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Removal of Alachlor and Pretilachlor by Laboratory-Synthesized Zerovalent Iron in Pesticide Formulation Solution

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Pesticides are of the main contaminants in the agricultural environment, as they have been extensively used in the control of pests and weeds. One of the main routes of pesticide contamination is movement from treated soil and crop into ground and surface waters. Pesticides can reach the ground water by leaching into the deeper soil and can also readily flow out into the aquatic environment from agricultural fields via runoff (Nakano et al 2004). The contamination of soil and water with pesticides poses potential threats to aquatic ecosystems and human health, as certain pesticides exhibit acute and chronic toxicity. Thus, technologies are required for the effective removal of pesticides from the water/soil environment.

The technologies involved in the removal of pesticides from agricultural waters include adsorption within the organic matrix, biological and chemical degradation and phytoremediation using plants. The chemical degradation using zerovalent iron (Fe^0) has proven a cost-effective treatment for the remediation of contaminated waters and soils. Fe^0 has been used to increase the dechlorination of halogenated chemicals (Lowry and Johnson 2004), chloroacetanilide and triazine herbicides (Gaber et al 2002; Gibb et al 2004) and the reduction of the nitro group of explosives (Gregory et al 2004). Using Fe^0 for treatment of pesticide-contaminated samples is based on the fact that many pesticides contain moieties that can be reduced when coupled to the oxidation of iron metal with Fe^0 and Fe(II) serving as reductants.

Alachlor and pretilachlor both belong to the chloroacetanilide class of herbicides, which have been used extensively in paddy fields in Korea since 1984. These herbicides are water soluble at a concentration range of 50 to 242 mg/L, and have been known to be toxic to aquatic animals (Tomlin 2003). Although the acetanilide herbicides are known to bind to humic acids of organic soils (Wang et al 1999), they have also been found in river and ground waters at variable concentrations (Spalding et al 2003; Tanabe et al 2001). Considering the potential that herbicides adsorbed to the soil matrix may be desorbed and may ultimately reach the water table and soil-water layer, technologies are needed to effectively remove and degrade them. The objective of the present study was to examine the removal of alachlor and pretilachlor by laboratory-synthesized zerovalent iron. The commercial purchase of Fe^0 in Korea is somewhat difficult, as most of countries that produce

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Fe^0 do not sell to other countries. Thus, an alternative approach for the removal of pesticides and other contaminants using Fe^0 involves the preparation of laboratory-synthesized iron metal. Batch experiments were conducted in order to investigate the removal of alachlor and pretilachlor from waters treated with the herbicide formulations.

MATERIALS AND METHODS

Reference standards of alachlor (purity 99.5%) and pretilachlor (96.0%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All solvents were HPLC grade and were purchased from Fisher Scientific (Pittsburgh, PA, USA). All other chemicals were of analytical grade and commercially available, unless otherwise stated.

Nanoscale zerovalent iron was synthesized by dropwise addition of 1.6 *M* $NaBH_4$ solution to 1 *M* $FeCl_3{\cdot}6H_2O$ solution at an ambient temperature with magnetic stirring as previously described (Wang and Zang 1997). The solution was stirred for 40 min and centrifuged at 8 000 x g for 10 min to obtain the Fe^0 precipitates. The Fe^0 precipitates were washed twice with acetone and dried at 110°C for 6 hr under a gentle stream of N_2. The resultant black zerovalent iron powder was then stored in N_2 purged desiccators until use.

For batch experiments of the removal of alachlor and pretilachlor, Fe^0 (0.6 g) was added to triplicate 50 mL centrifuge tubes containing 30 mL of pesticide-formulation solutions of Lasso (emulsifiable concentrate for alachlor) and Solnet (emulsifiable concentrate for pretilachlor) at 240 and 50 mg kg^{-1}, respectively. These concentrations were the rate of water solubility. Preliminary experiment showed that the 0.6 g of the iron was optimum for reacting with 30 mL of the pesticide solution. The tubes were capped and incubated at ambient temperature on a shaker at 150 rpm. Parallel experiments were also conducted without Fe^0 or the herbicide solution. Periodically, triplicate tubes were taken and centrifuged at 8 000 x g for 10 min. The supernatants were extracted with 50 mL of ethyl acetate and the organic phase was collected. The organic phase was dehydrated over anhydrous sodium sulfate and subjected to gas chromatographic analysis. The concentrations of alachlor and pretialchlor were determined quantitatively on the basis of their calibration curves. All experiments were conducted triplicate, otherwise stated. The statistical analyses were performed by using a Microsoft Excel computer program (Windows® NT).

Gas chromatographic analysis was conducted using a Hewlett Packard 6890 model gas chromatograph (GC) equipped with ^{64}Ni electron capture detector (ECD). The column was an HP-5 capillary column (0.25 mm i.d. × 30 m length, 1.0 μm thickness) and the carrier gas was helium at a flow rate of 1 mL/min. Injection was made in split mode of 50:1. The column temperature was held at 100°C for 2 min and increased to 280°C by a rate of 10°C/min. The injector and detector temperatures were 250 and 300°C, respectively.

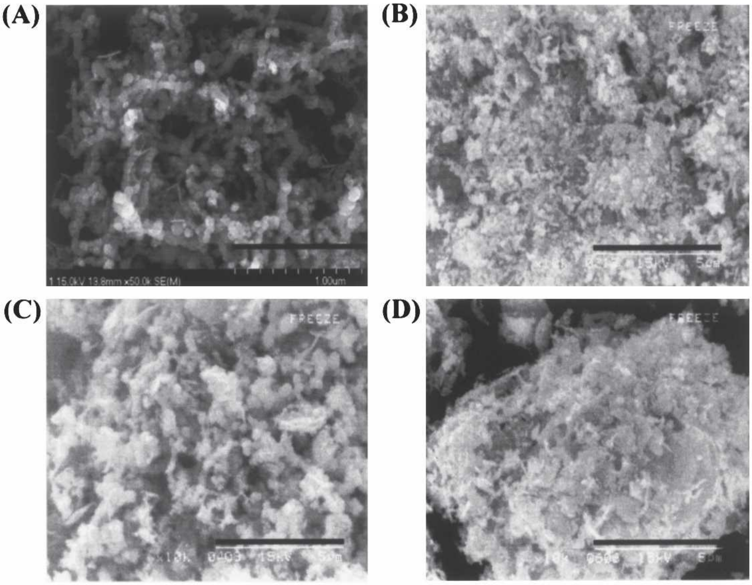

Figure 1. Scanning electron microscopy image of laboratory-synthesized zerovalent iron particles before (A) and after reaction with the pesticide solution for 6 (B), 12 (C) and 24 hr (D). Scale bars of the zerovalent iron before and after reaction are 1and 5 μm, respectively.

To determine the degradation products of alachlor and pretilachlor, GC/MS analysis was conducted using an Agilent model 5973N system with HP-5MS capillary column (0.25 mm i.d. × 30 m length, 1.0 μm thickness). GC conditions for mass spectrometric analysis were the same as described above. Mass spectroscopy was in the electron ionization (EI) mode at 70 eV. Mass value was scanned from 50 to 500 amu at 2.94 sec per scan. The scanning electron microscopy analysis was conducted using a JEOL model JSM-840A SEM (Japan) as described previously (Kanel et al 2005).

RESULTS AND DISCUSSION

Figure 1 shows the scanning electron microscopy (SEM) data of the zerovalent iron synthesized in this study. The zerovalent iron particles were measured in a size range of 10-100 nm by SEM (Figure 1A), which suggests that our zerovalent iron is nanoscale iron particles. When the nanoscale zerovalent iron (NZVI) was treated with the pesticide solutions and a time-course SEM analysis of NZVI was conducted, an increase in particle aggregation was observed (Figure 1B, 1C, 1D). Aggregation of zerovalent iron particles has been demonstrated in the reactions with the aqueous solutions containing chemicals or heavy metals (Comfort et al 2001; Hernandez et al 2004; Kanel et al 2006; Ponder et al 2001).

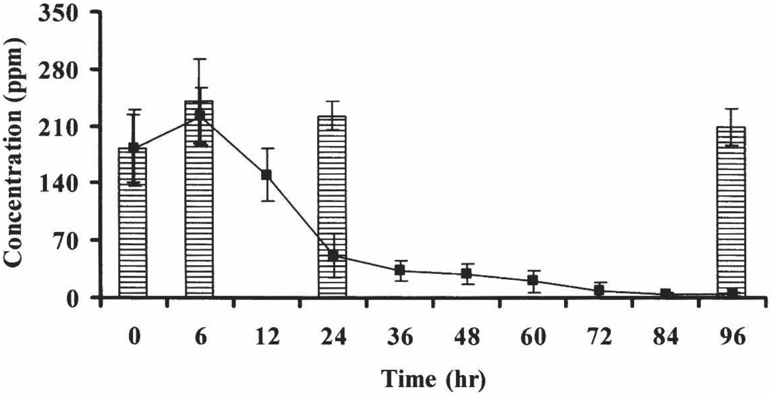

Figure 2. Time-course removal of alachlor from the pesticide solutions treated without (▤) and with (■) the laboratory-synthesized zerovalent iron in the batch experiments. Each value represents mean ± SD (*n* = 3).

In those studies, aggregation was suggested to be due to iron(Ⅲ) oxide/hydroxide formation during the iron reaction. The oxidation of zerovalent iron by water and oxygen generates ferrous iron, and the resulting Fe(Ⅱ) further reacts to give magnetite (Fe_3O_4), ferrous hydroxide ($Fe(OH_2)$) and ferric hydroxide ($Fe(OH)_3$) (Glaves et al 1995). It is, therefore, suggested that aggregation of NZVI was the result of oxidation of NZVI to give the iron oxide compounds.

The data of batch experiments of the time-course removal of alachlor and pretilachlor by NZVI treatment are presented in Figure 2 and Figure 3, respectively. Alachlor and pretilachlor were removed continuously with time by NZVI treatment. Alachlor showed approximately 70% removal in 24 hr by NZVI treatment (Figure 2), while pretilachlor exhibited approximately 90% removal by NZVI treatment (Figure 3) in 24 hr. Both herbicides were removed more than 95% of the initialed added in 72 hr. In contrast, the control samples did not show the removal of the pesticides throughout experiments. The pH of the reaction solution was decreased from approximately 6.8 to 4.7, and the formation of green rust was observed. A pH drop and green rust formation in the reaction of zerovalent iron with pesticides have been established in other studies (Gaber et al 2002; Shea et al 2004), which enhanced the reduction of chlorine-containing herbicides. The data of the batch experiments indicate that the removal of alachlor and pretilachlor was due to NZVI reaction in the pesticide solutions.

Pesticide concentrations in the control samples increased about 1.2 to 1.6 times after a 6 hr-incubation time (Figure 2 and 3). A possible hypothesis regarding the increased concentrations in the control samples was that the initially added-pesticides would bind to iron particles or the surface of the flask. Another possible hypothesis was that the added-pesticides would become more water soluble due to

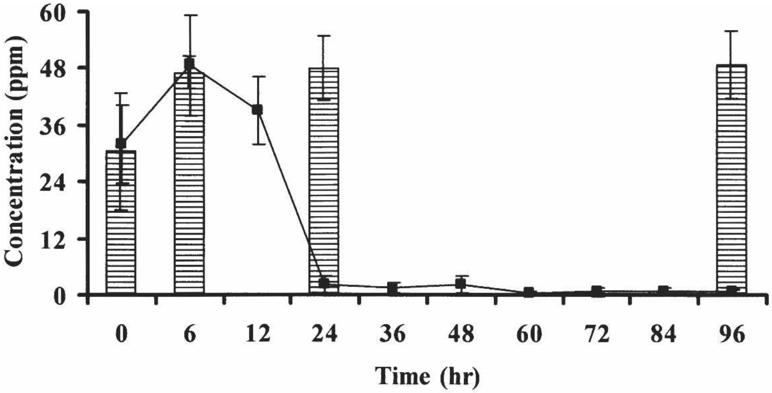

Figure 3. Time-course removal of pretilachlor from the pesticide solutions treated without (▤) and with (■) the laboratory-synthesized zerovalent iron in the batch experiments. Each value represents mean ± SD (*n* = 3).

the presence of surfactant in the pesticide solutions. The presence of surfactants in the solution would allow herbicide concentrations to exceed the aqueous solubility. This hypothesis was supported by the fact that the pesticide concentration in the control samples remained constant after 6 hr. To investigate if pesticides bound to NZVI particles, NZVI was also extracted with organic solvent after reaction and subjected to gas chromatographic analysis. A negligible pesticide concentration, less than 0.5 ppm in the extract suggested that the removal of herbicides was due to degradation by NZVI treatment.

To analyze the degradation products of alachlor and pretilachlor in the reaction solutions, the solutions were extracted with solvent and analyzed by GC/MS. GC/MS analyses identified M^+ peaks at *m/z* 235 (Figure 4A) and 277 (Figure 4C) as the main degradation products of alachlor and pretilachlor, respectively. These degradation products were identified as dechlorinated products, suggesting that dehalogenation mechanism was occurred by NZVI treatment. GC/MS analyses also identified an M^+ peak at *m/z* 207 as an alachlor degradation product (Figure 4B) and an M^+ peak at *m/z* 235 as an pretilachlor degradation product (Figure 4D). These products were identified as dealkylated by-products of the herbicides. The dealkylated by-products of acetanilide herbicides by NZVI treatment has not been reported elsewhere. The dealkylated by-products would be result of an abiotic degradation after dechlorination. Enhanced mineralization of the recalcitrant explosive hexahydro-1,3,5-trinitro-1,3,5-triazine after zerovalent iron treatment (Oh and Alvarez, 2002 and 2004) suggests that zerovalent iron may improve biodegradation processes. It is likely that our laboratory-synthesized NZVI similarly generated more biodegradable products of alachlor and pretilachlor, as the NZVI removed electron-withdrawing moieties such as chlorine, giving dechlorinated and dealkylated products.

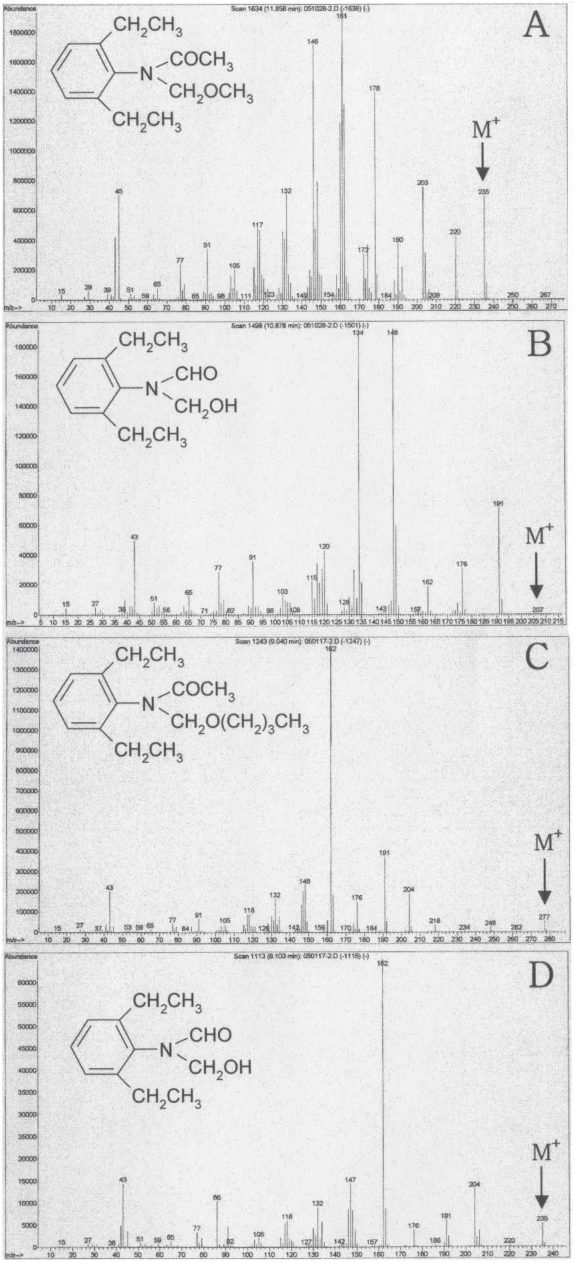

Figure 4. GC/MS spectra of the degradation products of alachlor (A, B) and pretilachlor (C, D) extracted from the reaction solutions in the batch experiments.

Overall, the data of batch experiments and GC/MS analyses indicate that our laboratory-synthesized Fe^0 functioned well as a reductant to react with chlorine-containing herbicides such as alachlor and pretilachlor. The use of Fe^0 for remediating ground water and soil contaminated with orgranochlorine pesticides have been demonstrated largely (Comfort et al 2001; Gaber et al 2002; Gibb et al 2004; Shea et al 2004). From these studies, Fe^0 has proven an effective application in removing these chemicals from waters and soils. Those studies were carried out by using pure chemicals and commercial zerovalent iron. In the present study, we examined the removal of alachlor and pretilachlor by treating their formulation mixtures with laboratory-synthesized nanoscale Fe^0. Our NZVI may be applicable for the remediation of waters contaminated with alachlor and pretilachlor.

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