. C. C.; Liu, C.-Y. Remediation of TCE contaminated soils by in situ EK-Fenton process. *J. Hazard. Mater.* **2001**, *B85*, 317–331.
- (25) Pignatello, J. J.; Baehr, K. Ferric complexes as catalysts for "Fenton" degradation of 2,4-D and metolachlor in soil. *J. Environ. Qual.* **1994**, *23*, 365–370.
- (26) Li, Z. M.; Peterson, M. M.; Comforta, S. D.; Horstb, G. L.; Shea, P. J.; Oh, B. T. Remediating TNT-contaminated soil by soil washing and Fenton oxidation. *Sci. Total Environ.* **1997**, *204*, 107–115.
- (27) Flotron, V.; Delteil, C.; Padellec, Y.; Camel, V. Removal of sorbed polycyclic aromatic hydrocarbons from soil, sludge and sediment samples using the Fenton's reagent process. *Chemosphere* **2005**, *59*, 1427–1437.
- (28) Bogan, B. W.; Trbovic, V.; Paterek, J. R. Inclusion of vegetable oils in Fenton's chemistry for remediation of PAH-contaminated soils. *Chemosphere* **2003**, *50*, 15–21.
- (29) Bier, E. L.; Singh, J.; Li, Z.; Comfort, S. D.; Shea, P. J. Remediating hexahydro-1,3,5-trinitro-1,2,5-triazine-contaminated water and soil by Fenton oxidation. *Environ. Toxicol. Chem.* **1999**, *18*, 1078–1084.
- (30) Wang, Q.-Q.; Lemley, A. T. Oxidation of carbaryl in aqueous solution by membrane anodic Fenton treatment. *J. Agric. Food Chem.* **2002**, *50*, 2331–2337.
- (31) Wang, Q.-Q.; Lemley, A. T. Kinetic model and optimization of 2,4-D degradation by anodic Fenton treatment. *Environ. Sci. Technol.* **2001**, *35*, 4509–4514.
- (32) Wang, Q.-Q.; Lemley, A. T. Competitive degradation and detoxification of carbamate insecticides by membrane anodic Fenton treatment. *J. Agric. Food Chem.* **2003**, *51*, 5382–5390.
- (33) Saltmiras, D. A.; Lemley, A. T. Atrazine degradation by anodic Fenton treatment. *Water Res.* **2002**, *36*, 5113–5119.

- (34) Saltmiras, D. A.; Lemley, A. T. Degradation of ethylene thiourea (ETU) with three Fenton treatment processes. *J. Agric. Food Chem.* **2000**, *48*, 6149–6157.
- (35) Saltmiras, D. A.; Lemley, A. T. Anodic Fenton treatment of treflan MTF®. *J. Environ. Sci. Health Part A: Toxic/Hazard. Subst. Environ. Eng.* **2001**, *A36*, 261–274.
- (36) Wang, Q.-Q.; Lemley, A. T. Oxidative degradation and detoxification of aqueous carfuran by membrane anodic Fenton treatment. *J. Hazard. Mater.* **2003**, *B98*, 241–255.
- (37) Wang, Q.-Q.; Lemley, A. T. Competitive degradation and detoxification of carbamate insecticides by membrane anodic Fenton treatment. *J. Agric. Food Chem.* **2003**, *51*, 5382–5390.
- (38) Wang, Q.-Q.; Lemley, A. T. Kinetic effect of humic acid on alachlor degradation by anodic fenton treatment. *J. Environ. Qual.* **2004**, *33*, 2343–2352.
- (39) Kong, L.; Lemley, A. T. Kinetic modeling of 2,4-dichlorophenoxyacetic acid (2,4-D) degradation in soil slurry by anodic Fenton treatment. *J. Agric. Food Chem.* **2006**, *54*, 3941–3950.
- (40) Ye, P.; Kong, L.; Lemley, A. T. Kinetics of carbaryl degradation by anodic fenton treatment in a humic acid amended artificial soil slurry. *Water Environ. Res.* **2008**, in press.
- (41) Arroyo, L. J.; Li, H.; Teppen, B. J.; Johnston, C. T.; Boyd, S. A. Hydrolysis of carbaryl by carbonate impurities in reference clay SWy-2. *J. Agric. Food Chem.* **2004**, *52*, 8066–8073.
- (42) Sumner, M. E.; Miller, W. P. Cation exchange capacity and exchange coefficients. In *Methods of Soil Analysis: Chemical Methods. Part 3*; Sparks, D. L., Ed.; Soil Science Society of America: Madison, WI, 1996; pp 1201–1229.
- (43) Ruiz-Hitzky, E.; Aranda, P.; Serratos, J. M. Clay–organic interactions: organoclay complexes and polymer-clay nanocomposites. In *Handbook of Layered Materials*; Auerbach, S. M., Carrado, K. A., Dutta, P. K., Eds.; Dekker: New York, 2004; pp 91–154.
- (44) Hermosin, M. C.; Martin, P.; Cornejo, J. Adsorption mechanisms of monobutyltin in clay minerals. *Environ. Sci. Technol.* **1993**, *27*, 2606–2611.
- (45) CambridgeSoft ChemBioOffice Ultra, 2008.
- (46) Glaser, R. *Biophysics*, 5th ed.; Springer: Berlin, Germany, 2001; p 60.
- (47) Rytwo, G.; Nir, S.; Margulies, L. A model for adsorption of divalent organic cations to montmorillonite. *J. Colloid Interface Sci.* **1996**, *181* (2), 551–560.
- (48) Wang, Q.; Lemley, A. T. Oxidation of diazinon by anodic Fenton treatment. *Water Res.* **2002**, *36* (13), 3237–3244.
- (49) Tunega, D.; Gerzabek, M. H.; Haberhauer, G.; Lischka, H. Formation of 2,4-D complexes on montmorillonites—an ab initio molecular dynamics study. *Eur. J. Soil Sci.* **2007**, *58* (3), 680–691.
- (50) Teppen, B. J.; Yu, C.-H.; Miller, D. M.; Schaer, L. Molecular dynamics simulations of sorption of organic compounds at the clay mineral/aqueous solution interface. *J. Comput. Chem.* **1998**, *19* (2), 144–153.
- (51) Yu, C.-H.; Newton, S.; Norman, M.; Schäfer, L.; Miller, D. Molecular dynamics simulations of adsorption of organic compounds at the clay mineral/aqueous solution interface. *Struct. Chem.* **2003**, *14* (2), 175–185.
- (52) Boyd, S. A.; Sheng, G.; Teppen, B. J.; Johnston, C. T. Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays. *Environ. Sci. Technol.* **2001**, *35*, 4227–4234.

Received for review June 23, 2008. Revised manuscript received September 2, 2008. Accepted September 3, 2008. The study was funded in part by the College of Human Ecology and the Department of Fiber Science and Apparel Design, Cornell University, and in part by the Cornell University Agricultural Experiment Station federal formula funds, Project NYC-329806 (W-1045), received from Cooperative State Research, Education, and Extension Service, U.S. Department of Agriculture. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors and do not necessarily reflect the view of the U.S. Department of Agriculture.

JF801922R