

# Fenton Electrochemical Treatment of Aqueous Atrazine and Metolachlor

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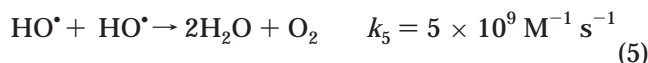
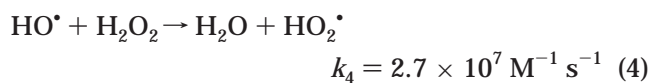
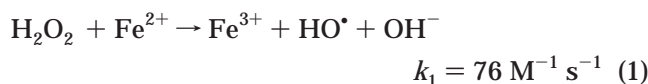
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A bench-scale Fenton electrochemical system was used to study the degradation of two widely used herbicides, atrazine and metolachlor. In this system the degradation of the herbicides occurs by attack of hydroxyl radicals which are produced from reaction of hydrogen peroxide with electrochemically generated ferrous iron. The goals of the study were to achieve degradation of the herbicides by optimizing reagent concentrations and to identify degradation pathways. Herbicide degradation was determined with respect to iron and hydrogen peroxide concentrations and their rate of addition. Effects of near-UV illumination and herbicide concentration on the degradation of the herbicides were also studied. Adding hydrogen peroxide in multiple smaller doses resulted in enhanced removal of the herbicides, especially metolachlor (greater than 99% degradation), as compared to adding it all at once at the beginning of the treatment. The degradation of atrazine, which was initially difficult, was enhanced (greater than 99% degradation) by using a small molar excess of hydrogen peroxide to iron (5:1) and maintaining the ratio for the entire period of treatment. Atrazine degradation in this system appears to be via N-dealkylation and dechlorination.

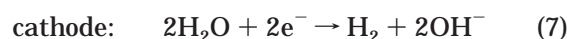
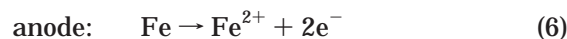
**Keywords:** Atrazine; degradation; electrochemical; Fenton; herbicides; hydroxyl; radicals; metolachlor

In a recent survey on agricultural chemical usage atrazine was reported as the most used herbicide, followed by metolachlor (U.S. Department of Agriculture, 1995). In Canada, metolachlor is heavily used in the Province of Ontario (Lau et al., 1995). Pesticides become potential contaminants when they are rinsed from application equipment, and in the past pesticide waste and rinsates were dumped on nearby soil for evaporation and further degradation. This method has proven to be environmentally unsafe as evidenced by the contamination of applicator sites and nearby wells (Aharonson, 1987). It is not always feasible to reuse the pesticide rinsewater in subsequent applications due to concerns of cross-reactivity or in situations where multiple cropping is employed (Ehart, 1988). Effective disposal of pesticide waste requires refined onsite pre-treatment/treatment methods that are both environmentally sound and cost-effective.

Recently, the use of advanced oxidation methods to treat contaminated wastewater has received attention. Oxidation methods such as the Fenton reaction that generate hydroxyl radicals are promising methods for treating polluted water. Traditionally, the Fenton system is a mixture of ferrous salt and hydrogen peroxide. Ferrous ion reacts with hydrogen peroxide to produce hydroxyl radical, hydroxide ion, and ferric ion (eq 1); the highly reactive hydroxyl radical then participates in other reactions (eqs 2–5) (Walling, 1975).



The hydroxyl radical is effective in attacking a wide range of organic compounds, and the Fenton system has been used by a number of researchers to bring about degradation of various organic pollutants. In previous work, Pratap and Lemley (1994) used a modified version of the Fenton system to degrade five herbicides belonging to three classes. Electrochemical delivery of iron was used instead of adding a ferrous salt, resulting in a higher final pH of the treated herbicide solution. In this system ferrous ion was produced at the anode, and water was reduced to hydrogen gas and hydroxide ion at the cathode.



Hydrogen peroxide was delivered to the electrochemical cell before electrolysis commenced in order to provide

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the conditions for the Fenton reaction. Control studies with electrochemical delivery of iron and no H<sub>2</sub>O<sub>2</sub> and with H<sub>2</sub>O<sub>2</sub> and no iron were also done to demonstrate that pesticide degradation was not due to other electrochemical or oxidative reactions. Although the Fenton electrochemical treatment was not as efficient in degrading the herbicides as the classic Fenton treatment, from a waste treatment perspective it has several attractive features; namely, (1) it is operable at circumneutral pH and (2) in-situ addition of ferrous ion from sacrificial iron electrodes in the reactor is easier to handle from a process perspective than external addition of large amounts of iron salt. The Fenton electrochemical approach looked promising but required further work.

The primary goal of the current study was to optimize the Fenton electrochemical method at circumneutral pH with respect to degradation of two herbicides, atrazine and metolachlor. Atrazine is of special interest because it was not degraded effectively in the previous study (Pratap, 1992). Neither herbicide undergoes rapid degradation in the environment. Attempts at optimization involved studying the system at different ratios of iron and hydrogen peroxide addition, their rate of addition, the concentration of herbicide, and the use of near-UV light. A second goal was to identify degradation products by HPLC. For atrazine, radiolabeled <sup>14</sup>C (both ring and side chains) compounds were used to determine degradation patterns.

#### MATERIALS AND METHODS

**Chemicals.** The herbicides used in this study were metolachlor (98% pure) and atrazine (99.0% pure) and their metabolites, deethylatrazine (DEA), deethyldeisopropylatrazine (DEIA), 2-hydroxyatrazine (OA), and 2-[(2-ethyl-6-methylphenyl)amino]-1-propanol, 99.1, 97, 99, and 98% pure, respectively, purchased from Chem Service Inc., West Chester, PA. Formulated atrazine (4L) and formulated metolachlor (8E) were obtained as gifts from the Plant Science Department, Cornell University, Ithaca, NY. Radiolabeled <sup>14</sup>C ring, ethyl and isopropylatrazine were received as gifts from the Agricultural Research Service Lab, USDA, Beltsville, MD. Reagent grade sodium chloride (NaCl) and analytical grade 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution were purchased from Fisher Scientific, Fair Lawn, NJ. Analytical grade sodium hydroxide (NaOH) was obtained from Mallinckrodt, Inc., Paris, KY. The biodegradable counting scintillant (BCS) was obtained from Amersham Corporation, Arlington Heights, IL. The solvents used in the HPLC analysis were methanol, acetonitrile, and water. HPLC grade methanol and acetonitrile were obtained from Fisher Scientific, Fair Lawn, NJ. Ultrapure water used for HPLC analysis and in the preparation of laboratory solutions was prepared by passing deionized water through a Barnstead NANOpure II 4-Module system followed by subsequent distillation in a Corning MEGA-PURE model MP-1 still.

**Experimental Procedures.** Preparation of the aqueous stock solutions of metolachlor used in the studies involved stirring the herbicide-water mixture for a few hours. The concentration of metolachlor used in most treatments ranged from 127 μM to 194 μM. In the case of atrazine, stock solutions were prepared by adding saturated amounts of the herbicide to distilled water and stirring it overnight to obtain concentrations near the limits of water solubility. A solubility of around 139 μM was achieved. The concentration of atrazine used in most treatments ranged from 120 μM to 139 μM. Lower concentrations of atrazine (14.8 μM) and metolachlor (23 μM) were used to study concentration effects.

A typical experiment involved electrolyzing 400 mL of the herbicide solution in a 600-mL beaker in the presence of hydrogen peroxide. The solution was kept well stirred with a magnetic stir bar to saturate the system with air. Sodium

chloride (0.2 g) was added as the electrolyte to improve conductivity in the solution. To electrolyze the pesticide solution, three 1/8-in. thick cold rolled steel plates separated by 1/8-in. gaps were used. The iron electrodes were immersed in the solution. Electrolysis was carried out by passing an appropriate amount of constant current for a given length of time. The level of iron generated in the system is governed by eq 8 which follows from Faraday's Law:

$$[\text{Fe}^{2+}] = (itgF)/V \quad (8)$$

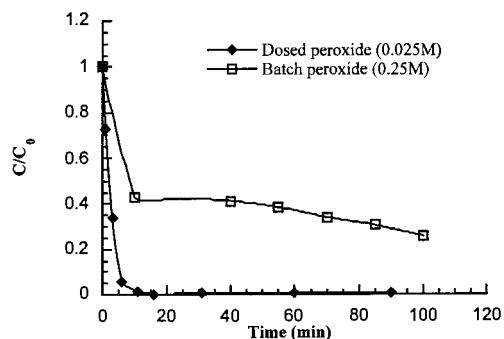
where *i* is the current in amperes, *t* is the time of electrolysis in minutes, *g* is the number of gaps between the electrodes, *F* is the design factor for the electrodes, and *V* is the volume of the solution in liters. The amount of current passed and the time were varied for given experiments. For 0.89 mM iron generation, 0.3 A constant current was passed for 2.5 min, while for 1.8, 3.6, and 7.1 mM iron the same current was passed for 5, 10, and 20 min, respectively. To generate 3.6 mM iron at currents of 0.6, 0.45, 0.15, and 0.08 A, electrolysis was carried out for 5, 7.5, 20, and 37.8 min, respectively. During electrolysis the solution initially turned yellow. Thereafter, reddish brown particulates of iron solids formed. When the mixture was allowed to stand, the particulates settled to the bottom of the beaker, leaving a clear supernatant at the top.

Three methods of hydrogen peroxide delivery were employed. In some experiments, 10 mL of 30% of hydrogen peroxide were added (batch addition) before electrolysis was commenced, while in other experiments, the reagent was added periodically (dosed addition), starting just before the iron was generated. Dosing was done every 5 min. A total of 10 doses were used in each treatment run. The treatments were carried out at two levels of hydrogen peroxide addition (1 and 0.25 mL), using the dosed method of addition. One and 0.25 mL of 30% hydrogen peroxide in 400 mL of solution amount to 0.025 and 0.006 M, respectively. The third method of hydrogen peroxide addition involved delivering the reagent via a syringe pump (Sage Instruments, model 220). This method of peroxide addition was incorporated in Fenton electrochemical treatments of atrazine only. The concentrations of hydrogen peroxide delivered via the syringe pump were such that a constant molar ratio of iron to hydrogen peroxide was maintained. This was accomplished by generating iron and adding peroxide continuously for the whole period of the treatment. Treatments were conducted under the conditions of 1:1, 1:5, and 1:10 molar ratios of iron to peroxide.

As soon as electrolysis was started, a 10-mL aliquot was withdrawn (*t<sub>0</sub>*) from the reaction beaker and quenched with an equal volume of HPLC grade organic solvent—acetonitrile for atrazine and methanol for metolachlor. At intervals of time, six to eight aliquots were taken and quenched with 10 mL of the appropriate solvent. These quenching compounds matched the mobile phases for HPLC analysis. The quenched samples were refrigerated and analyzed by HPLC the following day. The Fenton electrochemical treatments were performed with and without UV illumination. When UV illumination was not used, the beaker and the electrode assembly were wrapped in aluminum foil.

The UV illumination experiments were carried out inside a cardboard box, the inside of which was lined with aluminum foil. Near-UV illumination (330–400 nm) was used with the emission peak centered at 370 nm. The beaker containing the herbicide solution was placed in the center of the box over a magnetic stir plate. The beaker was surrounded by eight F15T8 BLB Sylvania black light fluorescent bulbs, with two bulbs to a side. Each pair of bulbs was placed approximately 27 cm away from the outer surface of the beaker. In the absence of any ventilation, illumination resulted in rise of solution temperature from 27 to 33 °C at the end of 1.5–2 h treatment. The pH values of the treated solutions were measured with an Accumet 25 pH meter using an Accumet 13-620-287 pH electrode.

**Mineralization Experiments.** Three sets of mineralization experiments were conducted with radiolabeled atrazine.



**Figure 1.** Effect of hydrogen peroxide dosing on the degradation of metolachlor in the Fenton electrochemical system: dark, 3.6 mM iron and 0.3-A current.

The experiments were conducted in an enclosed reactor containing a sidearm with 5 mL of 0.5 M sodium hydroxide (NaOH) used as a trap for  $^{14}\text{CO}_2$ . Treatments were conducted with 14.8  $\mu\text{M}$  atrazine solution and under conditions of constant molar ratio of 1:5 iron to peroxide and no light. Iron was generated at 0.08 A current with a total iron generated of 3.6 mM.

The first set of experiments consisted of Fenton electrochemical treatment of 400 mL of atrazine solution spiked with 0.6  $\mu\text{Ci}$  of [ $^{14}\text{C}$ ]ethyl atrazine. The second set of Fenton electrochemical treatments was performed with 1.1  $\mu\text{Ci}$  [ $^{14}\text{C}$ ]isopropylatrazine. The third set of treatments was conducted with 400 mL of atrazine solution spiked with 9.3  $\mu\text{Ci}$  of ring labeled [ $^{14}\text{C}$ ]atrazine.

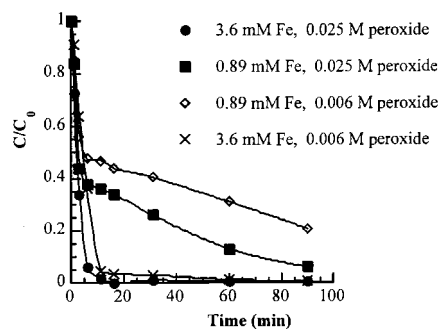
**Analytical Method.** Herbicide concentrations were analyzed with a Hewlett-Packard model 1090A high-performance liquid chromatograph equipped with a Rheodyne 7010 injection valve and a diode-array detector using a 150  $\times$  4.6 mm Supelcosil LC-8-DB analytical column (3.6- $\mu\text{m}$  packing) and a 2-cm guard column (Supelco Inc., Bellefonte, PA). In the case of metolachlor and its metabolite [2-(2-ethyl-6-methylphenyl)amino]-1-propanol, the mobile phase consisted of methanol and water in the ratio of 73:27 (methanol to water) (v/v). Atrazine was analyzed by using an isocratic gradient, 50:50 of acetonitrile to water (v/v). Quantitation of the parent compound was followed at 220 nm, the maximum absorbance in its ultraviolet-visible spectrum. For metolachlor analysis, a flow rate of 1 mL/min was used, while for atrazine a lower flow rate of 0.8 mL/min was used. The retention times for metolachlor and its degradation product were approximately 5.6 and 3.1 min, respectively. Atrazine eluted at 3.8 min. For all analyses, a sample loop of 200  $\mu\text{L}$  was used, and all the samples were filtered through 0.25 mm acrodisc nylon syringe filters prior to injection of the samples.

A different method was used to separate the degradation products of atrazine. The same column was used, but the solvent system was ramped over 30 min from 98% solvent A (water at pH 3) and 2% solvent B (90% methanol, 10% 50  $\mu\text{M}$   $\text{CH}_3\text{COONH}_4$ ) to 15% solvent A and 85% solvent B. The flow rate was 0.8 mL/min and the autosampler injection volume was set at 100  $\mu\text{L}$ . UV settings were the same.

All samples were analyzed in triplicate and compared to a calibration curve. Each electrochemical treatment run presented is the average of three runs. Differences presented are statistically significant at the 95% confidence level.

## RESULTS AND DISCUSSION

**Effect of Hydrogen Peroxide Dosing.** The efficiency of the Fenton electrochemical system is enhanced by adding a given amount of peroxide in smaller doses (dosed) rather than adding it all at once (batch). Figure 1 shows this enhanced degradation for metolachlor. With batch addition of hydrogen peroxide (0.25 M) at a given level of iron, the disappearance of metolachlor is initially rapid and then becomes slow. Complete removal of the parent compound is not



**Figure 2.** Degradation of metolachlor in the Fenton electrochemical system: dark, two different iron generations and two concentrations of hydrogen peroxide (dosed).

achieved. However, when the same amount of hydrogen peroxide is added in 10 doses (0.025 M) over the course of treatment, the removal of metolachlor is enhanced. At 3.6 mM iron and with dosing of peroxide (0.025 M), greater than 99% degradation of metolachlor is achieved. In essence, a lower initial concentration of hydrogen peroxide results in faster and more effective degradation of metolachlor. The batch addition of hydrogen peroxide most likely results in quenching of hydroxyl radicals via the reactions in eqs 4 and 5 whose rates are competitive with reactions of most herbicides with hydroxyl radicals as in eq 3 (Haag and Yao, 1992). Other experiments showed that metolachlor degradation is significantly decreased in the presence of methanol, a known hydroxyl radical quencher (data not shown), indicating that in the electrochemical Fenton system degradation of the herbicide does indeed occur by hydroxyl radical attack.

Some simple calculations can be made to determine what concentration of hydrogen peroxide produces significant hydroxyl radical reaction with a given herbicide at a given concentration. Equation 9 is a ratio of the rate of reaction of  $\text{OH}^\bullet$  with metolachlor and with hydrogen peroxide, which is assumed to be the most important competitive reaction due to the concentration of hydrogen peroxide.

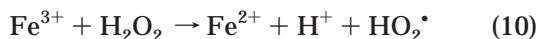
$$\text{fractn to metol} = \frac{k_{\text{OH}^\bullet + \text{metol}}[\text{metol}]}{\sum k_{\text{OH}^\bullet + \text{[Ci]}}} = \frac{k_{\text{OH}^\bullet + \text{metol}}[\text{metol}]}{k_{\text{OH}^\bullet + \text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]} \quad (9)$$

If a rate constant of  $10^9$  is assumed for the metolachlor reaction [based on similar reaction rates in Haag and Yao (1992)], a typical concentration of metolachlor is used (127  $\mu\text{M}$ ), the rate constant for the hydrogen peroxide reaction from eq 4 is used, and a hydrogen peroxide concentration of 0.25 M is used (the amount of  $\text{H}_2\text{O}_2$  used in the batch study), the fraction of radicals available to react with the metolachlor is 0.02. If it is assumed that all the iron produces hydroxyl radicals (3.6 mM) and 0.02 of that reacts with metolachlor, 72  $\mu\text{M}$  of metolachlor should react, roughly half of the initial concentration. These calculations describe what is seen in Figure 1. The batch experiment does not produce enough hydroxyl radicals to degrade all of the metolachlor. The lower concentration of  $\text{H}_2\text{O}_2$  (0.025 M) is low enough to degrade 720  $\mu\text{M}$  metolachlor. Thus, a lower concentration limit for  $\text{H}_2\text{O}_2$  can be determined for a given set of conditions, taking into account the competition for hydroxyl radicals and the amount required for the Fenton reaction.

Figure 2 depicts the degradation of metolachlor at two iron levels and two hydrogen peroxide concentrations.

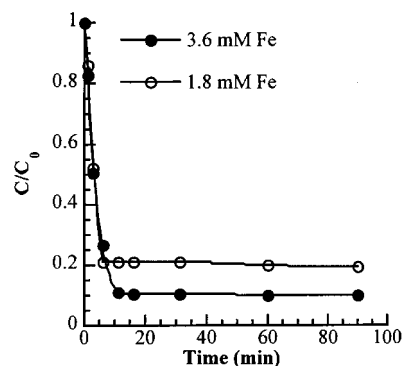
Hydrogen peroxide was added in the ten-dose method. Significantly better removal of metolachlor is achieved with 3.6 mM iron generation. Although the previous calculation would suggest that the 0.006 M addition of hydrogen peroxide would be more effective than the 0.025 M addition, at this level of iron the rate of degradation and the amount of metolachlor degraded are not affected by the concentration of peroxide used, indicating that the calculation is not sensitive to differences at these levels. Only two doses of peroxide are needed to degrade greater than 99% of metolachlor. This result is not surprising based on the previous calculation. However, with lower iron generation (0.89 mM), greater than 95% removal of metolachlor is only achieved with the higher peroxide concentration (0.025 M) and over a longer period of treatment. This result can be investigated by making some assumptions and using eq 9 to solve for the fraction of hydroxyl radicals that would react with metolachlor, assuming a 0.025 M concentration of hydrogen peroxide in each dose. If the concentration of Fe(II) generated were 3.6 or 0.89 mM and all of the Fe(II) were converted into hydroxyl radicals, these concentrations multiplied by the fraction to metolachlor from eq 9 gives the expected amount of metolachlor that would react with hydroxyl radicals. The initial concentration of metolachlor is 127  $\mu\text{M}$ , and the calculated metolachlor concentrations that could react with hydroxyl radicals are 720 and 178  $\mu\text{M}$  for 3.6 and 0.89 mM iron, respectively. The calculations predict that there should be just enough Fe(II) available in the 0.89 mM experiment (and more than enough in the 3.6 mM experiment) to produce hydroxyl radicals to degrade all the metolachlor. But the experimental results do not follow these predictions. If any Fe(II) is not available for the Fenton reaction, due to other reactions such as eq 2 or oxidation to Fe(III), the 0.89 mM iron addition does not provide enough iron to degrade all the metolachlor, as seen in the Figure 2. In these experiments, the iron becomes the limiting reagent for the initial degradation of metolachlor.

It can also be noted in Figure 2 that at 0.89 mM iron metolachlor degrades rapidly in the first few minutes, i.e., when electrolysis is on, and then degrades slowly in the postelectrolysis period of the treatment. The fact that at low levels of iron generation this slow degradation continues after electrolysis can be explained by the regeneration of ferrous ion via reaction 10, i.e., ferric ion catalyzes the decomposition of hydrogen peroxide (Sun and Pignatello, 1993) which is still being added.



This regeneration is possible because, with 0.89 mM iron generation, the final pH of treated metolachlor solution is 4.4, and the  $\text{Fe}^{3+}$  is still soluble. Initial and final pH values for metolachlor and atrazine solutions are shown in Table 1. The pH of the treatment mixture goes up slightly with increasing levels of iron due to the concomitant production of hydroxide anions at the cathode.

It is also known that the Fenton reaction is more efficient at lower pHs (2–3) (Pignatello and Baehr, 1994) due to higher solubility of  $\text{Fe}^{3+}$ . At pH 4.4, it is possible that some ferric ion (produced by reactions 1 and 2) exists as  $\text{Fe}^{3+}(\text{aq})$ , although at nanomolar levels (Stumm and Morgan, 1981). Therefore, at 0.89 mM iron, metolachlor degradation may be controlled post-electrolysis by reaction 10 in which a low concentration



**Figure 3.** Fenton electrochemical treatment of atrazine at two levels of iron generation: dark, dosed peroxide (0.025 M), and 0.3-A current.

**Table 1.** Influent and Effluent pH Values

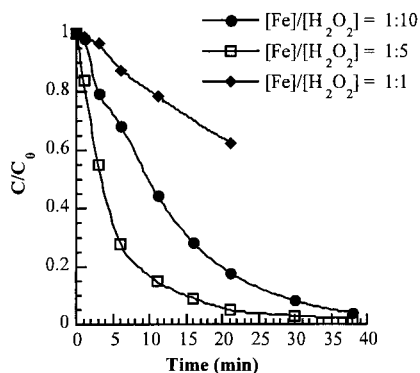
[Fe], mM	metolachlor		atrazine	
	initial pH	effluent pH	initial pH	effluent pH
0.89	5.8 ± 0.2	4.4 ± 0.1	5.5 ± 0.2	6.7 ± 0.1
1.8	5.8 ± 0.2	5.0 ± 0.2	5.5 ± 0.2	6.7 ± 0.1
3.6	5.8 ± 0.2	5.9 ± 0.3	5.5 ± 0.2	7.7 ± 0.2
7.1			5.5 ± 0.2	7.6 ± 0.6

of ferrous ion is regenerated and the Fenton reaction 1 is sustained.

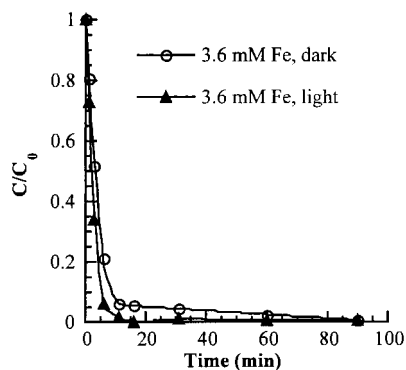
In Figure 3 the degradation of atrazine at 1.8 and 3.6 mM iron and 0.025 M hydrogen peroxide is shown. With the dosing method of peroxide addition, 90% removal of atrazine is achieved at 3.6 mM iron, but complete removal of the compound is not achieved. In general, greater removal of metolachlor is accomplished with lower levels of iron generation as compared to atrazine. For example, at 3.6 mM iron and 0.025 M hydrogen peroxide, metolachlor removal is greater than 99%, while for atrazine it is about 90%. The removal difference is more pronounced at the 0.89 mM iron level for the same concentration of hydrogen peroxide (94% versus 57%). Slightly better removal of atrazine (94%) is effected by increasing the level of iron generation to 7.1 mM (data not shown). Also, unlike metolachlor degradation, atrazine degradation reaches a plateau in the postelectrolysis period of the Fenton electrochemical treatment.

The difference in the reactivity of atrazine and metolachlor in the Fenton electrochemical system contrasts with their similar hydroxyl radical reaction rate constants reported in the literature. Atrazine and alachlor (which is structurally similar to metolachlor) react with hydroxyl radicals at rate constants of  $2.6 \times 10^9$  and  $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively (Haag and Yao, 1992). The pHs of treated atrazine solutions are reproducibly higher than for metolachlor (Table 1). These higher pH values were also found for the other triazines (Pratap and Lemley, 1994). At pH values greater than 6.0, the Fenton reaction is not efficient in degrading atrazine due to more oxidation to Fe(II) and precipitation of ferric oxides (Arnold et al., 1995).

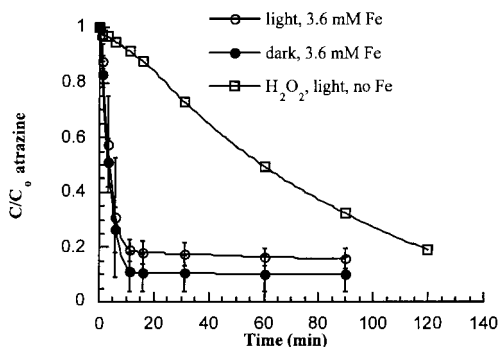
To effect greater degradation of atrazine, the system was further modified by continuous addition of lower concentrations of peroxide and by maintaining a constant molar ratio of iron to peroxide. Figure 4 shows the degradation of atrazine under three different molar ratios of iron to peroxide. This modification enhances atrazine removal; greater than 99% removal is achieved at the constant molar ratio of 1:5 iron to peroxide, which appears to be an optimum ratio among those tested. At a lower ratio of 1:1 the system is ineffective, probably



**Figure 4.** Effect of molar ratios of iron and hydrogen peroxide on the degradation of atrazine in the Fenton electrochemical system: dark, continuous addition of peroxide.



**Figure 5.** Effect of near-UV light (330–400 nm) on the degradation of metolachlor in the Fenton electrochemical system: 3.6 mM iron, 0.025 M dosed peroxide, and 0.3-A current.

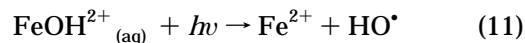


**Figure 6.** Effect of near-UV light (330–400 nm) on the degradation of atrazine in the Fenton electrochemical system: 3.6 mM iron, 0.025 M dosed peroxide, and 0.3-A current. Effect of 0.025 M dosed peroxide and near-UV light on degradation of atrazine with no iron addition.

due to lack of sufficient hydroxyl radicals, while at a higher ratio of 1:10 some quenching of hydroxyl radicals affects the degradation of the herbicide. With this modification, the Fenton electrochemical system becomes more efficient at degrading atrazine at a lower concentration of added peroxide (0.0018 M for 1:5 iron to peroxide) as compared to the dosed additions of 0.025 M. This method provides a constant source of hydroxyl radicals, matching it to the production of ferrous ions at the anode and thus sustaining the Fenton reaction.

**Effect of Near-UV Illumination.** Figures 5 and 6 show the effect of near-UV illumination on the degradation of the herbicides metolachlor and atrazine, respectively. The treatments were performed with 3.6 mM iron generation and dosed peroxide (0.025 M). Figure

6 also shows the effect of light (330–400 nm) with hydrogen peroxide addition in the absence of electrochemical addition of iron. Addition of light does not enhance the Fenton degradation of the herbicides (the two bottom curves in Figure 6 are the same within experimental error), although it could be expected if ferric ion in solution were able to react via reaction 11 (Sun and Pignatello, 1993) to regenerate ferrous ion.



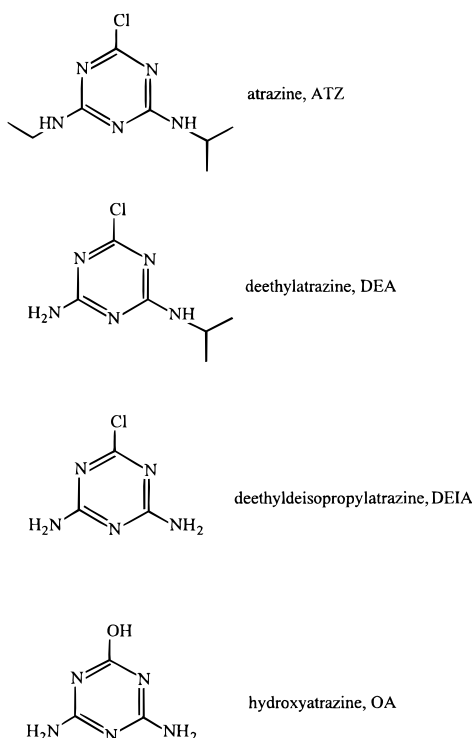
However, due to low solubility of ferric ion at circumneutral pH, the effect of this reaction is negligible. Also, it is assumed that the iron solids formed in the system attenuate the intensity of the light striking the target molecules. When hydrogen peroxide is added in the presence of light and absence of iron (Figure 6) atrazine disappears slowly until 80% removal is achieved. The energy of the light used is not sufficient to produce enough hydroxyl radicals via photolysis (Edwards and Curci, 1991) to degrade atrazine as efficiently as the Fenton system.

**Rate of Iron Delivery.** Another attempt at optimizing reaction conditions of the Fenton electrochemical system involved generating iron at different rates by adjusting the current passed in the electrochemical cell. Varying the rate of iron generation had no effect on the removal efficiency of either of the herbicides (data not shown).

**Effect of Herbicide Concentration.** The initial concentration of the herbicides does not appear to affect the degradation of the herbicides. In the case of metolachlor, the plots of logarithmic  $C/C_0$  versus time yield a linear relationship with slopes (rate constants) of 0.30 and 0.22  $\text{min}^{-1}$  for metolachlor levels of 23 and 192  $\mu\text{M}$ , respectively. Similarly, with atrazine the rate constants obtained from the slopes of the linear plots of logarithmic  $C/C_0$  versus time are 0.14 and 0.10  $\text{min}^{-1}$  for initial concentrations of 14.8 and 129  $\mu\text{M}$ . In the liquid phase most organics (containing C–H and C–C multiple bonds) react with hydroxyl radicals with rate constants near the diffusion-controlled limit ( $10^{10} \text{M}^{-1} \text{s}^{-1}$ ). The oxidation rates are usually limited by the rates of hydroxyl radical generation and competition by other radical scavengers in solution and not by the inherent reactivity of the compound with the radical (Haag and Yao, 1992).

**Formulated Herbicides.** With respect to formulated herbicides, metolachlor in the formulation 8E and atrazine in the formulation 4L were degraded as completely as the analytical standards in the Fenton electrochemical system. Apparently the presence of other organics in the formulation does not severely affect the degradation of the herbicides. In the case of atrazine, the formulation is a suspension of atrazine in water with 3% wetting agents and polymeric dispersing agents.

**Degradation Products.** The HPLC profiles of treated metolachlor show various peaks which elute before the parent compound. This result indicates that metolachlor probably does not undergo mineralization in the Fenton electrochemical system. In many of the studies on chemical oxidation, microbial degradation, or sunlight degradation of metolachlor reported in the literature mineralization was not observed (Chesters et al., 1989; Kochany and Maguire, 1994; Liu et al., 1995). A close match of a product peak (HPLC) with a standard



**Figure 7.** Atrazine and N-dealkylation degradation products, DEA and DEIA.

metabolite of metolachlor, [(2-ethyl-6-methylphenyl)-amino]-1-propanol, was obtained. However, this product is a minor product as judged by the area under the curve for the peak. Chloride estimation by using a chloride selective electrode was not performed because chloride ions (9 mM) present from the addition of sodium chloride would mask the estimation of chloride release from the herbicides which are at levels 100-fold lower than that of the salt. However, dechlorination of metolachlor is suspected in the system. This follows from the results reported in the literature. In a Fenton-like system (Pignatello and Baehr, 1994), chloride release was observed with the degradation of metolachlor. Dechlorinated products were also identified in the sunlight degradation of metolachlor (Kochany and Maguire, 1994).

There were at least five major HPLC peaks in the treated atrazine solution. Three peaks matched retention times with standards of deethyldeisopropylatrazine (DEIA), deethylatrazine (DEA), and 2-hydroxyatrazine (OA). The UV spectra of these peaks (taken with the diode array detector) are similar to those of the standards, further confirming their identity. This suggests that the degradation of atrazine in the Fenton electrochemical system occurs via N-dealkylation and dechlorination (Figure 7) as in the classic Fenton system (Arnold et al., 1995). Also, Fenton electrochemical treatments with  $^{14}\text{C}$ -labeled ethyl- and isopropylatrazine result in loss of radioactivity of 56% and 26%, respectively. It was extremely difficult to trap  $\text{CO}_2$  with the apparatus used in these studies due to the large headspace required with the electrodes and no positive pressure to carry the  $\text{CO}_2$  to the trap. New equipment is being designed to do further mineralization studies. The  $^{14}\text{C}$  results clearly indicate that N-dealkylation is one of the pathways of degradation of the herbicide in the system. Earlier studies reported in the literature show that N-dealkylation is the major pathway for degradation of atrazine by hydroxyl radicals in Fenton

and Fenton-like oxidative systems (Plimmer et al., 1971; Kearney et al., 1988; Larson et al., 1991; Arnold et al., 1995). In the recent study by Arnold et al. (1995), Fenton degradation of atrazine leads to the formation of DEIA as a major product and to other dechlorinated products.

No loss of radioactivity was observed with the Fenton electrochemical treatment of the  $^{14}\text{C}$  ring labeled atrazine. This result confirms the findings of earlier Fenton system studies. Mineralization has been observed in microbial degradation studies only. This suggests that breakdown of the triazine ring or, in other words, the cleavage of the C=N bond, is probably an enzyme-mediated reaction.

## CONCLUSIONS

In this study, the efficiency of the electrochemical Fenton system was enhanced by adding hydrogen peroxide in multiple smaller doses over the time of the experiment rather than all at once. This result indicates that the major pathway for removal of the hydroxyl radical is through its reaction with excess hydrogen peroxide (eq 4), which thereby inhibits the degradation of the herbicides. The use of excess hydrogen peroxide is unnecessary in this modified Fenton system, since it cannot be used to regenerate significant amounts of ferrous ion via reaction 9 due to restricted availability of aqueous ferric ion at circumneutral pH.

The Fenton reaction is not efficient for degrading atrazine under circumneutral pH conditions (pH greater than 6) as reported by Arnold et al. (1995). Thus, the efficiency of the Fenton electrochemical system, which has effluent pH values of 6.6–7.7 for atrazine solutions, is not surprising. Electrochemically generated ferrous ion undergoes various competing reactions that restrict its concentration in solution. It is oxidized to ferric ion via the Fenton reaction (eq 1), and it undergoes reaction with the hydroxyl radical (eq 2), reaction with oxygen in the air, and reaction with the organic peroxy radical. Among these reactions, the air oxidation of Fe(II) is important for pH values greater than 5 (Stumm and Morgan, 1981). The rate of oxidation is first order with respect to Fe(II) and  $\text{O}_2$  and shows second-order dependence with hydroxide anion concentration. There is a 100-fold increase in reaction rate for an increase of one pH unit. Under the pH conditions of the atrazine solutions, ferric iron will precipitate as oxyhydroxide complexes, the iron solids observed in the experiments. In addition, preliminary experiments showed that the Fenton electrochemical system will not work if peroxide is added after iron is generated. These results confirm that ferrous is oxidized to ferric quickly enough under these conditions so that not enough iron is present in solution to sustain the Fenton reaction.

Therefore, adding the peroxide while the system is generating ferrous ions is a logical approach to making the system operate efficiently at circumneutral pH. Dosed and continuous methods of hydrogen peroxide addition incorporate this approach and are successful at degrading the herbicides metolachlor and atrazine, with the continuous addition working better for atrazine. Controlled addition of peroxide, controlled iron generation, and maintenance of an optimum iron to peroxide concentration ratio are critical to maintaining an effective Fenton reaction in the system. If more iron is generated than peroxide addition, hydroxyl radical availability will be affected by the reaction of excess

ferrous ions with hydroxyl radicals (eq 2). If hydrogen peroxide is in great excess, hydroxyl radicals will be quenched (eqs 4 and 5). A slight excess of peroxide appears to be essential for the system to degrade the herbicides efficiently.

N-Dealkylation and dechlorination appear to be the major pathways of degradation for atrazine in the Fenton electrochemical system. No mineralization of the herbicide is observed. The results obtained in the study also indicate that the treatment efficiency of the Fenton electrochemical system depends not only on the concentrations of iron and hydrogen peroxide but also on the chemical nature of the herbicides, particularly as the pH of the solution is affected during degradation.

The Fenton electrochemical system was optimized to effectively degrade the analytical standards and formulated products of metolachlor and atrazine. It shows promise for wastewater treatment at circumneutral pH and should be investigated as a method to degrade other organic aqueous pollutants.

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