

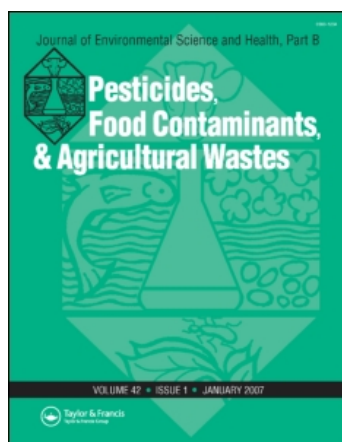
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Remediation of alachlor and atrazine contaminated water with zero-valent iron nanoparticles

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Zero-valent iron nanoparticles (nZVI, diameter < 90 nm, specific surface area = 25 m² g⁻¹) have been used under anoxic conditions for the remediation of pesticides alachlor and atrazine in water. While alachlor (10, 20, 40 mg L⁻¹) was reduced by 92–96% within 72 h, no degradation of atrazine was observed. The alachlor degradation reaction was found to obey first-order kinetics very closely. The reaction rate (35.5×10^{-3} – 43.0×10^{-3} h⁻¹) increased with increasing alachlor concentration. The results are in conformity with other researchers who worked on these pesticides but mostly with micro ZVI and iron filings. This is for the first time that alachlor has been degraded under reductive environment using nZVI. The authors contend that nZVI may prove to be a simple method for on-site treatment of high concentration pesticide rinse water (100 mg L⁻¹) and for use in flooring materials in pesticide filling and storage stations.

Keywords: Zero-valent iron (ZVI); iron nanoparticle; alachlor; atrazine; pesticide rinse water.

Introduction

Major non-point source pesticide contamination in the USA and the world has reduced markedly due to best management practices in agricultural.^[1–3] In contrast, point source contamination, especially from conventionally ignored sources, remains as a major concern. Such point sources include the pesticide handling facilities at farms.^[3] In addition, leftovers in pesticide containers, though in small quantities cause significant problem in terms of decontamination. Three critical steps are usually involved in pesticide handling and use at farms:^[3] (i) transfer of pesticides into spray tanks and their dilution (or dilution in nurse tanks), (ii) field application of pesticides, and (iii) management of pesticide leftover in containers. While there is very less pollution potential from field applications because of best management practices, the transfer step (step 1) remains as a high risk for contamination of soil and groundwater. Castillo et al.^[3] calculated that a few drops of a pesticide concentrate (containing about 1 g of the active pesticide) may amount to a groundwater pesticide

concentration of 0.1 µg L⁻¹ which is the European maximum contaminant level (MCL) for pesticides in drinking water.^[4] The potential pollution risk associated with steps 1 and 3 described above can be reduced by providing the farmers with a cost effective yet fast treatment option. The need for a fast and cost effective treatment is felt further in many developing countries as empty pesticide containers are used for domestic purposes including storage of water and other edibles^[5] (also, Bezbaruah per. obs.).

Alachlor and atrazine are two most extensively used pesticides in the United States. They are associated with a number of harmful effects on human and other biota. Alachlor (2-Chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide, C₁₄H₂₀ClNO₂) is used for the control of annual grasses and broadleaf weeds in field corn, soybeans, peanuts, grain sorghum, cotton, brassicas, oilseeds, radish, and sugar cane.^[6] Alachlor (trade names and synonyms:^[7] Alachlor, Lasagrin, Lassagrin, Lasso, Lazo, Metachlor, Pillarzo, Alanox, Alanex, Chimichlor) is a cream colored solid (MW = 269.8, water solubility = 240–242 mg L⁻¹, K_{oc} = 124, and log K_{ow} = of 2.6–3.1).^[6,8,9] It is the 16th most widely used pesticide in the USA with 3.5–4.0 million kg applied to agricultural land in 2001.^[10] Alachlor's high water solubility, relatively low K_{oc}, and high half-life in water make it a potential water contaminant. The US MCL for alachlor is 2 µg L⁻¹ and MCL goal (MCLG) is zero µg L⁻¹.^[11] World Health Organization (WHO) and the

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United States Environmental Protection Agency (USEPA) have classified alachlor as a carcinogen.^[11,12] The US Food and Drug Administration (FDA) has also classified alachlor as class II priority pesticide for monitoring because of its health hazards, toxicity, and carcinogenicity.^[13] Alachlor is identified as a Priority Hazardous Substance by the European Commission's Water Framework Directive.^[14]

Atrazine (6-Chloro-N-ethyl-N'-(methylethyl)-1,3,5-triazine-2,4-diamine) is the most used herbicide in the triazine class that is characterized by a heterocyclic ring containing three nitrogens at positions 1, 3 and 5. In 2001, 36×10^6 kg of atrazine was applied to agricultural land in the United States, making atrazine the second most widely used pesticide in the country.^[10] Atrazine provides broad-spectrum weed control and is priced competitively. It is used alone or in combination with other pesticides in maize, sorghum, sugar cane, pineapples, macadamia nuts, conifers, grapevines, and roses. Atrazine and its metabolites are among the most frequently detected agricultural chemicals in private wells.^[15] While only slightly water soluble (33 mg L^{-1} at 25°C), atrazine is moderately mobile in soils.^[9] It is a very persistent pesticide with a half-life of 77–146 d in soil.^[9] Short-term exposure to atrazine is associated with kidney problem and congestion of the heart and lungs. Long-term exposure at levels above the MCL ($3 \text{ } \mu\text{g L}^{-1}$) is associated with degeneration of the cardiovascular and retinal systems.^[11]

Based on relevant literature on existing pesticide treatment options, zero-valent iron (ZVI) based remediation may be a feasible and attractive option. Iron is inexpensive, non-toxic and environmentally compatible. The reported mode of contaminant degradation by ZVI is reductive dehalogenation.^[16] Although most remediation studies involving microscale zero-valent iron (mZVI) have focused on chlorinated hydrocarbons,^[16–18] there are some reports on pesticide remediation as well. Effectiveness of mZVI for remediation of chloroacetanilide herbicide (e.g., alachlor) contaminated soil^[19–21] and water^[21] has been demonstrated. Atrazine has been treated using ZVI to varying degrees of success.^[22–26]

There are several limitations inherent to traditional iron remediation that have restricted its applications. Iron filings and mZVI have been used in permeable reactive barriers (PRB) for groundwater remediation.^[16] However, they are expensive to install due to deep excavation requirement even though it is inexpensive to maintain them.

Dechlorination of organic compounds occurs on the ZVI surface and the extent of dechlorination depends on the available reactive surface area.^[27] Thus, it is logical to hypothesize that an increase in remediation performance can be achieved by increasing the iron surface area available for contact with the contaminant. For the last decade or so nanoscale zero-valent iron (nZVI) has been employed to remediate various contaminants with varying degrees

of success. These particles are characterized by many fold increase in available surface area as compared to mZVI and iron filings.^[28] Faster and more complete degradation can be achieved with nZVI.^[29] Further, nZVI can be injected into the subsurface^[30] with necessary surface modification to overcome non-target oxidation, limited transport (injectability), and lack of dispersion.^[31–34] Researchers have shown that nZVI can successfully degrade a number of environmental contaminants including chlorinated ethenes,^[29] chlorinated methanes,^[35] polychlorinated biphenyls,^[29] selected pesticides,^[28,36] arsenic^[37] and other metals.^[38]

The objective of the study described in this paper was to investigate the treatability of pesticides alachlor and atrazine with nZVI. The focus was on high pesticide concentrations representing acute spills that occur at pesticide handling and storage facilities in agricultural communities.

Materials and methods

Chemicals and supplies

All chemicals were used as received from the suppliers unless otherwise specified. Alachlor (99.2%, Chem Service), atrazine (99.5%, Chem Service), Fe(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%, Alfa Aesar), sodium borohydride (NaBH_4 , 98%, Aldrich), methanol (production grade, BDH), dichloromethane (99.9%, EMD), and ethanol (ACS grade, Mallinckrodt Chemicals) were used in the study.

Nanoparticle synthesis

Nanoparticles (nZVI) were synthesized by borohydride reduction of ferrous iron. The original method described by Liu et al.^[39] was modified slightly by the corresponding author's research group.^[28,33] The modifications by the research group^[28,33] include drying using alternating exposures to nitrogen gas and vacuum at 120°C . After thoroughly drying the iron, air was allowed to slowly bleed over the iron for a period of approximately 12 h to passivate the iron. The resulting black clusters of iron were ground, yielding fine nZVI powder and stored under a nitrogen environment in a glovebox (Innovation Technology Inc.) for later use.

Nanoparticle characterization

Nanoparticles were characterized by transmission electron microscopy (TEM, JEOL JEM-100CX II). X-ray diffraction (XRD) analysis of nZVI was performed on a Philips X'Pert MPD with Cu $K\alpha$ X-ray source. Brumaier-Emmett-Teller (BET) specific surface area of nZVI was determined by N_2 gas absorption (Micromeritics, ASAP 2000).

Alachlor and atrazine degradation batch studies

Batch studies were conducted in 0.5 L polyethylene terephthalate bottles (reactors). The bottles were fitted with fluoropolymer resin-coated silicone septum screw caps. An amount measuring 400 mL of deionized (Barnstead, 18 M Ω) water in the reactor was spiked with an alachlor stock solution (1.0 mg mL⁻¹ in methanol) to get 10, 20, and 40 mg L⁻¹ solution. The content in the reactor was deoxygenated by sparging it with ultra high purity grade N₂ gas. The pH (initial value \approx 6.0–8.0) was not adjusted and no buffer was used. A measured amount (1.60 g) of nZVI was added to each reactor and the headspace was purged with N₂ gas. The reactor was wrapped with aluminum foil to prevent possible alachlor photodegradation reported by Bahena and Martínez.^[40] Blanks (i.e., only deionized water with no nZVI and alachlor) and controls (i.e., with deionized water and alachlor but nZVI) were prepared exactly the same way as for the reactors. The reactors were rotated (28 rpm) end-over-end in a custom built rotary shaker at room temperature (22 \pm 2°C). Aliquots (2 mL) were periodically withdrawn from each reactor, blank, and control, filtered with syringe filter (0.02 μ m pore size, Whatman, Anotop 10), and stored at 4°C, when needed, and analyzed within 48 h of collection. All trials were run in triplicates unless otherwise specified.

Atrazine batch studies were conducted following the general scheme as for alachlor. 10, 20, and 40 mg L⁻¹ solutions of atrazine were used. It is important to note that 40 mg L⁻¹ was above the solubility limit of atrazine but was selected to be consistent with alachlor batch study.

Analytical methods

Alachlor and atrazine concentration in the sample was measured by reverse phase high performance liquid chromatography (HPLC) using a C-18 column (ZORBAX RX-C18, 5 μ m, 4.6 \times 250 mm, Agilent Technologies) with a mobile phase of water and acetonitrile (ACN:Water 60:40 for alachlor analysis, 40:60 for atrazine). HPLC method details: injection volume, V = 20 μ L; Alachlor R_T = 8.10 min; Atrazine R_T = 8.76. Method detection limit was not specifically found, but method was repeatable down to 0.05 C₀. Standard calibration methods were followed. Gas chromatography-mass spectrometry (GC-MS, 6890 Plus, HP; 5973 MSD, HP) equipped with a fused silica capillary column (ZB-35, 30.0 m \times 250 μ m \times 0.25 μ m, Phenomenex) and helium carrier gas was used for alachlor byproduct detection. The injection volume (V) used was 1 μ L. Extraction to dichloromethane (DCM):10 mL sample extracted to 1 mL DCM. Extracts were injected in the splitless mode with the inlet maintained at 250°C. Oven conditions were as follows: 50°C (hold 1 min) and increase 20°C min⁻¹ to 280°C (hold 10.5 min). The carrier gas (He) flow rate was maintained at 1.0 mL min⁻¹. Atrazine byproducts analysis was not necessitated as no atrazine degradation was achieved (see Results and Discussion). Chloride ion con-

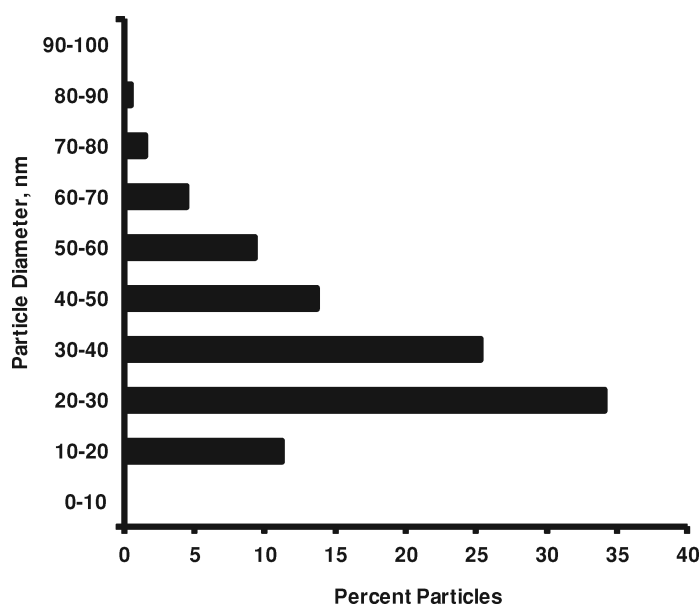


Fig. 1. Particle size distribution for the nZVI synthesized in this study. Particle diameter ranged from 10 to 90 nm with an average diameter = 35 nm.

centration (in alachlor batch studies) was determined by ion chromatography (IC) analysis (DX-120, Dionex).

Results and discussion

Nanoparticle characterization

The average particle diameter was determined to be approximately 35 nm (Fig. 1). The diameter is consistent with that reported by Li et al.^[41] A thin (2–5 nm) oxide shell was formed around the nZVI particle during particle passivation.^[31–33] The shell is reported to be made of amorphous iron oxide/hydroxide (FeOOH) and core is zero-valent iron.^[42] BET surface area for nZVI synthesized was found to be 25 m² g⁻¹^[28,33] and that is in agreement with others (22 m² g⁻¹ reported by Ponder et al.^[38] and 36 m² g⁻¹ reported by Liu et al.^[39]). XRD spectra of the synthesized nZVI show peaks for only Fe⁰.^[28] However, SEM-EDX spectrum of fresh nZVI synthesized in the laboratory show ~16% oxygen possibly because of the oxide layer on the outside surface of the particles (results not shown). For an average diameter of 35 nm and bulk density of iron of 7.87 \times 10⁶ g m⁻³, a spherical shape of particle gives the theoretical surface area as 22 m² g⁻¹ which is in close agreement with measured BET surface area of 25 m² g⁻¹.^[28] Based on this calculation, the authors have assumed the nZVI to be spherical in shape.

Atrazine degradation

Atrazine did not degrade during the study period (Fig. 2). Three different atrazine concentrations (10, 20, and 40 mg L⁻¹) were tried. As in the case of alachlor, no pH adjustment or buffering was done. There are number reported

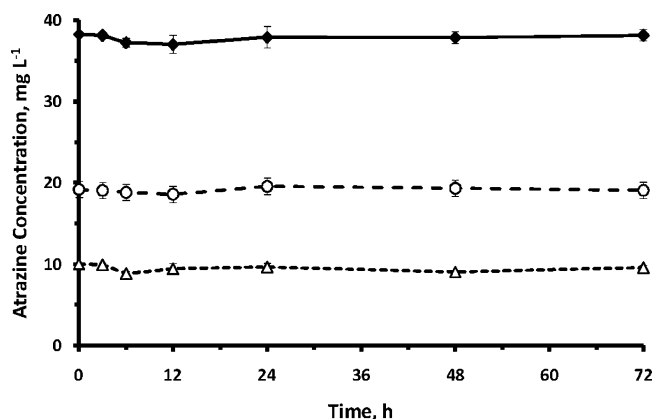


Fig. 2. Degradation of atrazine over time (—◆— 40 mg L⁻¹, —○— 20 mg L⁻¹, —△— 10 mg L⁻¹). The controls were run for each atrazine concentration and the plots nearly overlap the respective plots shown here. The vertical error bars indicate \pm standard deviations. The data points are joined by straight lines for ease of reading only and they do not represent any trend.

studies with differing results on atrazine degradation by ZVI. Some researchers reported unsuccessful atrazine degradation trials with ZVI^[24] while another group reported rapid degradation.^[22] Ghauch and Suptil^[22] conducted a series of experiments on ZVI mediated reduction of atrazine and proposed a first-order kinetic model. They concluded that the pesticide underwent reductive dechlorination. The present study results contradict these observations. No atrazine reduction was achieved (in 10 and 20 mg L⁻¹ solutions) apparently because the Fe⁰/Fe²⁺ system has insufficient redox potential to reduce atrazine.^[22] At 40 mg L⁻¹ (which is above 33 mg L⁻¹ solubility limit of atrazine at 25°C) the insoluble atrazine might have covered the surfaces of nZVI thereby making them further ineffective for atrazine remediation.

Alachlor degradation

Rapid degradation of alachlor in all trials was observed (Fig. 3). The initial alachlor concentrations of 10, 20 and 40 mg L⁻¹, decreased to 0.78 (92% reduction), 1.17 (94%) and 1.67 mg L⁻¹ (96%), respectively, over a 72 h period. The experiments were continued beyond 72 h with less frequent

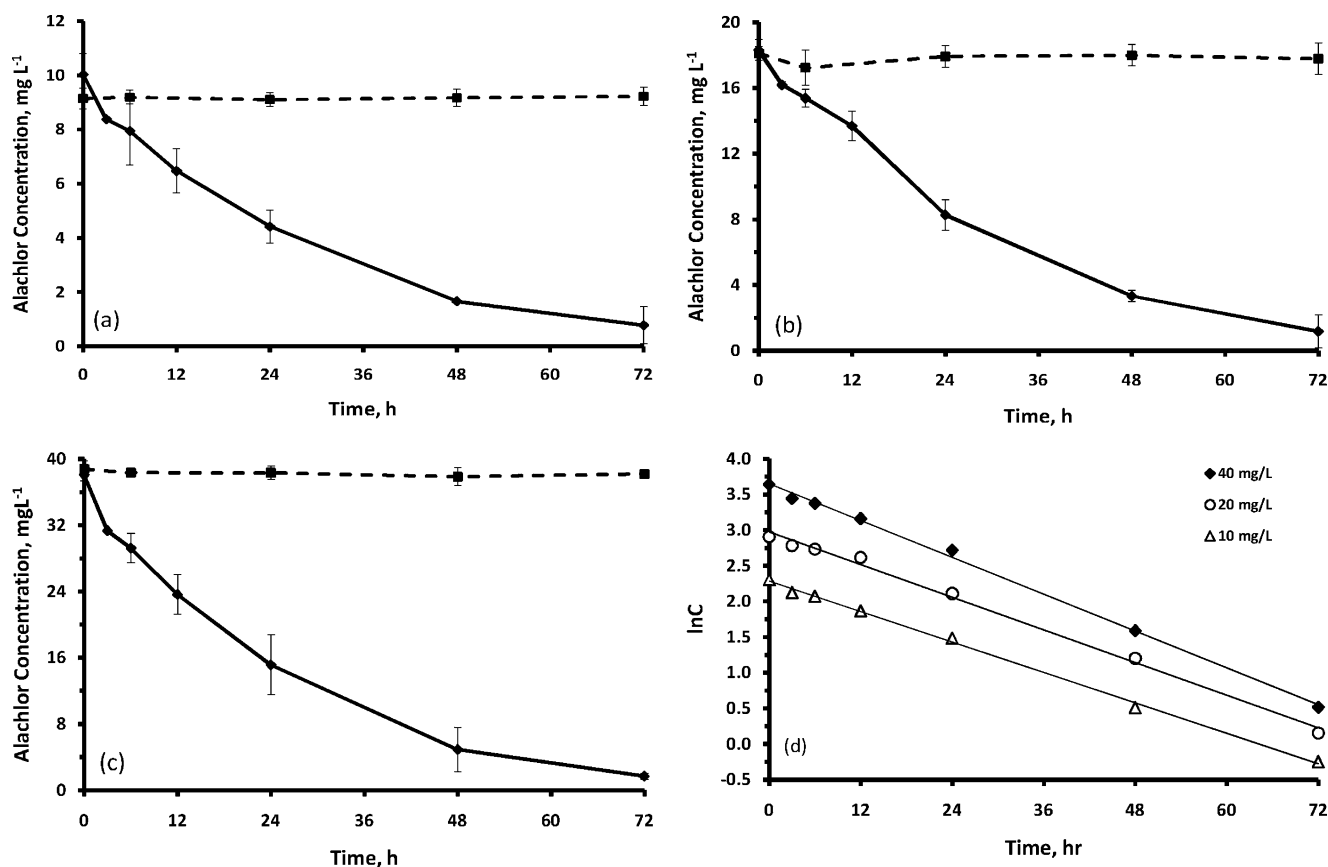


Fig. 3. Degradation of alachlor over time (—◆— trial and —■— control in (a) – (c)): (a) 10 mg alachlor L⁻¹, (b) 20 mg alachlor L⁻¹, (c) 40 mg alachlor L⁻¹, and (d) first order model for alachlor degradation (— model trendline). The vertical error bars in (a) – (c) indicate \pm standard deviations. The data points in (a) – (c) are joined by straight lines for ease of reading only and they do not represent any trend.

Table 1. Rate data analysis for order of the reaction and reaction rate.

Alachlor conc. (mg L ⁻¹)	0-order		1st-order		2nd-order	
	R ²	k _{obs} (h ⁻¹)	R ²	k _{obs} (h ⁻¹)	R ²	k _{obs} (h ⁻¹)
10	0.9169	12.5 × 10 ⁻³	0.9979	35.5 × 10 ⁻³	0.9248	15.6 × 10 ⁻³
20	0.94	24.1 × 10 ⁻³	0.995	38.1 × 10 ⁻³	0.8669	10.1 × 10 ⁻³
40	0.9059	48.7 × 10 ⁻³	0.9977	43.0 × 10 ⁻³	0.8653	7.2 × 10 ⁻³

sampling and no alachlor was detected after 5 d (data not reported).

Alachlor degradation data over time were plotted to see whether zero-, first-, and second-order kinetics was followed. The results from this analysis are presented in Table 1. The reaction was found to obey first-order kinetics very closely (Fig. 3d). First order reaction is common for dehalogenation of organic compounds by ZVI.^[17] The reaction rate for the first order reaction increased with increasing alachlor concentration.

Alachlor degradation byproduct

Only one byproduct could be identified in samples during degradation of alachlor in the presence of nZVI. The byproduct was identified by comparing its GC-MS mass spectrum with those presented by Potter and Carpenter.^[43] The byproduct's spectrum matched with that of N-(2,6-Diethylphenyl)-N-(methoxymethyl) acetamide (i.e., dechlorinated alachlor), providing confirmation of reductive dechlorination. Primary peak @ m/z = 161 matches Potter and Carpenter.^[43] Major secondary peaks at 148, 178, 45, 203 and 235 match Potter and Carpenter^[43] very well. No other byproduct was detected. The typical mode of contaminant degradation by ZVI is reductive dehalogenation,^[16] as shown below (Eq. 1).

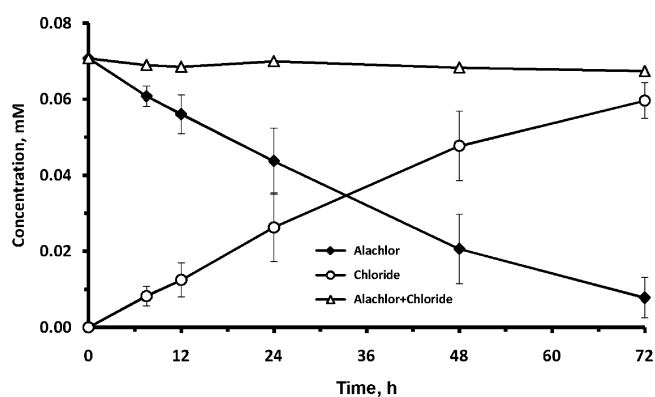


Fig. 4. Chloride mass balance over time (—△— alachlor and chloride, —◆— alachlor, —○— chloride). The vertical error bars indicate ± standard deviations. The data points are joined by straight lines for ease of reading only and they do not represent any trend.

Ekyholt and Davenport^[21] reported a significant level of a dealkylated, dechlorinated byproduct in addition to the dechlorinated byproduct in their studies on alachlor degradation. Ekyholt and Davenport^[21] speculated that photolysis might be responsible for N-dealkylation. In the present experiment, the reactors, stock solution and samples were covered with aluminum foil to avoid exposure to light and that might have precluded the generation of N-dealkylation byproducts. Comfort et al.^[20] reported that dechlorinated metolachlor (a structurally similar chloroacetanilide herbicide) was five times more biodegradable than the parent compound. Thus, it seems likely that the dechlorination of alachlor results in some degree of improvement in biodegradability. This, however, needs to be confirmed through separate biodegradation studies.

An analysis of chloride concentration was conducted to both verify dechlorination and confirm mass balance (Fig. 4). At least 95% of the mass was accounted for in each sample. The small loss can be considered acceptable and attributed to instrumental and/or experimental errors. The stoichiometric conversion of chlorine in alachlor to Cl⁻ ion strongly implies a reductive dechlorination degradation path.

Conclusions

The results of the investigation showed that alachlor can be rapidly reduced by nZVI in an anoxic environment. The degradation pathway was reductive dechlorination and the end product was found to be dechlorinated alachlor. It is likely that dechlorinated alachlor is environmentally benign and more biodegradable than its parent compound. The alachlor degradation reaction was found to be first-order. No degradation of atrazine was observed and it was concluded that atrazine is not amenable with nZVI under normal environmental conditions.

Results from the study suggest that nZVI may be applicable to concentrated alachlor remediation. Boparai et al.^[23] worked on similar agrichemical spills and discharge situations and successfully used mZVI/ZVI filings with carbon amendments to remediate soil contaminated with metolachlor (170 mg kg⁻¹). Metalachlor concentration decreased to below 1 mg kg⁻¹ after 95 days of treatment with 5% (w/w) ZVI when applied in combination with Al₂(SO₄)₃. They proposed that when high contaminant

concentrations inhibit natural attenuation of pesticide in soils, chemical treatment (with ZVI) can be used to promote degradation. The results from the present study indicate that highly contaminated and localized groundwater could be effectively remediated by injecting nZVI slurry. There may, however, be a need to modify the nZVI surface (i.e., coat the nZVI) with an organic ligand to increase its injectability and dispersibility while decreasing non-target oxidation.^[31,32] The authors also contend that nZVI may prove to be a simple method for on-site treatment of high concentration pesticide rinse water which contains about 100 mg L⁻¹ atrazine.^[44] For example, according to the proposed first order kinetic model, treating rinse water to below the MCL (2 µg L⁻¹) in 100 h would require approximately 10 g nZVI L⁻¹. The cost would be \$0.66 L⁻¹ at the current nZVI market price of \$66 kg⁻¹.^[45] This calculation is based on projected reaction rate for 100 mg L⁻¹ alachlor. From the data presented in Table 1 it is apparent that there is a linear relationship between alachlor concentration (C) and first order reaction rate constant, k_{obs} ($k_{\text{obs}} = 0.0002 \cdot C + 0.0331$, $R^2 = 0.9998$). Based on this relationship k_{obs} for $C = 100 \text{ mg L}^{-1}$ is $53.1 \times 10^{-3} \text{ h}^{-1}$. When normalized for surface area (25 m²/g nZVI, for 1.60 g nZVI used in 400 ml test solution, $k_{\text{SA}} = 100 \text{ m}^2 \text{ L}^{-1}$ here^[28]) the reaction rate constant becomes $k_{\text{SA}} = 53.1 \times 10^{-5} \text{ L m}^{-2} \text{ h}^{-1}$. This reaction rate is used for calculations. It should, however, be noted that the amount of iron needed will not be exclusively determined by stoichiometry but a variety of environmental factors. Such a treatment method available to farmers will result in appreciable cost savings in terms of travel time and cost otherwise needed to take care of the used pesticide containers. Presently the farmers have to travel to specified locations or the county has to organize collection events for such containers and left-over pesticides.

Acknowledgments

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