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Electrochemical Peroxide Treatment of Aqueous Herbicide Solutions

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The treatment efficiencies of an electrochemically mediated iron–hydrogen peroxide system and the classic Fenton reagent system have been investigated with the goal of developing simple accessible methods for treatment of pesticide-contaminated wastewater, such as pesticide rinsewater. These treatment methods were screened by applying them to aqueous solutions of alachlor, metolachlor, atrazine, cyanazine, and picloram. Electrochemically mediated iron precipitation, achieved by electrolyzing the pesticide solutions in the presence of sacrificial iron electrodes, studied as a control method, was not effective in removing the herbicides from their respective aqueous solutions. A modified Fenton system consisting of electrochemical generation of iron in the presence of hydrogen peroxide (electrochemical peroxide) was effective in removing/degrading the herbicides within a few hours, with 90% or greater efficiency in all cases except cyanazine. The classic Fenton system was effective in removing the herbicides within 1.5 h with greater than 99% efficiency. The final pH values of the electrochemical peroxide treated solutions ranged from 5 to 7.5, while the pH of the classic Fenton reagent treated solutions ranged from 2 to 3.2.

In the United States hundreds of millions of pounds of pesticides are applied annually to control weeds and insect pests. According to estimated figures, herbicides comprised about 85% of pesticide use in 1990 (Curtis and Walsh, 1991). Such large-scale use of pesticides poses a potential threat to groundwater (Williams et al., 1988) and surface water through runoffs, leaching, and accidental spills. In the developing countries of Africa and Asia the problems of pesticide pollution are aggravated by lack of trained personnel, absence of strict government regulations, lack of good storage facilities, and stockpiles of unwanted pesticides which have to be disposed of (Jensen, 1992). Pesticides also become potential contaminants when they are rinsed from application equipment. Significant volumes of aqueous rinsewater are generated by commercial pesticide applicators and private farmers. Use of such rinsates as diluent in subsequent applications may not always be practical (Ehart, 1988). A typical rinsewater may contain pesticide amounts ranging from 100 to 1000 ppm (Seiber, 1988).

Many methods have been used to remove pesticides from aqueous wastewater. While separation techniques such as activated carbon have had some success, the ultimate problem of disposal must still be handled. Strong degradative techniques that employ oxidation are more likely to eliminate environmental toxicity (Hapeman-Somich, 1992). Electrochemistry has been used by some workers to generate hydroxyl radicals from hydrogen peroxide to produce such a degradative system. The hydroxyl radical so produced is a potent oxidizing agent (Walling, 1975). Several studies have investigated the effectiveness of electrochemical peroxide treatments on degradation of certain industrial pollutants. In one work (Tomat and Vecchi, 1971), oxidative addition of hydroxyl radical to benzene was found to be effective. In another study, Sudoh et al. (1986) investigated the oxidative degradation of phenol effluent by hydrogen peroxide which was generated by electroreduction of oxygen dissolved in the effluent.

The classic Fenton reaction has also been used to degrade environmental pollutants. Fenton's reagent is a mixture of ferrous salt and hydrogen peroxide and represents a class of metal–hydrog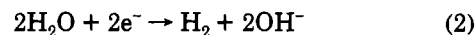en peroxide aqueous systems. Ferrous ion reacts with hydrogen peroxide to produce hydroxyl ion, hydroxyl radical, and ferric ion (Walling, 1975). The classic Fenton system has been studied with a wide variety of compounds of environmental concern such as chlorobenzene, polychlorinated biphenyls, and polychlorinated phenols (Sedlak and Andren, 1991a,b; Barbeni et al., 1987; Watts et al., 1990; Leung et al., 1992). Some workers have investigated the system with pesticides (Plimmer et al., 1972; Larson et al., 1991; Pignatello et al., 1992). Most of the Fenton reagent studies reported in the literature have been conducted at pH values between 0 and 3.

An electrochemical precipitation method for removal of contaminants was developed by Andco Environmental Processes, Inc., Amherst, NY. The Andco electrochemical cell generates ferrous ion when current is applied across the sacrificial iron electrodes which are immersed in aqueous solution. Equations 1–3 represent the reactions that occur in the cell:
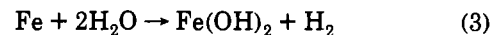
at anode

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

at cathode

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

overall

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \tag{3}$$

In certain wastewaters ferrous hydroxide chemically reacts with hexavalent chrome and coprecipitates with other heavy metals such as Cu, Co, and Ni. The method has also proved to be effective in removing color from dye-laden textile wastewaters (Kiener and Uhrich, 1987). In another study with dye-laden wastewater, significant reductions in BOD and COD were achieved (Demmin and Uhrich, 1988). Recently, studies of azo-based acid dyes (McClung and Lemley, 1992) demonstrated some chemical reduction of the azo linkage.

In this study, an electrochemical Fenton system (electrochemical peroxide method) for treating aqueous solu-

tions of herbicides was screened for its effectiveness in removal/degradation of five herbicides. The method is an adaptation of the electrochemical method described above; the addition of hydrogen peroxide to the solution in conjunction with the generation of ferrous ion produces an electrochemical Fenton system at circumneutral pH. The purpose of the study was to determine if the electrochemical Fenton system is effective at removal/degradation of the parent compound when compared to a second method, the classic Fenton reagent treatment. A third method, the electrochemical method developed by Andco, was investigated as a control for evaluating the electrochemical-peroxide method.

The five herbicides studied are from three classes and are widely used. Alachlor and metolachlor are chloroacetanilides; atrazine and cyanazine are s-triazines; and picloram is a picolinic acid derivative (4-amino-3,5,6-trichloropicolinic acid).

MATERIALS AND METHODS

Chemicals. Alachlor (99% pure), metolachlor (98% pure), picloram (97% pure), atrazine (99% pure), and cyanazine (97% pure) were purchased from Chem Service Inc., West Chester, PA. Laboratory grade sodium chloride (NaCl), analytical grade 30% hydrogen peroxide (H_2O_2) solution, ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), and reagent grade hydrochloric acid (HCl) were purchased from Fisher Scientific, Fair Lawn, NJ. Analytical grade sodium hydroxide (NaOH) was obtained from Mallinckrodt, Inc., Paris, KY, and a 0.2% solution of anionic acrylamide coagulant polymer (Andco 2600) was contributed by Andco Environmental Processes Inc. The solvents used in the HPLC analysis were methanol and water. HPLC grade methanol used was from Fisher Scientific. 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. Aqueous solution of 1 M tetrabutylammonium dihydrogen phosphate (ion pair reagent) was purchased from Aldrich Chemical Co., Milwaukee, WI.

Experimental Procedures. All experiments were conducted at ambient temperature (22–27 °C). Aqueous solutions of herbicides were used in electrochemical, electrochemical peroxide, and Fenton reagent treatments. Preparation of the herbicide stock solutions involved stirring the herbicide–water mixture for several hours. In the case of atrazine, 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 30–32 mg/L was achieved instead of the reported solubility of 70 mg/L (*Merck Index*, 1983). The concentrations of all the herbicide solutions except metolachlor were approximately 30 ppm. The concentrations of metolachlor solutions ranged from 45 to 170 mg/L.

(A) *Electrochemical Treatment.* Electrochemical treatment experiments were conducted with the Andco bench-top scale electrochemical cell (L-cell). In a typical electrochemical treatment, 400 mL of the herbicide solution was measured into a 600-mL beaker. To the solution was added 0.2 g of sodium chloride as the electrolyte. The solution was electrolyzed by applying a constant direct current of 0.3 A across the iron electrodes for a given amount of time. The amount of ferrous iron generated is governed by Faraday's law. According to this law, in any electrolytic process the amount of chemical change is directly proportional to the quantity of electricity (current × time) passed. Since the current was kept constant, the amount of iron generated was proportional to the time of electrolysis. For all experiments, current was applied for 20 min, generating 400 ppm of total iron. For these experiments and for the electrochemical peroxide experiments (*vide infra*), the iron concentration was determined spectrophotometrically on the basis of the iron(II)–1,10-phenanthroline complex method used by Harvey et al. (1955). The herbicide solution was stirred over a magnetic stir plate, and the pH was checked at regular intervals. After

electrolysis, the solution was stirred vigorously for 5 min to vent hydrogen gas. The pH of the solution was checked and adjusted to between 8.5 and 8.9 with 0.5 M sodium hydroxide and 0.5 M hydrochloric acid whenever necessary. Following pH adjustment, 1 mL of the anionic polymer (Andco 2600) was added to the solution to aid in coagulation/flocculation of the precipitate. The mixture was then filtered through Whatman No. 5 filter paper. The filtrate was subsequently analyzed by HPLC.

Preliminary precipitate analysis was performed to determine the mechanism of pesticide removal from aqueous solution. The precipitate obtained after the electrochemical treatment was thoroughly washed and dried overnight. Any bound herbicide was extracted by rinsing the precipitate three times with 10 mL of HPLC grade methanol. The resulting methanolic solution was then allowed to dry. Any remaining residue (actually not visible to the naked eye) was dissolved in double-distilled water and analyzed by HPLC.

(B) *Electrochemical Peroxide Treatment.* Electrochemical peroxide treatment was conducted by generating iron in the presence of hydrogen peroxide. Into a 600-mL beaker was measured 400 mL of the herbicide solution, followed by addition of 0.2 g of sodium chloride (electrolyte). The beaker and the electrode assembly were covered with aluminum foil to inhibit hydroxyl radical generation by light radiation from ambient light sources. The solution was kept well stirred with the aid of stir-bars. Ten milliliters of 30% hydrogen peroxide was added before the start of electrolysis. A constant current of 0.3 A was applied across the iron electrodes for a given length of time. The duration of electrolysis varied from 5 to 20 min. After electrolysis, the electrodes were removed ($t = 0$), and thereafter, at timed intervals, 10-mL aliquots of the reaction mixture were withdrawn and immediately analyzed by HPLC. Solution pH was checked periodically. Hydrogen peroxide concentration in the electrochemical peroxide treatment was checked over the course of time using the iodimetric titration method (Vogel, 1962).

For the case of alachlor, which exhibited some adsorption in the electrochemical treatment, the iron hydroxide precipitate obtained in the electrochemical peroxide treatment method was analyzed at timed intervals for any bound alachlor. The precipitate was separated from the filtrate using a Whatman No. 42 filter paper. The precipitate was washed and allowed to dry overnight. Any bound alachlor was extracted by rinsing the precipitate three times with 10 mL of HPLC grade methanol. The solvent was evaporated by drying the solution under a stream of air; remaining residue was dissolved in double-distilled water and analyzed by HPLC.

(C) *Fenton Reagent Treatment.* In addition to the electrochemical treatments, classic Fenton reagent treatments (dark) were conducted on the herbicides and compared with the electrochemical treatments. A typical experiment involved preparation of a reaction mixture in a 250-mL Erlenmyer flask containing 200 mL of herbicide solution to which appropriate amounts of ferrous sulfate heptahydrate and 5 mL of 30% hydrogen peroxide were added. The flask was wrapped with aluminum foil to inhibit generation of hydroxyl radical via radiation from ambient light sources. The reaction mixture was well stirred using magnetic stir-bars. The course of the reaction was followed by withdrawing 10-mL aliquots of the reaction mixture at intervals of time and analyzing them by HPLC. Periodically, the pH of the reaction system was checked.

Analytical Methods. 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 × 4.6 mm Supelcosil LC-8-DB analytical column (3.6-μm packing) and a 2-cm guard column (Supelco Inc., Bellefonte, PA). In the case of alachlor and metolachlor, the mobile phase consisted of methanol and water solutions used in the ratio of 73:27 (methanol/water) (v/v). For the triazines (atrazine and cyanazine), the HPLC method was adapted from work reported in the literature (Vermuelen et al., 1982), using an isocratic gradient of 55:45 methanol/aqueous ammonium acetate (pH 7.4). Picloram was analyzed by using a mobile phase of methanol/water in the ratio 36:64 (v/v), which was 0.005 M in the ion pair reagent, tetrabutylammonium phosphate (TBAP). Quantification of alachlor, atrazine, cyanazine, and metolachlor was followed at 220 nm, the maximum

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Table 1. Electrochemical Treatment

herbicide	initial concn (ppm)	final concn (ppm)	% removal
alachlor	30.1	18.1	40.1
	25.9	15.3	40.9
	30.2	14.7	51.2
metolachlor	71.7	70.9	1.1
	91.7	88.4	3.6
atrazine	26.2	25.6	2.2
	25.4	24.6	3.3
	24.8	24.1	2.8
cyanazine	30.1	28.9	3.8
	24.3	23.3	4.1
	36.3	35.2	3.1
picloram	30.1	29.2	3.0
	30.0	29.1	3.0
	30.4	29.5	2.6

absorbance in their ultraviolet–visible spectra. Though picloram has an absorbance maximum around 220 nm, the analysis was performed at 230 nm to avoid the interference of TBAP at wavelengths below 230 nm. For all of the analyses, a flow rate of 1 mL/min and a sample loop of 200 μL were used. The retention time for the chloroacetanilides was approximately 5.6 min, for the triazines 8 min, and for picloram 10 min. All of the samples were filtered through 0.25-μm acrodisc nylon syringe filters prior to injection of the samples.

Iron concentrations were confirmed colorimetrically with a Perkin-Elmer Lambda II UV–visible spectrophotometer. The total iron generated in the electrochemical and in the electrochemical peroxide system was reduced with hydroxylamine, and the concentration of the reduced iron–phenanthroline complex was determined at 511 nm.

To help characterize the nature of degradation products, simple batch hydrolysis experiments were conducted by adding sodium hydroxide.

RESULTS AND DISCUSSION

Electrochemical Treatment. The efficiency of removal of the herbicides by the electrochemical method was found to be low in the absence of hydrogen peroxide. The results of electrochemical treatment conducted on five herbicides are reported in Table 1. Among the herbicides, best removal was achieved for alachlor. Metolachlor was poorly removed as compared to alachlor. It is not completely understood why this is so, other than the fact that metolachlor has a higher water solubility (530 mg/L) than alachlor (240 mg/L). Very little removal was observed with the triazines and picloram. These results form a basis for evaluating the electrochemical peroxide degradative system.

The chromatograms of electrochemically treated herbicide solutions contained only the parent peak. The chromatograms of the herbicides extracted from iron hydroxide precipitates revealed only parent peaks. These results suggest that any removal of herbicides in the electrochemical treatment system occurs by the process of adsorption.

The low-efficiency removal of herbicides by the electrochemical method contrasts with the greater than 90% removal of dyes and heavy metals from textile wastewaters by the same method. This poor adsorption of the herbicides can be explained if the structure of the iron hydroxide precipitate and the structure of the adsorbent are taken into consideration. The ferrous hydroxide precipitate that is initially produced in the electrochemical system is oxidized by air to the black precipitate $Fe_2O_3 \cdot nH_2O$. On addition of the flocculating polymer, iron possibly complexes with the polymer. A visual charac-

terization of the flocculated iron hydroxide precipitate performed by Wilcock et al. (1988) using the scanning electron microscope revealed two layers: a loosely packed stringy upper layer and a coarse lower layer consisting of closely packed particles. The upper layer was assumed to be iron complexed with the flocculating polymer, and the lower layer was assumed to be particles of iron. While the actual mechanism of dye and heavy metal removal is not known, it has been assumed that removal in such a system is probably accomplished by electrostatic attraction or physical entrapment. The presence of extended π-electrons in dyes presumably facilitates their adsorption to the hydroxide matrix via electrostatic attraction, while the small size of the heavy metals poses no hindrance for adsorption by physical entrapment. In contrast to the dyes and metals, the herbicides used in the study do not have extended π-electrons, and their sizes are much larger than those of the heavy metal atoms. Presumably, these factors affect the efficiency of removal of the herbicides in the simple electrochemical treatment system.

Electrochemical Peroxide Treatment. Herbicide concentration vs time profiles at different iron concentrations, but the same initial hydrogen peroxide concentration, are depicted in Figures 1–5. Each reaction or treatment was followed for a maximum of 5 h or until no further decrease in the concentration of the parent compound was obtained. The iodimetric titration method indicated that under the electrochemical peroxide treatment conditions the hydrogen peroxide concentration decreased 100-fold from 0.75% to 0.07% within 35 min. The final pH values of the herbicide solutions in this treatment system were in the range 5–7.5, the pH of most natural waters. The pH of the treated herbicide solutions of alachlor, metolachlor, and picloram ranged from 5 to 5.2 at different amounts of iron generation, while in the case of the triazines the final pH of the solutions varied from 6.5 to 7.5.

Figure 1 represents the removal of alachlor at two iron concentrations, 100 and 200 ppm. Initially, the rate of removal of alachlor was rapid. Thereafter, the disappearance of the parent compound was slow. At 200 ppm generation of iron, almost complete removal of alachlor was achieved within 3.5 h. At 100 ppm of iron, the system was not as efficient. At both iron concentrations, the iron hydroxide precipitate analysis performed at timed intervals showed no adsorption of the parent herbicide. This result may be due to the absence of the coagulating anionic polymer which was used in the electrochemical treatment experiments; it also suggests that removal of alachlor in the electrochemical peroxide system occurs by degradative pathways.

The disappearance of metolachlor at 100 and 200 ppm of iron generation is also described by an initial rapid rate of removal followed by a slower rate in the later phase of the reaction (Figure 2). The concentrations of metolachlor that were used for treatment were higher than those used for the other herbicides. Therefore, complete removal of metolachlor was not observed, though greater than 90% removal of the parent compound was achieved within 5 h of treatment at 200 ppm of iron.

The removal of alachlor and metolachlor in the electrochemical peroxide system seems to be governed by complex kinetic pathways. Simple first-order rate equations do not fit the experimental data. These results are not surprising, since hydrogen peroxide is quickly decomposed and its concentration cannot be considered to be constant. This suggests that degradation of alachlor
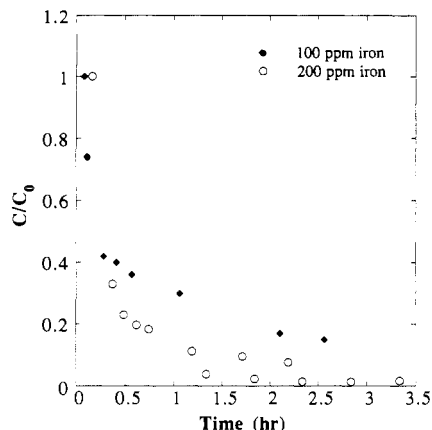
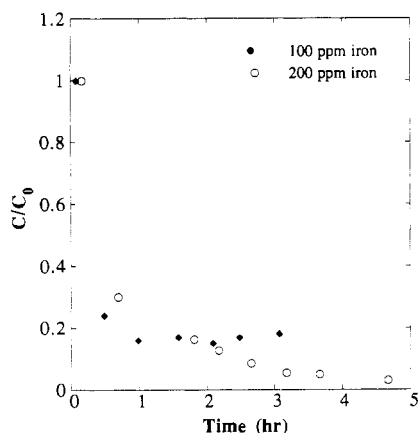**Figure 1.** Disappearance of alachlor in the electrochemical peroxide system.

Figure 2. Disappearance of metolachlor in the electrochemical peroxide system.
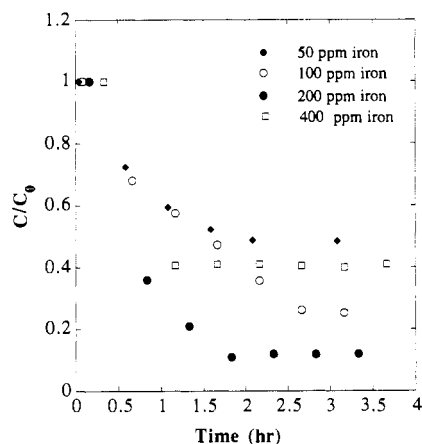

Figure 3. Disappearance of atrazine in the electrochemical peroxide system.

and metolachlor is rate limited by something other than the herbicide concentrations.

In the case of atrazine, treatments were performed at 50, 100, 200, and 400 ppm of iron concentrations. Figure 3 represents the concentration vs time curves generated at each of the iron concentrations. An analysis of the plots shows that at concentrations of 50 and 100 ppm of iron, in the initial phase of the reactions, there is a gradual change in the concentration of atrazine. At 200 and 400 ppm of iron generation the change is fairly rapid. For each iron concentration, the change in the initial concentration of atrazine reaches a given value after which no further removal is observed. At 200 ppm of iron generation,
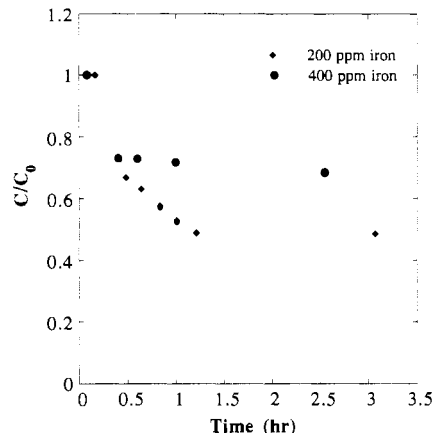

Figure 4. Disappearance of cyanazine in the electrochemical peroxide system.
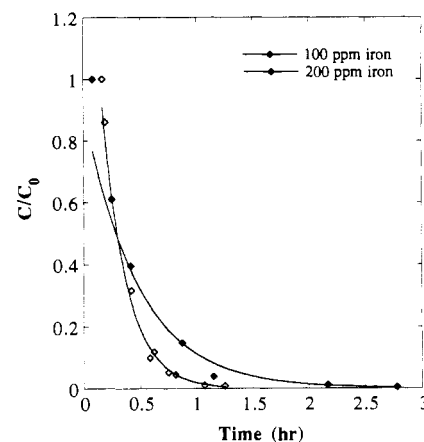

Figure 5. Disappearance of picloram in the electrochemical peroxide system.

the most efficient level of treatment, the plateau effect is seen at 10% of the initial atrazine concentration, while at other iron concentrations the plateau effect is observed at higher atrazine concentrations.

Figure 4 represents the concentration vs time profiles of cyanazine at 100 and 200 ppm generation of iron. Removal of cyanazine is not as efficient as removal of atrazine. At 200 ppm generation of iron, the percent removal is higher as compared to the removal at 100 ppm of iron, and the concentration of cyanazine changes gradually until it finally levels off between 40% and 50% of the original concentration for the 200 ppm of iron treatment.

As in the case of the chloroacetanilides, the degradation of atrazine and cyanazine in the electrochemical peroxide system does not follow simple first-order kinetics. Disappearance of cyanazine in the electrochemical peroxide system is rather slow as compared to that of atrazine. This slow reactivity of cyanazine in the electrochemical peroxide system may be due to its unique molecular structure, as discussed for classic Fenton treatment (vide infra).

Effective degradation of picloram is achieved in the electrochemical peroxide system at 100 and 200 ppm of iron generation (Figure 5). Greater than 99% removal of the parent compound is achieved within 3 h of treatment. In contrast to the rest of the herbicides, degradation of picloram is efficient at both 100 and 200 ppm of iron. When the data are constrained to a first-order plot, the time at which half the herbicide has been degraded can be calculated. The values, 2.1 h^{-1} at 100 ppm of iron and 4.7 h^{-1} at 200 ppm of iron, can then be compared to those derived in the classic Fenton treatment.
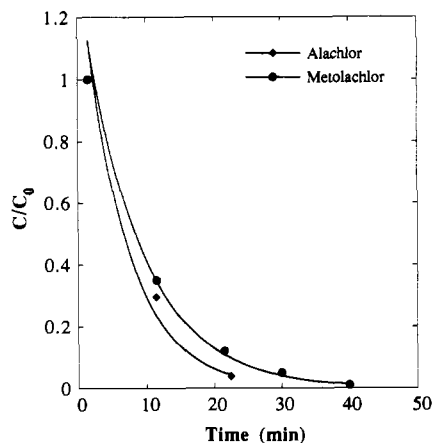
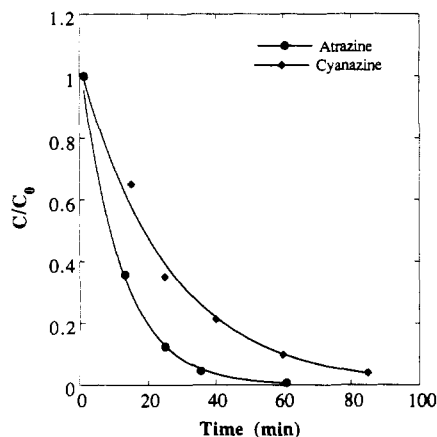**Figure 6.** Disappearance of alachlor and metolachlor in the Fenton system.

Figure 7. Disappearance of atrazine and cyanazine in the Fenton system.

The results of these dark electrochemical peroxide treatments indicate that the disappearance of herbicides involves complex degradative pathways. The degradation rates may be dependent on ferrous ion, ferric ion, and hydroxyl radical concentrations. The iron concentration is changing due to precipitation, and the hydroxyl radical is quickly dissipating. Only a complete kinetic study of the system, beyond the scope of this screening study, could elucidate these mechanisms. The efficiency of the treatment method varies with the herbicides, which have very different structures. Degradation of the herbicides in the electrochemical peroxide and the classic Fenton system are compared in subsequent sections.

Classic Fenton Reagent Treatment. Fenton reagent treatment was conducted at iron concentrations of 50 and 200 ppm of iron. The final pH values of the solutions of treated herbicides were between 3.2 and 2.3, depending on the amount of iron salt added to the system. The disappearance profiles of the different herbicides at 50 ppm of iron addition are shown graphically in Figures 6–8. At 200 ppm of iron, the reactions were too fast to follow kinetically. At both iron concentrations, each of the herbicides disappeared beyond levels of analytical detection. The disappearance of the respective herbicides was constrained to a first-order kinetic fit at 50 ppm of iron addition for purposes of comparison. The times at which half of the herbicides was degraded are listed in Table 2.

One of the primary goals of this study was to determine whether the dark electrochemical peroxide treatment was effective in degrading the herbicides present in the aqueous
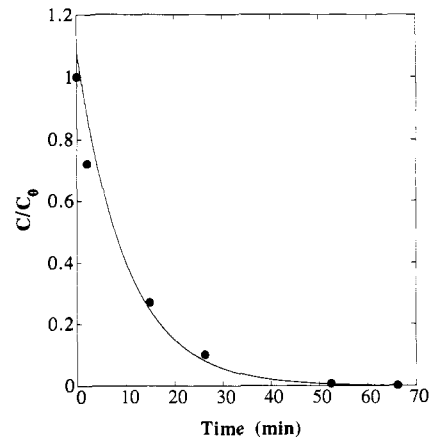

Figure 8. Disappearance of picloram in the Fenton system.

Table 2. Time to Half-Removal ($t_{1/2}$) of Herbicides in the Classic Fenton System

herbicide	iron concn (ppm)	$t_{1/2}$ (min)
alachlor	50	4.3
metolachlor	50	6.9
atrazine	50	7.7
cyanazine	50	17.3
picloram	50	6.9

solutions. The disappearance profiles of the herbicides show that the method is indeed effective with respect to degradation of most of the herbicides, though with lower efficiency than the classic Fenton reagent treatment. Disappearance of the herbicides is slower in the electrochemical peroxide system as compared to that in the classic Fenton system. This could be due to several reasons: (1) The pH of the electrochemical peroxide system was found to be several units higher than that of the classic Fenton system; with increasing pH (pH >3), the rate of oxidation of ferrous ion to ferric ion increases rapidly, as does the rate of precipitation of ferric ion from solution. Loss of iron as ferric precipitates probably limits the sustenance of radical reactions in the electrochemical peroxide system. (2) The efficiency of oxidation in this system could be reduced by the reduction of the hydroxyl radical to the hydroxyl anion at the cathode or by other cathodic reductions such as the reduction of hydrogen peroxide to water. These reactions will be sorted out in future work with other electroanalytical techniques.

Alachlor is removed easily in both peroxide systems. A slower removal of metolachlor as compared to alachlor needs to be investigated by determining the sites of hydroxyl radical attack and degradation products of both herbicides.

Among the herbicides, triazines, especially cyanazine, react slowly in the electrochemical peroxide as well as in the classic Fenton system. This is probably due to the inherent chemical stability of the triazine ring present in their structures. In the case of cyanazine, the presence of the very strong electron-withdrawing cyano group in the N-isopropyl side chain of the molecule makes that site of cyanazine less susceptible to attack by the electrophilic hydroxyl radical.

Picloram degrades as easily in the electrochemical peroxide as in the classic Fenton system. The disappearance rate of picloram at 200 ppm of iron, unlike those of the other herbicides in the electrochemical peroxide system, approaches the rate obtained in the Fenton system at 50 ppm of iron. The higher efficiency of the electrochemical peroxide system in degrading picloram as compared to the other herbicides could be due to the structure

of picloram, which contains many sites for attack. These mechanisms will be investigated in further studies.

Qualitative Characterization of Degradation Products. The formation of degradation products in the electrochemical peroxide and classic Fenton systems was inferred from the presence of additional peaks in the chromatograms of treated herbicide solutions. For each of the herbicides, both treatment methods produced similar elution profiles. Identification of the products was not possible with the analytical methods used.

Peroxide oxidation (electrochemical peroxide and Fenton reagent) of alachlor and metolachlor gives a chromatographic peak which disappears within a few hours of electrochemical peroxide treatment and within an hour of the classic Fenton reagent treatment. Chromatographic profiles of base-hydrolyzed alachlor and metolachlor also give peaks at the same retention times. Despite flow rates of 1 mL/min, the match of the two alachlor peaks and the two metolachlor peaks suggests that this intermediate product may be a hydroxy product formed by substitution of OH⁻ for Cl⁻ on the chloroacetyl group or by oxidation of the alkyl side chains. This result is in good agreement with the findings reported by Somich et al. (1988). In their study, photolysis of alachlor produced various dechlorinated hydroxy products that retained the aromatic ring and the carbonyl carbons, while ozonation oxidized the alkyl side chain and opened the ring.

In the case of the triazines, the major products that are formed seem to be persistent, both in the electrochemical peroxide system and in the classic Fenton system. These major product peaks may represent dealkylated triazines. In other studies which involved peroxide oxidation, ozonation, or photolysis/H_2O_2 of atrazine, dealkylated compounds, especially deethylatrazine, were identified as the major products (Plimmer et al., 1972; Hapeman-Somich et al., 1992; Adams and Randtke, 1992; Kearney et al., 1988; Larson et al., 1991).

The formation of small amounts of degradation products of picloram in the peroxide systems is seen in the chromatograms. These peaks disappear within a few hours of electrochemical peroxide treatment and classic Fenton reagent treatment. A photochemical degradation study of picloram (Gear et al., 1982) showed that, in the photolysis of picloram, dechlorination/hydroxylation is the major photochemical process, followed by decarboxylation, loss of aromaticity, and deamination as significant reactions. The mechanisms of degradation in the peroxide systems and in photochemical versions of them will be studied in future work.

This work reports a screening study of treatment methods for pesticide-laden wastewater applied to five widely used herbicides. The results demonstrate that electrochemical peroxide treatment and classic Fenton reagent treatment are effective in removal/degradation of these herbicides in aqueous solution. The electrochemical system has the advantage that it can be conducted at circumneutral pH. The system was investigated in the dark and without hydrogen peroxide concentration optimization. This study serves as a foundation for future work which will include the use of UV light and optimization of hydrogen peroxide addition. Formulated herbicides and spiked rinsewater will also be studied, and the results will be compared to this study which used analytical standards.

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