

Application of Nano-Zero Valent Iron for Treating Metolachlor in Aqueous Solution

P. Suntrornchot, T. Satapanajaru, and S.D. Comfort

Abstract—Water, soil and sediment contaminated with metolachlor poses a threat to the environment and human health. We determined the effectiveness of nano-zerovalent iron (NZVI) to dechlorinate metolachlor [2-chloro-n-(2-ethyl-6-methyl-phenyl)-n-(1-methoxypropan-2-yl)acetamide] in pH solution and the presence of aluminium salt. The optimum dosage of degradation of 100 mL⁻¹ metolachlor was 1% (w/v) NZVI. The degradation kinetic rate (k_{obs}) was $0.218 \times 10^{-3} \text{ min}^{-1}$ and specific first-order rates (k_{SA}) was $8.72 \times 10^{-7} \text{ L m}^{-2} \text{ min}^{-1}$. By treating aqueous solutions of metolachlor with NZVI, metolachlor destruction rate were increased as the pH decrease from 10 to 4. Lowering solution pH removes Fe (III) passivating layers from the NZVI and makes it free for reductive transformations. Destruction kinetic rates were $20.8 \times 10^{-3} \text{ min}^{-1}$ for pH4, $18.9 \times 10^{-3} \text{ min}^{-1}$ for pH7, $13.8 \times 10^{-3} \text{ min}^{-1}$ for pH10. In addition, destruction kinetic of metolachlor by NZVI was enhanced when aluminium sulfate was added. The destruction kinetic rate were $20.4 \times 10^{-3} \text{ min}^{-1}$ for 0.05% $\text{Al}(\text{SO}_4)_3$ and $60 \times 10^{-3} \text{ min}^{-1}$ for 0.1% $\text{Al}(\text{SO}_4)_3$.

Keywords— destruction, kinetic rate, metolachlor, nano-zerovalent iron

I. INTRODUCTION

Organic pollutants which are important contaminants in soil water and groundwater, threat ecology system and environment. These pollutants are emitted from various sources such as pesticides from agricultural land or chemical from production process.

Metolachlor [2-chloro-n-(2-ethyl-6-methyl-phenyl)-n-(2-methoxy-1-methyl ethyl) acetamide] is one of the more popular chloroacetanilide and is used a variety of commercial blends to control annual grasses and small-seeds broadleaf weeds. A national well wall water survey involving more than 6 million private and commercial was indicated a 1% detection of metolachlor (approximately 60,000 wells) at concentrations of $\geq 0.03 \mu\text{L}^{-1}$ [1]. Surface water have also been affected by metolachlor in at least 14 states, with maximum

S. Suntrornchot is with in the Department of Environmental Science, Faculty of Science, Kasetsart University, P.O. Box 1072, Phahon Yothin Rd, Chatuchak, Bangkok 10903, Thailand. (email: g5164246@ku.ac.th).

T. Satapanajaru is with in the Department of Environmental Science, Faculty of Science, Kasetsart University, P.O. Box 1072, Phahon Yothin Rd, Chatuchak, Bangkok 10903, Thailand. (corresponding author to provide phone: +66(2)-942-8036 Fax: +66(2)-942-8715; e-mail: fscitus@ku.ac.th).

S.D. Comfort is with the School of Natural Resource Institute of Agriculture and Natural Resource, University of Nebraska Lincoln, 68503, USA.

concentration of $138 \mu\text{gL}^{-1}$ (USEPA, 1987). While attention to agrichemical use and the environment has centered on mitigating nitrate contamination, this focus may shift, or at least broaden as more state and federal regulators became attuned to problems associated with pesticide use and can recommend or endorse reliable remediation treatments for pesticide-contaminated soil and water. Metolachlor is a health hazard, thus it is necessary to remove from environmental [2]. There are several methods for treating it such as incineration, fenton-oxidation and biodegradation [3]. Although these methods are easy but they are expensive. In recently, nanotechnology represents a new generation of environmental technology that provides high effectiveness solutions to environmental cleanup and remediation by using nano-zerovalent iron (NZVI) (particle size 1-100 nm) as chemical reductant [4]. The high effectiveness of NZVI is due to its high surface area and surface reactivity which higher than microscale zerovalent iron (ZVI) about 10 – 10,000 times. Therefore, the objectives of this study were to determine the effectiveness of nano-zerovalent iron (NZVI) to destruction metolachlor and to investigate the effects of the iron dosage, solution pH and aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$).

II. MATHERIALS AND METHODS

A. Materials

Nano-zerovalent iron (Nanofer 25S) was obtained from NANOIRON,s.r.o.(Czech Republic). Metolachlor was prepared from the commercial product Dual 8E (Syngenta, Greenboro, NC). The chemical structure of metolachlor was shown in fig. 1. Commercial grade-aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3$) were purchase from Aldrich chemical Co. (Milwaukee,WI). Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were purchased from Fisher Scientific Co Ltd. HPLC grade- acetonitrile was purchase from EMD.

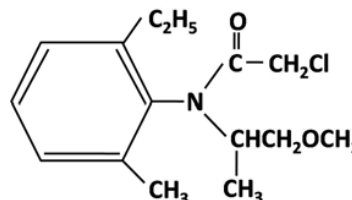


Fig. 1 chemical structure of metolachlor

B. Preparation of Nano-zerovalent iron (Nanofer 25s)

Before using, Nanofer 25s suspension was centrifuged at 4,000 rpm for 40 min under anaerobic condition. Then, suspension was withdrawn and the solid Nanofer 25s was dried by nitrogen gas.

C. Characterization of Nano-zerovalent iron

The surface morphology and quantify of Nanofer 25s were studied by mounting with carbon tabs, sputter-coating with gold-palladium, and observing with a Philips: XL30 & EDAX scanning electron microscope (SEM) operated at 15 KV connected with electron dispersive X-ray (EDX).

D. Batch experiments

Batch experiments were conducted to compare the efficiencies of NZVI to destruction metolachlor in aqueous solution. Metolachlor solutions were prepared in ultra pure water at initial concentration of 100 mgL⁻¹. The 100 mL of metolachlor solution was moved to 250 mL Erlenmeyer flask and then 0.5%, 1% and 5% (w/v) of NZVI was added. The flask was agitated on an orbital shaker. Samples were collected at 0, 10, 20, 30, 40, 50, 60, 80, 100 and 120 minutes. The samples were transferred to 1.5 mL polypropylene micro centrifuge and centrifuged at 14,000 rpm for 5 minutes. The concentration of metolachlor was determined by high performance liquid chromatography (HPLC), hybersil gold column connected to a Shimadzu (Kyoto, Japan) photodiode array detector with quantification at 220 nm. The mobile phase was 50:50 acetonitrile-water at flow rate of 1.0 mLmin⁻¹. To investigate the effect of initial pH and effect of aluminium sulfate (Al₂(SO₄)₃) on destructions of metolachlor by NZVI. Metolachlor solution was adjusted pH at 4, 7 and 10 using H₂SO₄ 0.5 M and NaOH 0.5 M before treatment by optimum NVZI dosage. Aluminium sulfate was added at 0.1%, 0.05%(w/v) with NZVI.

III. RESULTS AND DISCUSSIONS

A. Characterization of NZVI

Fig.1 represents the scanning electron microscope (SEM) and electron dispersive x-ray (EDX) image of NZVI. The particle morphology of NZVI is roughly spherical and aggregated (Fig. 1a). The element composition of NZVI was identified through EDX element mapping (Fig. 1b). The element iron was 76.63%.

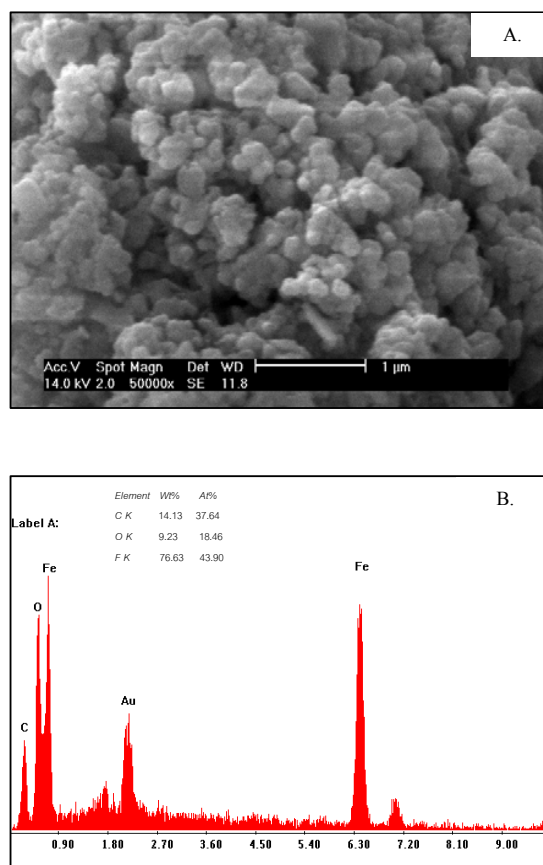


Fig. 2 (A) SEM (×50000) and (B) EDX image of NZVI

B. Destruction of Metolachlor by NZVI

Metolachlor degradation increased as the NZVI dosage increased (Fig. 3). Because of NZVI had the tiny size and high surface area. Therefore, its have a stronger reaction with organic pollutant molecules [5]. The destruction of metolachlor followed pseudo first-order kinetic reaction. First order metolachlor degradation kinetic rate (k_{obs}) was observed as in (1):

$$-\frac{d[\text{Metolachlor}]}{dt} = k_{obs} [\text{Metolachlor}] \quad (1)$$

The optimum dosage of degradation metolachlor was 1% NZVI (Table 1). The degradation kinetic rate (k_{obs}) was $0.218 \times 10^{-3} \text{ min}^{-1}$ for NZVI. For comparison, degradation kinetic rates can be normalized by the specific surface area of iron. The specific surface area for 10 gL⁻¹ iron(1% w/v) of NZVI was 250 m²L⁻¹. (k_{obs}) = (k_{SA}) ρ_a , where k_{SA} is the specific reaction rate constant (L m⁻²min⁻¹), and ρ_a is the surface area concentration of NZVI (m²L⁻¹) [6]. Specific first-order rates was $8.72 \times 10^{-7} \text{ L m}^{-2} \text{ min}^{-1}$ for NZVI.

Wang and Zhang [7] reported k_{SA} for synthesized nanoscale iron particle was $3.0 \times 10^{-3} \text{ Lm}^{-2}\text{h}^{-1}$ which was higher than k_{SA} for commercially available iron particles (generally below $1.0 \times 10^{-3} \text{ Lm}^{-2}\text{h}^{-1}$). In conclusion, the higher specific surface area, the higher surface reactivity to dechlorinate atrazine by nano ZVI.

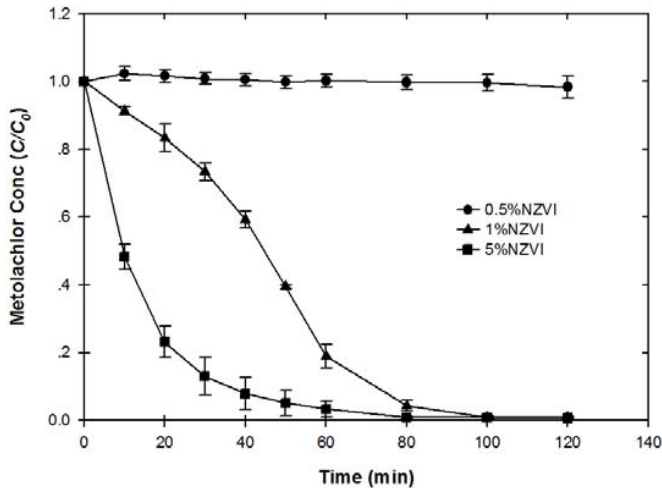


Fig. 3 Destruction of 100 mgL^{-1} metolachlor with NZVI

TABLE I
 k_{obs} and k_{SA} for destruction of 100 mgL^{-1} metolachlor by NZVI

Parameter	k_{obs} (10^{-3} min^{-1})	k_{SA} ($10^{-7} \text{ Lmin}^{-1}\text{m}^{-2}$)
100 mgL⁻¹ Metolachlor	0.5% NZVI	0.002
	1% NZVI	0.218
	5% NZVI	0.699

C. The Effect of pH on Metolachlor destructions by NZVI

The optimum NZVI dosage in destruction of metolachlor was used in studying the effect of pHs. Metolachlor destruction rate constant (k_{obs}) increased as the pH decreased from 10 to 4 (Fig. 4). Destruction kinetic rates were $20.8 \times 10^{-3} \text{ min}^{-1}$ for pH4, $18.9 \times 10^{-3} \text{ min}^{-1}$ for pH7, $13.8 \times 10^{-3} \text{ min}^{-1}$ for pH10. Slower destruction kinetics with increasing pH has observed while treating metolachlor [8], nitrite [9] or nitrate [10] with NZVI. Several factors may explain this trend. One is the formation of secondary reductants (Fe(II) or Fe(II)-containing oxides and hydroxides) on the surface of NZVI [9]. Various iron hydroxides such as goethite formed at high pH passivate the iron surface [8],[11]. Low pH would remove these passivating layers from NZVI core and render it free for reaction with the halogenated molecules [8],[12].

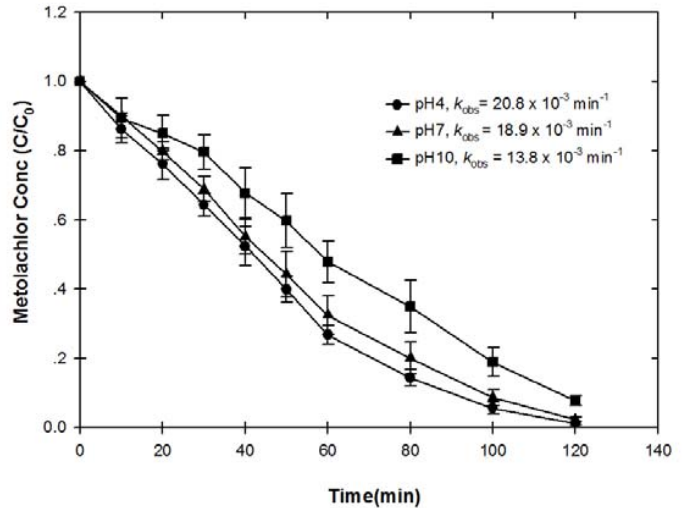


Fig. 4 The effect of pH on 100 mgL^{-1} metolachlor by 1% (w/v) NZVI

D. The effect of aluminum salt on metolachlor by NZVI

The efficiency of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) on metolachlor by 1% (w/v) NZVI, shows in fig. 5. Metolachlor degradation rate constants (k_{obs}) were enhanced when Al (III) salts were added. Destruction kinetic rate were $20.4 \times 10^{-3} \text{ min}^{-1}$ and $60 \times 10^{-3} \text{ min}^{-1}$ when 0.05% (w/v) and 0.1% (w/v) $\text{Al}_2(\text{SO}_4)_3$, respectively. Past researched has shown that high concentration of salt can slow passivation by moving the reaction products away from NZVI surface [13]. Moreover, availability of Al (III) during NZVI oxidation facilitates incorporation into the oxidized Fe structure [10],[14] and result in release of Fe(II) into bulk solution. Beside of formerly reason, sulfate has been show sustain higher rate corrosion, apparently by dissolving the oxide film that coat the surface during oxidation [15],[16].

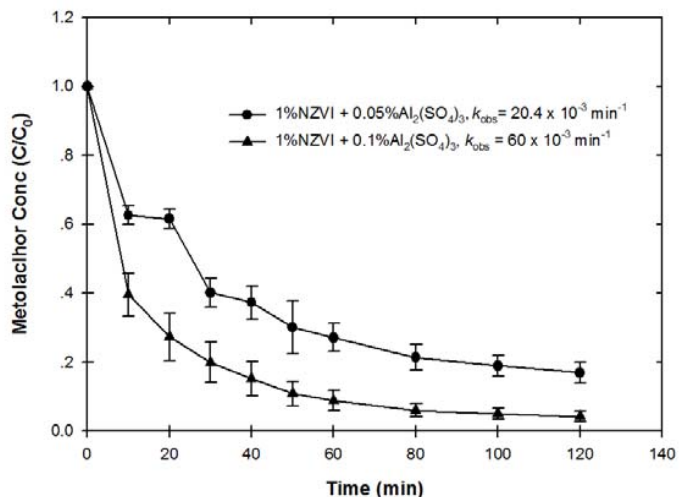


Fig. 5 The effect of aluminium salt on 100 mgL^{-1} metolachlor by 1% (w/v) NZVI

IV. CONCLUSION

Our result indicated that NZVI had efficiency for remediating metolachlor contaminated water. NZVI [1% (w/v)] was successful in removing metolachlor within 2 hours. Lowering the pH from 10 to 4 increased the destruction kinetic rate of metolachlor by NZVI. Moreover, aluminium salt can successfully increase destruction of metolachlor by NZVI. Result from this study can be applied to remediate metolachlor contaminated sediment in field.

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