

REMEDICATION OF ATRAZINE IN CONTAMINATED SOIL BY NANO ZEROVALENT IRON

ABSTRACT

Pesticide contaminated soil may require remediation to mitigate ground and surface water contamination. Nanoscale iron particles (because of their large surface areas and high surface reactivity) represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. We determined the effectiveness of nano zerovalent iron (nano ZVI) covered with urea-choline chloride to dechlorinate atrazine (2-chloro-4ethylamino-6-iso-propylamino-1,3,5-triazine) in contaminated soil. This study determined the effects of nano ZVI and solution pH in factorial design. Atrazine (0.4g/20g) was treated with 0.3g of nano ZVI (4.5%). Lowering the pH from 8.5 to 6 decreased the destruction (concentration) of atrazine by nano ZVI. Our results indicate that nano ZVI can be used in alkaline soil to remediate atrazine.

KEY WORDS: Atrazine, nano zerovalent iron, remediation, soil

INTRODUCTION

Atrazine [2-chloro-4ethylamino-6-iso-propylamino-1, 3, 5 -triazine] is among the most commonly used herbicides in the world. In USA, atrazine has been classified as a Restricted Use Pesticide (RUP) due to its potential for groundwater contamination (Ware 1986). Atrazine is transported in the natural environment through the diffusion and adsorption binding of suspended solids. This process is damaging to the ecosystem and humans (Hesketh et al. 1996). Atrazine has been identified as an endocrine disrupting chemical and a Type C carcinogen, and has become a growing concern in water quality management (Moore et al. 2000). Atrazine runoff and leaching from application sites into rivers, streams, lakes, reservoirs and groundwater is an ecological concern. In some aquatic ecosystems contaminated by atrazine, photosynthesis of algae, a primary producer in food chain, may be inhibited (Stratton 1984). Meisner et al. (1993) indicates potential toxic effects on animals from atrazine metabolites, particularly from adducts of nitroso derivatives. Some pesticides that are persistent in aerobic environments are more readily degraded under reducing conditions (Comfort et al. 2001). Thus generating a reducing (electron-rich) environment in soils, sediments, and aquifers has become a popular treatment option. One application of this technique uses zerovalent iron (ZVI) as a chemical reductant. Under aerobic conditions, oxygen is the usual electron acceptor, while in anaerobic environments, electron release from the reaction of ZVI with water can be coupled to the reaction of chlorinated and nitroaromatic compounds (Gillham and O'Hannesin 1994). Recent researches indicate that nanoscale zerovalent iron particles provide more surface area and are more reactive than microscale ones to chemically reduce halogenated hydrocarbons (Wang et al.1997). Elliott and Zhang (2002) and Nurmi et al. (2005) suggest that Fe nanoparticles are more effective for the degradation of halogenated organic contaminants. However, the investigations into its application for persistent organic pollutants have been limited.

Materials and Methods

Materials

Atrazine was obtained from Sigma Aldrich Chemical Co., Germany. Ferrous sulfate [FeSO₄·6H₂O] and sodium borohydrate [NaBH₄] were purchased from Merck Chemical Co. All other reagents were of analytical grade. Acetonitrile was purchased from Merck chemical co. and it was HPLC grade.

Preparation of Nano ZVI

Nanoscale zerovalent iron (nano ZVI) was synthesized by adding 1:1 volume ratio of NaBH₄ (0.8 M) solved in urea choline chloride into FeSO₄.6H₂O (0.2 M) and mixing the solution vigorously under room temperature for 5 min. Ferric iron was reduced by borohydrate and nano ZVI was formed according to the following equation (Sun et al.2006):



Nano ZVI was washed twice with DI water to get rid of excessive borohydrate. 20ml urea choline chloride was added in nZVI.

Soil Incubation Experiments

Soil was air-dried and then screened through a sieve (dia =2 mm) prior to hand-milling. Particle size distribution was determined using hydrometer techniques (American Society for Testing and Materials 1998; Method D422-63). Percent of soil organic matter was determined by standard methods (Nelson and Sommer 1982). CEC (cation exchange capacity) was analyzed by method of Rhoades (1982). Soil was spiked with Atrazine to get the initial concentration of 20 mg atrazine kg⁻¹ soil. Atrazine adsorbed on soil particles was extracted by acetonitrile with the aid of a sonic disruptor to determine percent recovery of atrazine. The sonic disruptor bombarded soil with sonic waves, facilitating the transfer of atrazine into ACN. After 12h, the aliquots were removed and transferred to 1.5 ml microcentrifuge tubes for HPLC analysis. The supernatant was filtered before the measurement. The quality of the analysis was censured by averaging the results obtained from triplicate analyses. Twenty milliliters of water were added to the tubes. Experimental units were initially prepared for each treatment and incubated for up to 3 weeks at room temperature. At preselected times. Three experimental units were removed and centrifuged at 6,000 rpm to separate supernatant from soil. Supernatant solutions were removed and transferred to 1.5 ml and kept under aerobic condition. Soil samples were also extracted by sonic disruptor method to determine atrazine.

Effects of pH

Atrazine destruction by nano ZVI was investigated under 3 pHs. The soil solutions were maintained at pH 6, 7 and 8 before treatment with nZVI. Acidic pH was adjusted by 0.1 N HCl while basic pH was adjusted by 0.2 N NaOH. Temporal changes in atrazine concentration were measured in samples at end of 21 days.

Sample Preparation and Analysis

After extraction the aliquots were transferred to 2 ml glass vials. Atrazine analysis was performed with HPLC (Shimadzu1100 series) by injecting 20 µl of sample into a 4 by 250 mm Hypersil ODS column connected to UV detector with quantification at 220 nm. The mobile phase was 70:30 CH₃CN/H₂O at a flow rate of 0.9 ml min⁻¹.

RESULTS

Characteristics of soil that used in present study are shown in table1. Atrazine concentration was decreased by elevation of pH. Amount of atrazine in soil was detected by HPLC. Graphical analysis of treated and untreated soil was shown in figure 1 and 2. Mean of atrazine concentration in soil was illustrated in figure 3. Atrazine concentration in acidic condition without Iron treatment and Iron treatment sample in basin pH is not significantly different. Iron nano particles were useful in atrazine decreasing in contaminated samples. Decreasing the pH from 8.5 to 6 decreased the destruction of atrazine by nano ZVI.

DISCUSSION

When pH level is increased, atrazine concentration decreased. These results are in agreement with Satapanajaru et al. (2003). Atrazine concentration in acidic condition without Iron treatment and Iron treatment sample in basin pH is not significantly different. Dechlorination of organic substance is pH dependent. These results indicate that Iron nano particles are useful in atrazine decrease in contaminated samples. Present experiment shows that pH treatment is significant (fig.3). Other researches indicate that dechlorination is pH dependent reaction (Zhang, 2003; Sung et al. 2009).

Organic destruction in low pH is more successful, but with this new cover basin pH is suitable for atrazine dechlorination. Dechlorination of chloroacetanilide herbicides by dithionite and dithionite-treated aquifer sediment and soil is a remediation option in natural environments (Boparai et al., 2006). Also Song and Carraway (2005) used from nanosized iron for reduction of chlorinated ethanes. The degradation one- and two-carbon chlorinated hydrocarbons was carried with granular or microscale iron (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Johnson et al., 1996). Also, degradation was done on chlorinated solvents (Zhang et al., 1998; Lien and Zhang, 1999, 2001, 2005; Zhang, 2003), polychlorinated biphenyls (PCBs) (Wang and Zhang, 1997), chlorinated benzenes (Xu and Zhang, 2000), perchlorate (Cao et al., 2005), and heavy metals (Cao and Zhang, 2006; Li and Zhang, 2006, 2007) in laboratory studies and field applications. Other potentially amenable contaminants and contaminant classes, including nitrate, pesticides, radionuclides, and toxic metals were studied (Cheng et al., 1997; Sayles et al., 1997; Gu et al., 1998; Blowes et al., 2000; Alowitz and Scherer, 2002).

CONCLUSION

Lowering the pH from 8.5 to 6 decreased the destruction (concentration) of atrazine by nano ZVI. This study shows that there is no significant difference between nZVI treatment in basin pH and Iron free treatments in acidic condition. Our results indicate that nano ZVI can be used in alkaline soil to remediate atrazine in soil. But we need more information to make decision for using this material.

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Soil pH	7.56
Texture	Silty loam
Organic matter	% 0.45
EC e	2.6 ds/m
CEC	2.5 meq/100g
Soil	is not alkaline and belong to ustorthents

Table 1. Soil characteristics of subsurface soils used in the study

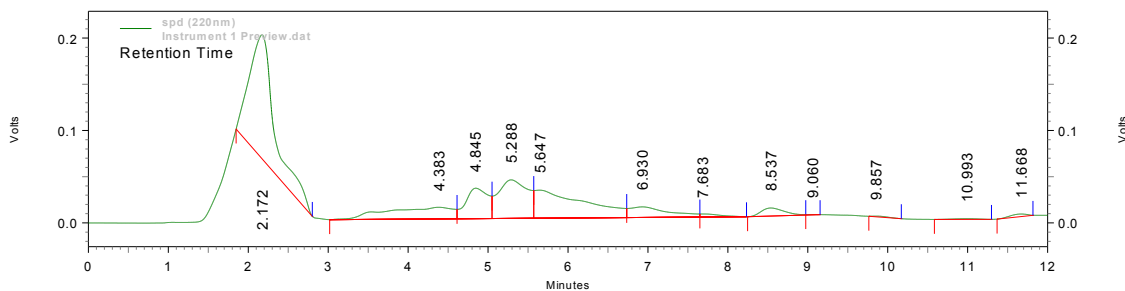


Fig.1 Atrazine contaminated sample

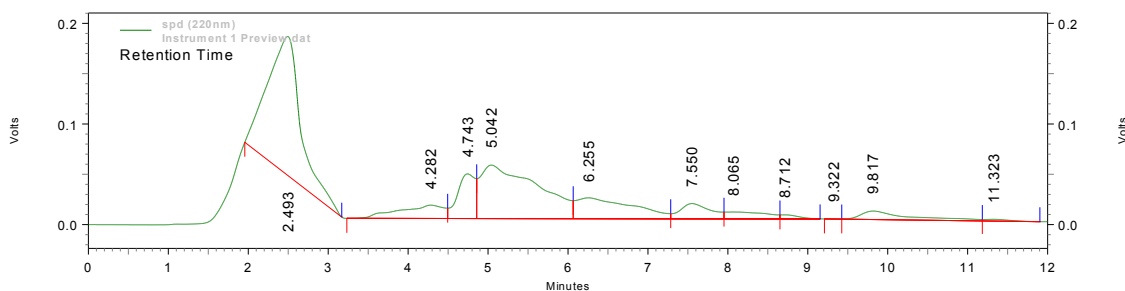


Fig.2 Atrazine contaminated soil with nano zerovalent Iron.

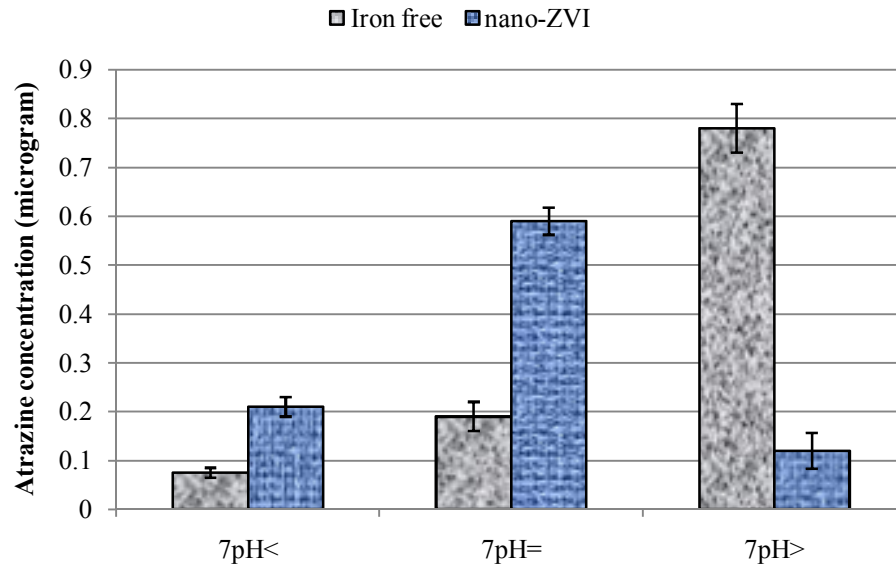


Fig.3- Mean (\pm SE) concentration of Atrazine (μ g) under different acidity of soil and with and without nano-iron treatment.

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