

Dechlorination of atrazine using zero-valent iron (Fe⁰) under neutral pH conditions

Geonha Kim^{a,*}, Woohyeok Jeong^b, Seunghee Choe^c

^a Department of Civil and Environmental Engineering, Hannam University, Ojungdong, Daejeon 306-791, Republic of Korea

^b Daejeon Development Institute, Dunsandong, Daejeon 302-789, Republic of Korea

^c Research Institute for Environmental Technology and Sustainable Development, Korea University, Anamdong, Seungbukgu, Seoul 136-701, Republic of Korea

Received 13 April 2007; received in revised form 11 October 2007; accepted 26 November 2007

Available online 7 March 2008

Abstract

Zero-valent iron (Fe⁰) is frequently used for the dechlorination of pesticides, because it is economical, easily acquired and stable. The kinetics of dechlorination by Fe⁰ are improved at low pH, but this requires additional acid addition, while dechlorination hardly occurs under basic conditions. Due to the buffer capacity of geological materials such as clay and sediment, however, the addition of acid to obtain a low pH may not be effective. In this research, the dechlorination constants of atrazine by Fe⁰ were measured with the addition of buffer solution to simulate the buffer capacity of sediment. In the presence of the buffer solution, the pH values remained neutral, while dechlorination occurred more slowly than that observed under acid additions but faster than that without any buffer. When the initial concentrations of atrazine were 10 mg/L, 30 mg/L, and 50 mg/L, its dechlorination was explained using pseudo-first order reaction kinetics. The pseudo-first order constants were $3.01 \times 10^{-2} \text{ d}^{-1}$ at 10 mg/L, $3.23 \times 10^{-2} \text{ d}^{-1}$ at 30 mg/L and $3.38 \times 10^{-2} \text{ d}^{-1}$ at 50 mg/L. In addition, the half-lives of atrazine were 8.91 d at 10 mg/L, 9.32 d at 30 mg/L, and 10.00 d at 50 mg/L. Acid addition may not be omitted to obtain acidic pH conditions when dechlorination is necessary in geologic materials.

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Keywords: Atrazine; Buffer capacity; Dechlorination; Kinetics; Zero-valent iron

1. Introduction

Toxic chemicals including pesticides from point or nonpoint sources are common contaminants of source water [1,2]. These pesticide contaminants are very harmful for humans and difficult to remediate. Pesticide spillage from nonpoint sources acts in combination with suspended solids and deposits on the waterbed at low water velocity forming sediment [3–5]. Remediation is necessary due to the high concentration range of pollutants in sediment pore water [6,7].

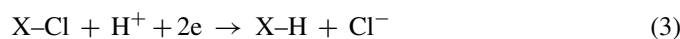
Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is one of the most important triazine herbicides and is used in large quantities worldwide [6,8]. Atrazine is transported in the natural environment through the diffusion and adsorption binding of suspended solids [9]. This process is damaging to the

ecosystem and humans [9]. Atrazine has been identified as an endocrine disrupting chemical and a Type C carcinogen, and has become a growing concern in water quality management [10]. Atrazine degradation products, such as hydroxyatrazine, were found to be substantially less toxic than the parent compound [11,12]. Atrazine has low volatility, low solubility in water (=33 mg/L) and a half-life of 244 d through hydrolysis [13]. The log K_{ow} of atrazine, an indicator of its hydrophobicity, is 2.69, which is similar to that of toluene and trichloroethylene (TCE). Its lethal dose (LD₅₀, rat) is 672 mg/kg and its lethal concentration (LC₅₀, 96 h) is 16 mg/L.

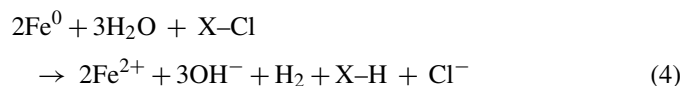
Technologies have been developed for the remediation of various chlorinated organic compounds. Studies in the past few years have demonstrated that metals such as iron and zinc can effectively reduce the amount of chlorinated organic compounds. Zero-valent iron (Fe⁰) has frequently been used, because it is economical, easily acquired and stable. Fe⁰ has been shown to be an effective material to remediate groundwater contaminated with chlorinated organic compounds [14–20].

* Corresponding author. Tel.: +82 42 629 7534; fax: +82 42 629 8366.
E-mail address: kimgh@hannam.ac.kr (G. Kim).

Fe^0 acts as both a reactant and surface substrate during the reduction of chlorinated organic compounds of the form X–Cl. Gillham and O'Hannesin [21] described the following general reactions:



Combining the reactions corresponding to Eqs. (1)–(3) gives the following:



Eq. (1) shows the oxidation of iron, while Eq. (2) shows the increase of pH brought about when water gains an electron, H_2 is released as gas and OH^- is generated. Eq. (3) is very slow under natural conditions, but more rapid at low pH. The overall reaction in Eq. (4) is a competition between water and chlorinated organic compounds. Eq. (4) shows that for each mole of reduced chlorinated organic compound, two moles of Fe^0 are oxidized to Fe^{2+} and three moles of OH^- are generated. At higher pH values, oxide and hydroxide coatings are undoubtedly produced, which hinder access to the Fe^0 surface. Therefore, the level of pH is important in the dechlorination of atrazine. The effect of dechlorination using Fe^0 is restrictive at low pH, and ineffective at high pH. The dechlorination process is highly dependent on the pH level, due to the reducibility of Fe^0 . We must investigate this pH variation and monitor its tendency, because dechlorination proceeds with difficulty under basic conditions.

Many geological materials such as clay and sediment have a pH buffering capacity which acts under both acidic and basic conditions, implying that the pH does not change significantly under buffered conditions [22,23].

Therefore, a dechlorination kinetic study needs to be undertaken under natural conditions and the object of this research was consequently to confirm and measure the dechlorination of atrazine under natural pH conditions in water with Fe^0 .

2. Materials and methods

This study was performed as a batch test to confirm the dechlorination of atrazine by Fe^0 under neutral pH conditions maintained with the aid of buffer solution. Atrazine was prepared from Supelco (purity 98%). Fe^0 powder (250-mesh) was provided by Junsei in extra pure grade. The pH buffer material was 0.1 M MOPS (4-morpholinepropane-sulfonic acid, $\text{C}_7\text{H}_{15}\text{NO}_4\text{S}$) solution prepared by Sigma Co.

Batch bottles, consisting of 125 mL glass bottles with a Teflon cap, were used. The batch systems were prepared by adding 93 mL of atrazine solution at concentrations of 10 mg/L, 30 mg/L, or 50 mg/L, 20 g of Fe^0 , and 7 mL of 0.1 M MOPS solution to each bottle. Atrazine was dissolved in ethanol and further diluted with deionized water. A concentration of atrazine of 50 mg/L is above its solubility limit. In pore water, a higher concentration range than the solubility limit is often found in the

field, as the majority of the solute adsorbs on the sediment surface [6]. Quality assurance and quality control are more reliable in the higher concentration range and the kinetics can be measured more quickly. In addition, additional bottles containing atrazine solution at a concentration of 30 mg/L without MOPS solution were prepared for the control experiment. All of the bottles were used once only at the settling time: one bottle every 10 min during the initial 30 min followed by one bottle every 30 min until an elapsed time of 10 h. Fifty-six batch bottles were prepared, 42 with MOPS solution (14 each at atrazine concentrations of 10 mg/L, 30 mg/L, and 50 mg/L) and 14 without MOPS solution.

We used a rotary shaker, at a temperature of 25 °C to ensure sufficient mixing of atrazine and Fe^0 . The bottles were fixed in a circular plate at 15 cm from the arbor. The rotation speed was 60 rpm in all cases. After the samples were extracted from the opened bottles, the ORP electrode was placed into the bottle and the entrance sealed to isolate it from the air. Data was read 30 min after inserting the electrode. The pH data was read with the ORP data using the same method. Three to five milliliters of high performance liquid chromatography (HPLC) grade methanol were added to 1–2 mL of the extracted specimen, and the resulting specimen was shaken for 3 min and then centrifuged. The supernatant was filtered before the measurement. The quality of the analysis was ensured by averaging the results obtained from triplicate analyses. If a deviation of more than 10% occurred between the repeated measurements, the experiment was repeated.

The temperature, pH and ORP were measured using an ion selective meter (Orion, 710A⁺). Atrazine was analyzed on a gas chromatograph (DS6200, Donam Instrument, Inc., Sungnam, Republic of Korea) equipped with a flame ionization detector (FID), autosampler (HT300A) and capillary column (DB-624, J&W Scientific Inc., Folsom, CA, USA). The injector and detector temperatures of the gas chromatograph were both 250 °C, while the oven program was 40 °C for 3 min.

3. Results and discussion

Fig. 1 shows the batch test results for the pH change corresponding to the degradation of atrazine by Fe^0 as functions of time and buffering. When Fe^0 and MOPS were placed in the batch bottle, the pH data were expressed in one graph, regardless of the atrazine concentration, because the pH ranges and tendencies were nearly united. In the presence of the pH buffer solution, the pH values were maintained at neutral pH or less than 8 at the highest in this study, implying that the amount of MOPS injected was sufficient to keep the pH of the solution neutral. In addition, the pH data for the batch bottles at an initial atrazine concentration of 30 mg/L without MOPS are also shown. As shown in Eq. (4), two moles of Fe^0 are oxidized to Fe^{2+} and three moles of OH^- are generated for each mole of reduced chlorinated organic compound. Therefore, the cause of the pH increase seems to be the reduction of atrazine in the absence of pH control. Chen et al. [17] reported that the degradation of halogenated substances using Fe^0 was possible when the pH was lower than 8, whereas it was hardly possible

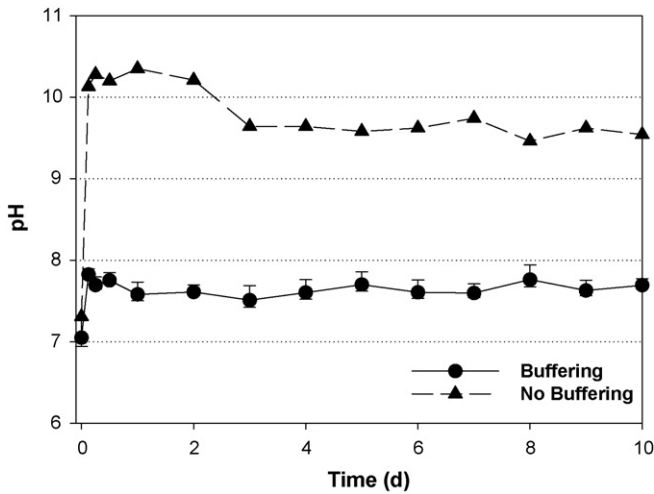


Fig. 1. Batch test results of pH change of dechlorination of atrazine by Fe⁰ as functions of time and buffering.

under basic conditions, mainly due to the precipitation of iron oxide. The influence of pH on the degradation rate is probably the result of both the maintenance of the available iron surface area for the reaction and the protonation of the triazine ring [12].

Fig. 2 presents the monitoring results of the ORP when atrazine is dechlorinated by Fe⁰, with and without pH buffer solution. In the case of the initial atrazine concentrations of 10 mg/L, 30 mg/L and 50 mg/L with buffer solution, the ORP data are presented in one graph because of their similar range and tendency. The ORP showed a low level of less than -300 mV from the first day in the presence of the buffer solution. This result demonstrated the potential for continuous dechlorination in the presence of the buffer solution. On the other hand, the ORP rapidly decreased during the first 24 h in the case where no buffer solution was present. Thereafter, the ORP remained steadily at around -30 mV. It was presumed that the dechlorination reaction was stopped due to the increase of pH that occurred if the solution was not buffered. This also explains the rapid pH

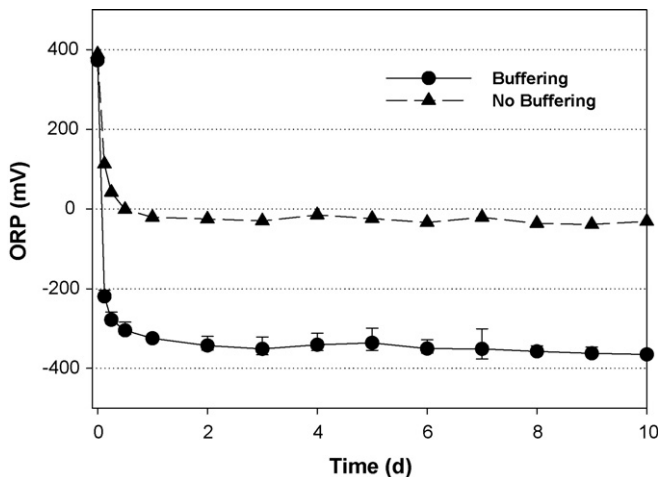


Fig. 2. Batch test results of oxidation reduction potential (ORP) change of dechlorination of atrazine by Fe⁰ as functions of time and buffer solution.

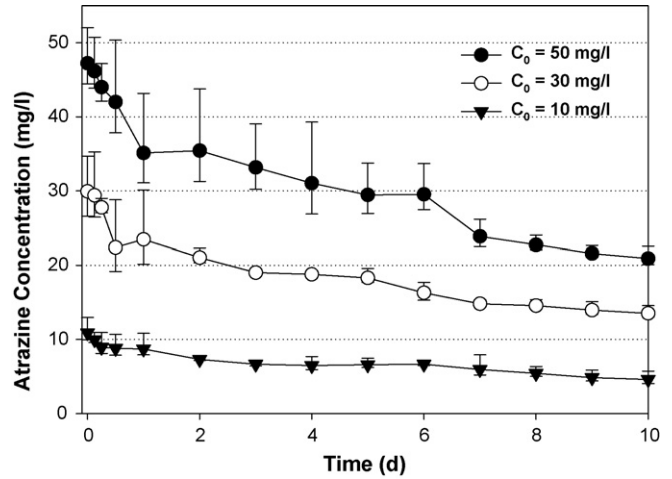


Fig. 3. Atrazine concentration change as a function of time when initial concentrations of atrazine (C_0) with buffer solution added.

increase that was observed when the solution was not buffered, as shown in Fig. 1.

Fig. 3 shows the degradation of atrazine with time according to the initial Fe⁰ concentration. When the initial concentration of atrazine was greater than 30 mg/L, the error bars were large because of the large fraction of atrazine present in the solid phase corresponding to the proportion above its solubility (=33 mg/L). After 10 days, when the initial concentration of atrazine was 50 mg/L, 30 mg/L and 10 mg/L, the concentrations were decreased to 20.92 mg/L, 13.53 mg/L and 4.6 mg/L, respectively. These results correspond to decreasing efficiencies of 58.16% at 50 mg/L, 54.90% at 30 mg/L, and 54.00% at 10 mg/L.

The rate of atrazine dechlorination by Fe⁰ was analyzed according to pseudo-first order kinetics to measure the dechlorination constant. Only the atrazine concentration was considered as an independent factor by assuming that all other conditions including the Fe⁰ content were the same. Eqs. (5)–(6) correspond to the equations of the concentration variation with time.

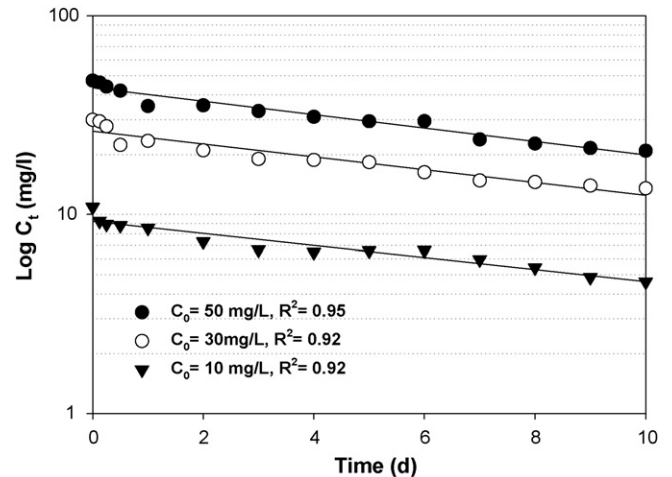


Fig. 4. Determination of kinetic constant for initial concentrations of atrazine (C_0) as the pseudo-first order reaction.

Table 1
Observed dechlorination constant, half-life of atrazine, coefficient of determination

Initial atrazine concentration (mg/L)	$k_{\text{obs}} (\times 10^{-2} \text{ d}^{-1})$	$t_{1/2}$ (d)	R^2
10	3.01	10.00	0.92
30	3.23	9.32	0.92
50	3.38	8.91	0.95

Fig. 4 was plotted on the basis of the linear regression results obtained from Fig. 3.

$$\frac{d[C]}{dt} = -k_{\text{obs}}[C] \quad (5)$$

$$\log \frac{[C]}{[C]_0} = k_{\text{obs}}t \quad (6)$$

$$t_{1/2} = \frac{1}{k_{\text{obs}}} \log 2 \quad (7)$$

where $[C]$ is the atrazine concentration at time t (mg/L); $[C]_0$ the initial atrazine concentration (mg/L); k_{obs} is the pseudo-first order constant (d^{-1}).

The dechlorination constant varied proportional to the initial concentration of atrazine, being $3.01 \times 10^{-2} \text{ d}^{-1}$ at an initial concentration of 10 mg/L, $3.23 \times 10^{-2} \text{ d}^{-1}$ at 30 mg/L and $3.38 \times 10^{-2} \text{ d}^{-1}$ at 50 mg/L. These values were considerably smaller than the value of 4.36 d^{-1} reported in the study of Dombek et al., in which similar conditions were used except that the pH was maintained at 3.8 [12].

The dechlorination constant was applied to Eq. (7), which gave rise to a half-life of atrazine of 10.00 d at an initial atrazine concentration of 10 mg/L, 9.32 d at 30 mg/L and 8.91 d at 50 mg/L. The dechlorination constant, half-life of atrazine and coefficient of determination measured in this study are summarized in Table 1.

4. Conclusions

Many geological materials such as clay and sediment have a pH buffering capacity which enables them to keep the pH of pore water neutral. In this research, a kinetic study of the dechlorination of atrazine by Fe^0 was undertaken under neutral conditions and the object of this research was consequently to confirm and measure the dechlorination of atrazine under neutral pH conditions in water with Fe^0 .

We were able to keep the pH in the neutral range between 7 and 8 and the ORP at the required level for the reduction of pore water by using a pH buffer solution. The ORP was maintained at less than -300 mV throughout the experiments, demonstrating the potential for the continuous dechlorination of atrazine by the addition of buffer solution. The dechlorination of atrazine followed pseudo-first order kinetics. The dechlorination kinetics were slow under neutral pH conditions, as compared with those reported in other studies conducted under acidic conditions. However, when present in the concentration range of 10–50 mg/L, atrazine was dechlorinated in 10 days, suggesting

that acidic additions may not be necessary for remediating geological materials. In the future, we will use geological materials such as sediment or clay under natural conditions with Fe^0 and monitor the levels of dechlorination, pH, and the ORP.

Acknowledgment

This research was supported by a research grant from the Small and Medium Business Administration, Korean Government.

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