

Reductive Dechlorination of Chloroacetanilide Herbicide (Alachlor) Using Zero-Valent Iron Nanoparticles

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Abstract

Nanoscale zero-valent iron (NZVI) was used for the first time to reductively degrade the chloroacetanilide herbicide, alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide], in laboratory studies. NZVI was synthesized by the borohydride reduction method and characterized using transmission electron microscopy and Brunauer–Emmett–Teller surface area analysis. Resulting particles had an average diameter of 35 nm and a Brunauer–Emmett–Teller surface area of 25 m² g⁻¹. Alachlor degradation in the presence of NZVI was rapid and complete. Parallel comparison trials with commercial microscale zero-valent iron (surface area = 1–2 m²/g⁻¹) were also conducted. Surface area-normalized rate constants (k_{SA}) for NZVI and microscale zero-valent iron were found to be 38.5 × 10⁻⁵ and 3.8–7.7 × 10⁻⁵ L h⁻¹/m⁻², respectively. A reaction product was identified as dechlorinated alachlor [N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide]. Based on results obtained in the research, the authors stipulate that NZVI may be a viable option for both site remediation and treatment of low-volume, high-concentration pesticide waste generated during pesticide application operations and in storage.

Key words: alachlor; chloroacetanilide; NZVI; remediation; dehalogenation; pesticides; zero-valent iron; nanoparticle

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ALACHLOR [2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide, C₁₄H₂₀ClNO₂] (Fig. 1) is used as a herbicide for the control of annual grasses and broadleaf weeds in field corn, soybeans, peanuts, and grain sorghum (Shea *et al.*, 2004; Fernández *et al.*, 2006; Chirnside *et al.*, 2007). Alachlor (also known as Lasso) belongs to the class of chloroacetanilide herbicides. In 2001, 3.5–4.0 million kg of alachlor was applied to agricultural land in the United States, making alachlor the 16th most widely used pesticide in the country (USEPA, 2004). Moreover, total chloroacetanilide (alachlor plus its sister compounds, e.g., metolachlor) usage remains high (USEPA, 2004).

Although responsible agricultural practices might have limited nonpoint source pesticide groundwater contamination to some extent, contamination due to point sources remains a major ongoing concern (Shea *et al.*, 2004; Chirnside *et al.*, 2007). Present extensive applications and occasional inappropriate usages of alachlor can lead to contamination of

water, soil, and air (Fernández *et al.*, 2006). Pesticide handling by farmers also creates low-volume high-concentration wastewater, which needs to be treated to avoid groundwater contamination (Felsot *et al.*, 2003). Alachlor has high water solubility (240 mg L⁻¹) (USDA, 2007), moderate organic carbon partition coefficient (K_{oc} = 124 mL g⁻¹), and high half-life in water, creating a potential for groundwater leaching resulting from spills. Half-life for hydrolysis of alachlor has been reported as ~3 h to ~22 days at room temperature and pH 7 (Sharma, 2002; Carlson *et al.*, 2006). The World Health Organization has classified alachlor as a carcinogen (WHO, 1996). The ability of alachlor to serve as an alkylating agent via reaction with nucleophiles may be linked to its carcinogenicity (Dearfield *et al.*, 1999; Lippa *et al.*, 2004). Other possible mechanisms are also suggested by researchers (Dearfield *et al.*, 1999) and it is also possible that dechlorination byproducts of alachlor are carcinogens and even more toxic than alachlor. To limit human exposure to alachlor in drinking water, the USEPA has established a maximum contaminant level (MCL) of 2 µg L⁻¹ and a MCL goal of 0 µg L⁻¹ (USCFR, 2001; USEPA, 2009). Alachlor is considered a priority hazardous substance by the Water Framework Directive of the European Commission (Farré *et al.*, 2005).

Traditional alachlor remediation techniques such as land-farming, land-filling, and incineration are not always cost effective or environmentally acceptable (Shea *et al.*, 2004).

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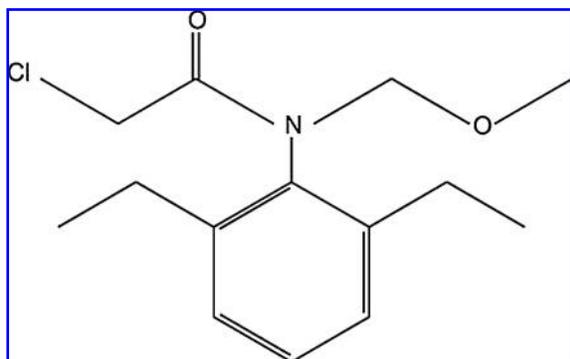


FIG. 1. Alachlor chemical structure.

Phytoremediation (Kawahigashi *et al.*, 2005) is economically favorable, but removal rates are reduced at high alachlor concentration. Ferrate oxidation (Zhu *et al.*, 2006) and advanced oxidation techniques such as TiO_2 -UV (Kim *et al.*, 2005) and photo-Fenton (Lapertot *et al.*, 2006) can remove alachlor very quickly. However, these techniques are better suited for use in wastewater treatment processes and not for *in situ* remediation (Lapertot *et al.*, 2006).

One potentially attractive remediation technique is reductive dechlorination by zero-valent iron (ZVI). This is an appealing technology because iron is inexpensive and can be easily used *in situ* even though there are some toxicity concerns recently being raised by a number of researchers (Aufan *et al.*, 2008; Lee *et al.*, 2008; Neal 2008; Kim *et al.*, 2009; Phenrat *et al.*, 2009). The typical mode of contaminant degradation by ZVI is reductive dehalogenation (Matheson and Tratnyek, 1994), as shown below (Eq. 1):



Although most research involving microscale ZVI (mZVI) remediation has focused on remediation of chlorinated hydrocarbons (Johnson *et al.*, 1996), a sizable body of research has been accumulated on pesticide remediation as well. Chloroacetanilide herbicides, such as alachlor, have been shown to be particularly susceptible to iron-mediated reduction. Studies have demonstrated the effectiveness of mZVI in the remediation of chloroacetanilide pesticides such as alachlor (Eykholt and Davenport, 1998; Comfort *et al.*, 2001; Shea *et al.*, 2004). However, several limitations including slow reaction rate and reaction inhibition due to oxide deposition inherent to traditional iron remediation have restricted its usefulness.

In recent years, nanoscale ZVI (NZVI), with its high specific surface area, has been employed for various contaminants with varying degrees of success. In addition to the obvious advantage of faster and more complete dechlorination, NZVI has the potential to be injected into the subsurface (Elliot and Zhang, 2001) with necessary surface modifications using modifiers including polymers (Saleh *et al.*, 2007; Krajangpan *et al.*, 2009). Surface modification also promotes better contaminant degradation. Research has shown that NZVI can successfully degrade chlorinated ethenes, chlorinated methanes, polychlorinated biphenyls, and selected pesticides (Joo *et al.*, 2004).

The objective of this study was to investigate the efficacy of NZVI to treat alachlor. Experiments were focused on high

alachlor concentrations representative of acute spills or pesticide handling wastewater. Such high concentrations of alachlor are typically found at pesticide storage and handling facilities. This study lays the foundation for future work on *in situ*, on-site, and point-of-use treatment of alachlor and similar pesticides. The words pesticide and herbicide are alternatively used throughout this article to describe alachlor.

Materials and Methods

Alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide] (99.2%; Chem Service, West Chester, PA), Fe(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%; Alfa Aesar, Ward Hill, MA), sodium borohydride (NaBH_4 , 98%; Aldrich, Milwaukee, WI), iron powder ($<10 \mu\text{m}$, 99.9%; Aldrich), methanol (production grade; BDH, Poole, United Kingdom), dichloromethane (99.9%; EMD, Gibbstown, NJ), and ethanol (ACS grade; Mallinckrodt Chemicals, St. Louis, MO) were used as received from the suppliers unless otherwise specified.

Iron nanoparticles were synthesized by borohydride reduction of ferrous iron following a method previously described by Liu *et al.* (2005a) and Bezbaruah *et al.* (2009). Particle morphology was characterized by transmission electron microscopy (TEM; Jeol JEM-100CX II, Peabody, MA). A concentrated NZVI sample was prepared in ethanol, sonicated, and placed on a Formvar[®] (SPI Supplies, West Chester, PA) coated 300-mesh copper grid for analysis at an accelerating voltage of 80 kV. Some sample oxidation might have occurred during preparation and was considered unavoidable. Surface area analysis was conducted on a Coulter SA 3100 surface area analyzer. Sample was outgassed at 105°C under constant He gas flow for 8 h before analysis. The specific surface area of the synthesized NZVI was measured using micromeritics analyzer (ASAP 2000; Micromeritics Instrument, Norcross, GA) using Brunauer-Emmett-Teller (BET) gas adsorption with N_2 .

Batch studies were conducted in 500-mL polyethylene terephthalate bottles with fluoropolymer resin-coated silicone septum screw caps. Sorption to caps and vials was not observed and so it was considered negligible. Vials were covered with aluminum foil to prevent possible photodegradation. Four-hundred milliliters of deionized (Barnstead, 18 M Ω) water was pipetted into the bottles and spiked with an alachlor stock solution (1.0 mg mL^{-1} in methanol) at varying levels to yield 10–40 mg L^{-1} pesticide solution. The pesticide solution was then sparged for 15 min with nitrogen gas (ultra-high-purity grade) to deoxygenate the solution. Samples were not withdrawn before sparging, and thus the effects of possible volatilization were not considered in the analysis. Initial pH ($\text{pH}_0 \approx 7.0$) was not adjusted, and trials were not buffered. Although pH values were not rigorously monitored, the solution pH at the end of the trials was ~ 8.5 . NZVI particles (1.60 g) were placed in each vial, and the headspace was purged with nitrogen gas. Parallel mZVI trials were also conducted under identical conditions, replacing NZVI with 200 g of mZVI (Aldrich; used as received). This mass was selected on the basis of preliminary trials to determine an appropriate mZVI mass that yielded a reaction timescale similar to that observed in the NZVI trials. Trial, comparison, blank (without alachlor), and control (without iron) vials were placed on a custom-built rotary shaker (28 rpm) at room

temperature ($22^{\circ}\text{C} \pm 2^{\circ}\text{C}$). Aliquots (2 mL) were periodically withdrawn by syringe and passed through a $0.02\text{-}\mu\text{m}$ pore-sized syringe filter (Whatman, Maidstone, United Kingdom; Anotop 10). Samples were stored at 4°C and analyzed within 48 h of collection. All trials were run in triplicate unless otherwise specified.

Aqueous alachlor concentration was monitored by reverse phase HPLC (1100 Series; Agilent Technologies, Santa Clara, CA) using a C-18 column (ZORBAX RX-C18, $5\ \mu\text{m}$, $4.6 \times 250\ \text{mm}$; Agilent Technologies) and diode array detector. High-performance liquid chromatography mobile phase consisted of 60:40 water:acetonitrile. Water was buffered with triethanolamine at pH 7.5. Alachlor retention time of $\sim 8.10\ \text{min}$ was determined at a wavelength of 222 nm. The flow rate was $1\ \text{mL min}^{-1}$. Byproducts were identified using gas chromatography–mass spectrometry (MS) (6890 Plus [HP]; 5973 MSD [HP]; Agilent Technologies, Santa Clara, CA) equipped with a fused silica capillary column (ZB-35, $30.0\ \text{m} \times 250\ \mu\text{m} \times 0.25\ \mu\text{m}$; Phenomenex, Torrance, CA). Aqueous samples (10 mL) were extracted with 1 mL dichloromethane. Extracts were injected in the splitless mode with the inlet maintained at 250°C . Oven conditions were used as follows: 50°C (hold 1 min) and increase of $20^{\circ}\text{C min}^{-1}$ to 280°C (hold 10.5 min). The carrier gas (He) flow rate was maintained at $1.0\ \text{mL min}^{-1}$. Chloride ion concentration was determined by ion chromatography analysis (DX-120; Dionex, Sunnyvale, CA) with an IonPac AS14 anion exchange column ($4 \times 250\ \text{mm}$; Dionex) and a conductivity detector. The eluent consisted of $3.5\ \text{mM Na}_2\text{CO}_3$ and $1.0\ \text{mM NaHCO}_3$ at a flow rate of $1.16\ \text{mL min}^{-1}$.

Results and Discussion

Particle morphology and size were determined by TEM (Jeol JEM-100CX II; Fig. 2). Average particle diameter was determined to be $\sim 35\ \text{nm}$ (Fig. 3) by analysis of the TEM image (number of particles measured, $n \approx 200$). Past studies

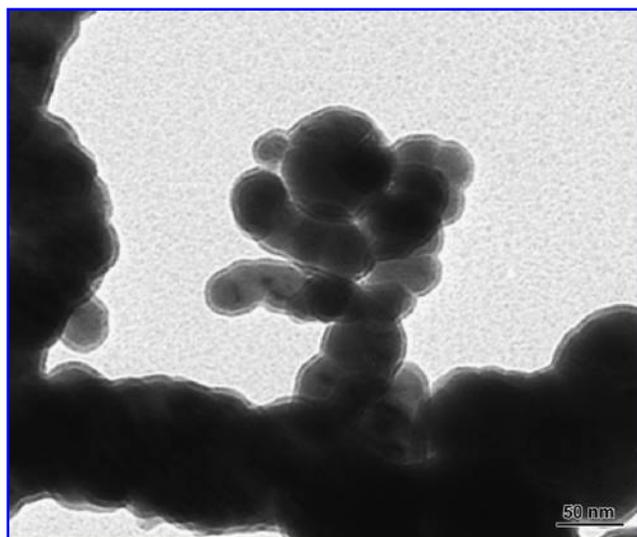


FIG. 2. Transmission electron microscopy image of an NZVI cluster. A thin (2–5 nm) oxide shell is formed around the NZVI particle during the passivation process. NZVI, nanoscale zero-valent iron.

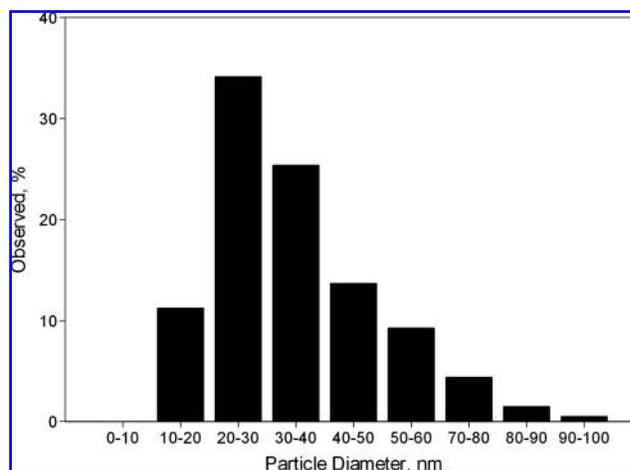


FIG. 3. Zero-valent iron nanoparticle size distribution ($n \approx 200$) indicated average particle diameter to be 35 nm and synthesized particle diameters were $\leq 90\ \text{nm}$.

have reported similar average particle diameters (Li *et al.*, 2006). A thin (2–5 nm) shell, presumably oxide, (Fig. 2) was formed during particle passivation. Martin *et al.* (2008) documented that the agglomerates of nanocrystalline Fe particles were always surrounded by a thin shell of amorphous FeOOH .

BET surface area of the synthesized NZVI was found to be $25\ \text{m}^2\ \text{g}^{-1}$ (based on duplicate samples). This value is in agreement with others who used similar NZVI synthesis techniques [$22\ \text{m}^2\ \text{g}^{-1}$ by Ponder *et al.* (2000) and $36\ \text{m}^2\ \text{g}^{-1}$ by Liu *et al.* (2005a)].

Alachlor degradation proceeded rapidly for all trials (Fig. 4). The initial alachlor concentrations of 10, 20, and $40\ \text{mg L}^{-1}$ decreased to 0.78, 1.17, and $1.67\ \text{mg L}^{-1}$, respectively, over the 72-h period. The alachlor concentration did not affect the reduction efficiency by NZVI. Alachlor was not detected after 5 days. The reaction was found to obey first-order kinetics very closely. This is common for the dehalogenation of organic compounds by both NZVI and mZVI (Johnson *et al.*, 1996;

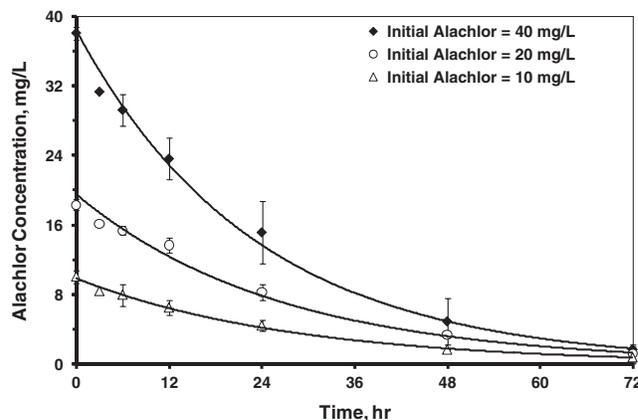


FIG. 4. Alachlor degradation results in the presence of NZVI at different initial concentrations. Iron mass loading was $4\ \text{g L}^{-1}$. Solid lines represent the first-order models. Error bars represent \pm standard error. Controls (not shown) do not display appreciable alachlor degradation.

TABLE 1. SUMMARY OF NANOSCALE ZERO-VALENT IRON AND MICROSCALE ZERO-VALENT IRON ALACHLOR DEGRADATION COMPARISON TRIALS

	Average diameter	Surface area ($m^2 g^{-1}$)	ρ_A ($m^2 L^{-1}$)	κ_{obs} (h^{-1}) ^a	κ_{SA} ($L m^{-2} h^{-1}$) ^a	R^2 ^b
NZVI	35 nm	25	100	38.5×10^{-3}	38.5×10^{-5}	0.999
mZVI	3 μm	1–2 ^c	500–1000	38.7×10^{-3}	$3.8\text{--}7.7 \times 10^{-5}$	0.987

^aReported reaction rate constants are based on the average of the three examined concentrations of alachlor (10, 20, 40 mg L⁻¹).

^b R^2 is related to κ_{obs} .

^cManufacturer's estimate. Accordingly, a range of values is proposed here for the kinetic parameters.

NZVI, nanoscale zero-valent iron; mZVI, microscale zero-valent iron.

Nurmi *et al.*, 2005). In the case of heterogeneous reactions, such as ZVI-mediated dehalogenation, it is instructive to normalize k_{obs} with respect to (iron) surface area. It should be noted that the validity of the area normalized rate constant (k_{SA}) has been debated. Cwiertny and Roberts (2005) contended that surface area-normalized rate constants do not relate linearly with iron loading, whereas Matheson and Tratnyek (1994) observed linearity. Because the linearity of k_{obs} and iron area was not tested in this work, the area-normalized rate constants must be viewed with these caveats in mind. The use of k_{SA} in this work should not be construed as an acceptance of the overall validity of k_{SA} . Johnson *et al.* (1996) have presented the following surface area normalized rate equation:

$$\frac{dC}{dT} = \kappa_{SA} \rho_A C \quad (2)$$

where k_{SA} is the surface area-normalized rate constant ($L m^{-2} h^{-1}$) and ρ_A is the iron surface area concentration ($m^2 L^{-1}$). The rate constant results are summarized in Table 1.

An analysis of chloride concentration was conducted to verify dechlorination and to confirm mass balance. Mass balances for alachlor and chloride indicate minor losses over time (Fig. 5). The small losses were considered acceptable and attributed to instrumental and/or experimental error. The losses in chlorides could also be attributed to some adsorption onto iron particles, especially after formation of iron corrosion products (Ghauch *et al.*, 2009; Noubactep, 2009). The stoichiometric conversion of chlorine in alachlor to Cl⁻ ion strongly implies degradation via reductive dechlorination.

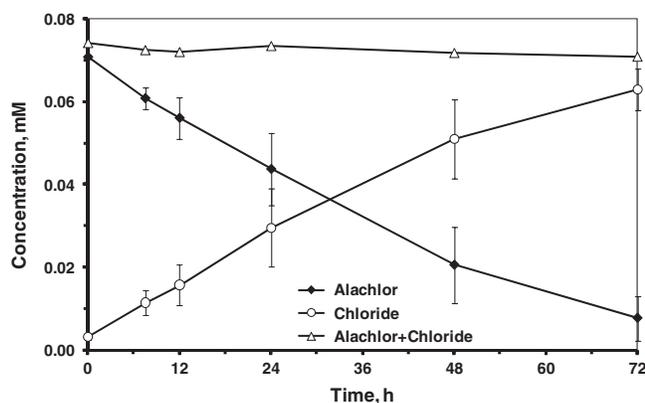


FIG. 5. Mass balance during alachlor degradation by NZVI. Iron mass loading was 4 g L⁻¹. Error bars represent \pm standard error. Initial nonzero chloride concentration is the background value and the same has been reported.

Gas chromatography–MS analysis was used for reaction product identification. The only observed product was identified by comparing its mass spectrum (Fig. 6) with those presented by Potter and Carpenter (1995). This work along with Mangiapan *et al.* (1997) is provided as authoritative references on alachlor MS spectral patterns. The product's spectrum matched that of dechlorinated alachlor [*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl) acetamide], providing further confirmation of reductive dechlorination. No other reaction product was detected. This, however, does not preclude the formation of short-lived intermediates or products with poor partitioning to the extractant (methylene chloride), as both would not be detectable under the study conditions. In similar studies, Eykholt and Davenport (1998) and Kim *et al.* (2006) reported a significant level of a dealkylated, dechlorinated byproduct in addition to the dechlorinated byproduct detected in this study. Although neither group reported a mechanism for *N*-dealkylation, Eykholt and Davenport (1998) speculated a photolysis mechanism. It was assumed that the care taken to shield reactors, stock solutions, and samples from light in this study precluded the accumulation of *N*-dealkylation reaction products. This should be read with the caveat that Carlson *et al.* (2006) have reported abiotic *N*-dealkylation of alachlor in the dark too under certain conditions. Although the toxicity and biodegradability of the reaction product have not yet been characterized, inferences can still be made. Comfort *et al.* (2001) found that dechlorinated metolachlor (a structurally similar chloroacetanilide herbicide) was five times more biodegradable than the parent compound. Thus, it seems possible that the

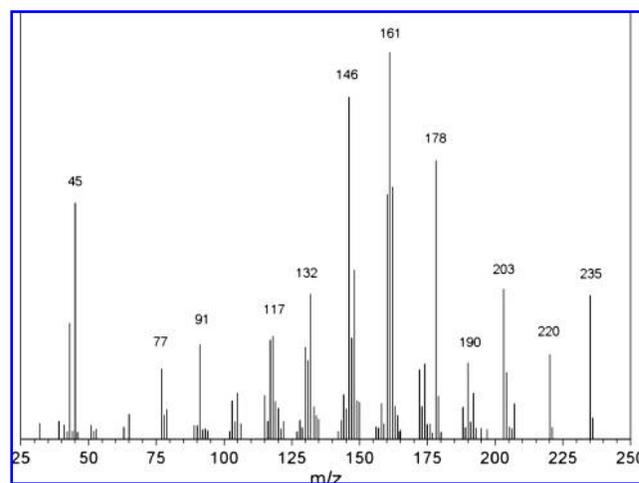


FIG. 6. Mass spectrum of dechlorinated alachlor. *N*-(2,6-Diethylphenyl)-*N*-(methoxymethyl) acetamide was determined to be a degradation product.

dechlorination of alachlor results in some degree of improvement in biodegradability. This, however, needs to be confirmed through separate biodegradation studies.

The results of the NZVI/mZVI comparison experiment are summarized in Table 1. The surface area-normalized rate constant, k_{SA} , was determined to be about 5–10 times greater for NZVI than mZVI. It should also be noted that the specific surface area of mZVI might have changed after manufacturer measured it. Although some degree of error in mZVI reaction rate is likely due to uncertainties in the surface area estimate given by the manufacturer, this alone cannot account for the observed difference. Further, greater surface area-normalized rates for NZVI compared with mZVI have been reported in the literature. Lien and Zhang (1999) observed similar difference (≈ 5 times) with respect to chlorinated methane degradation. They attributed this to the relative “freshness” of the synthesized NZVI compared with the commercial mZVI. Liu *et al.* (2005a) also found a slightly greater rate constant for trichloroethylene (TCE) degradation by NZVI (same as the one used by the authors) compared with mZVI. They attributed this to the ability of this particular type of NZVI to activate and use H_2 in the system for dechlorination. This hypothesis was verified in a later paper by the same research group (Liu *et al.*, 2005b). Their work indicated that these particles possess a nano effect.

The results of the investigation showed that the herbicide, alachlor, can be rapidly dechlorinated by NZVI. The reaction rate displayed pseudo first-order kinetics. The degradation pathway was determined as reductive dechlorination and the end product was found to be dechlorinated alachlor. The study further suggests that NZVI may be applicable to alachlor spill remediation. Although this study focused on high-concentration spills and pesticide wastewater, future research may examine lower concentrations likely encountered in nonpoint source alachlor contamination.

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Author Disclosure Statement

No competing financial interests exist.

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