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Electroreduction of Acetochlor at Silver Cathodes in Aqueous Media

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We report electroreduction of acetochlor at silver cathodes in aqueous media to provide insight related to electroreduction as a practical application for remediation of haloorganic pollutants. Cyclic voltammetry was used to determine the electrochemical behavior of acetochlor in water as a function of pH. Electrolysis was employed as a means for bulk reduction, with both constant-potential (CPE) and constant-current electrolysis (CCE) considered. CPE offers high selectivity and is preferred for mechanistic analysis, however, long electrolysis times are required for complete reduction. In contrast, CCE was found to provide an alternative for fast electroreduction of acetochlor, with the caveat that current densities must be chosen carefully, to retain selectivity against competing reactions (e.g., proton reduction). In addition, the effect of cell configuration (divided vs undivided) was explored. Finally, an undivided parallel-plate flow cell, in single pass, was employed for flow CCE. The effect of applied current, flow rate, and interelectrode gap were considered for optimal results.

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Halogenated organic compounds are used commonly in health and agriculture as antimicrobial agents and pesticides. Unfortunately, these compounds often accumulate in wastewater and contaminate the environment, where they can be toxic to plants, animals, and humans.[1,2] For this reason, many organohalides have been banned or phased out from commercial applications. An example of such organohalides is 2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide, commonly known as acetochlor, which was registered with the U.S. EPA in 1994 as a chloroacetanilide herbicide.[3] The U.S. Geological Survey estimates an annual usage between 28–38 million pounds of acetochlor in 2012, which increased to over 40 million pounds within four years.[4,5] In light of possible environmental and health hazards, acetochlor and its degradation products were listed as drinking water contaminants in 2016.[6,7] However, acetochlor use continues today, augmenting the need for detection and degradation of halogenated pollutants. One promising avenue of research is electrochemical remediation.

Water treatment via electrochemical technologies have been discussed previously in detail.[8–11] Electrooxidation is most popular,[12–17] as transformation of organic pollutants to mineral products (e.g., CO_2) occurs through a relatively nonselective process. These methods can be performed by direct means (typically with boron-doped diamond, or BDD, electrodes) or mediated by an electroactive species.[17,18] To date, mediated oxidation is achieved most commonly via the electro-Fenton process, where Fe(II) is generated from oxidation of a sacrificial Fe anode or from addition of a Fe(II) salt. Hydrogen peroxide is produced cathodically, which then reacts with Fe(II) to form highly oxidizing $OH^{\cdot}$ and Fe(III).[13,14,19] Fe(II) is regenerated through (1) reduction at the cathode, (2) reaction with H_2O_2, or (3) reaction with $OOH^{\cdot}$ formed as a result of (2). Although efficacy of electrooxidation processes are apparent, there are major drawbacks, including the high cost associated with BDD electrodes, especially in the case of electrodes with large surface area.[20] Mediated (electro-Fenton) treatment also suffers from low pH requirements (pH 2–4) for optimal performance and generates large amounts of ferric-ion sludge.[12,14] For both direct and mediated oxidation, formation of undesired by-products is not uncommon and can lead to reaction termination or production of substances with higher toxicity than the parent substrate.[8] As an alternative to electrooxidation, electroreduction provides a more controlled option typically focused on dehalogenation of haloorganic compounds.[21–24] Dehalogenation of pollutants have been shown to decrease toxicity,[25,26] enhance pollutant biodegradability,[27,28] and possibly produce useful materials.[24]

Recently, our group led an investigation of acetochlor electroreduction in dimethylformamide at carbon and silver cathodes.[29] Although catalysis of carbon–chlorine bond cleavage was observed at silver, bulk electrolysis resulted in lower product yields compared to carbon cathodes. Acetochlor was proposed to undergo a two-electron transfer followed by protonation (Scheme 1). The proposed mechanism was supported on the basis of deuterium-labeling studies, and agrees with the proposed mechanism for reduction of alachlor (isomer of acetochlor).[30]

In the present work, electroreduction of acetochlor was investigated at silver cathodes in aqueous media containing phosphate salts. Cyclic voltammetry was performed to assess the electrochemical behavior of acetochlor in water over a range of pH values. Bulk electrolyses were performed in batch under constant-potential (CPE) and constant-current (CCE) conditions. To improve the feasibility of this method for industrial applications, we pursued electroreduction under flow conditions. Recent reviews have described flow electrochemistry as an advantageous way to improve mass transfer, maximize the surface-to-volume ratio between electrode and solution, and minimize heat exchange.[31–34] In this context, flow electrolyses were performed under constant-current in single-pass mode, and optimized for applied current, flow rate, and cell volume.

Materials and Methods

Chemicals and materials.—Each of the following chemicals was purchased and used as received: 2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide (common name acetochlor, Toronto Research Chemicals, 95%); *N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide (referred to as deschloroacetochlor, Enamine Building Blocks, 95%); *N*-phenylacetamide (Sigma Aldrich, 99%), potassium phosphate dibasic (K_2HPO_4, JT Baker, 99.6%); phosphoric acid (H_3PO_4, Sigma Aldrich, ⩾99.999%); and ethyl acetate (Fisher Scientific, 99.5%). Solutions were made with deionized water (18.2 MΩ.cm, Millipore). Ultrapure argon (Air Products, 99.999%) was used to deaerate the solvent.

Electrochemical methods.—Cyclic voltammetry was performed with the aid of a BioLogic SP-300 potentiostat and a conventional three-electrode glass cell. The working electrode was a silver-disk electrode (0.071 cm^2 geometric area), and the counter electrode was a coiled platinum wire. The reference electrode was a homemade saturated calomel electrode (SCE) for all electrochemical

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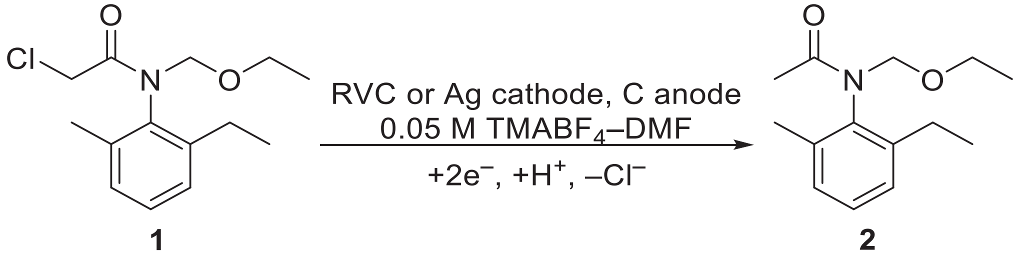

Scheme 1. Overview of acetochlor reduction.[29] RVC = reticulated vitreous carbon, $TMABF_4$ = tetramethylammonium tetrafluoroborate, DMF = *N,N*-dimethylformamide.

experiments (except flow electrolyses). Prior to each voltammetric scan, the silver electrode was polished on a rotary polishing pad (Buehler) wetted with 0.05-μm alumina (Buehler) slurry, followed by sonication in deionized water.

CPE and CCE were performed with silver-mesh cathodes (estimated surface area of 20 cm^2). Details for construction of silver cathodes from silver gauze (99.9%, 0.356 mm-diameter wire mesh woven, Alfa Aesar) can be found elsewhere.[35,36] A graphite rod served as the counter electrode (anode). CPE was performed with a PARC model 173 potentiostat at –1.0 V vs SCE, in a divided cell, as described in previous work.[21,37] CCE was performed with a BioLogic SP-300 potentiostat, either in a two-compartment cell, or in an undivided (beaker-type) cell. For experiments in a divided cell, the anode was separated from the cathode compartment by fritted glass backed by an agar plug in water–phosphate. For experiments in an undivided cell, the solution was continuously sparged with argon as a means to remove oxygen formed due to water oxidation. Data processing and analysis were accomplished with OriginPro 2018 software.

Flow electrolyses were conducted under constant current in a homebuilt parallel-plate flow cell, in single pass mode. The flow cell was adapted from the design reported by Waldvogel and co-workers.[38] Electrodes were purchased from Goodfellow Corporation and consisted of silver and carbon foil (60 × 20 × 3 mm, 99.95%) mounted in Teflon holders. An EPDM gasket (2 mm, Goodfellow Corporation) was placed in between the Teflon holders to separate the electrodes and ensure seal of the cell. A variable electrode gap was achieved by placing two gaskets in between the electrodes. Electrodes were polished manually with a polishing cloth prior to each experiment. Electrolyte solution was introduced in the flow cell by means of a syringe pump (Harvard Apparatus Model "11" single syringe). The first 5 ml of solution electrolyzed were discarded, and the following 10 ml were collected for product analysis.

$$\mathrm{ClC_{14}H_{20}NO_2 + e^- \rightarrow C_{14}H_{20}NO_2^{\bullet} + Cl^-} \quad (1)$$

$$\mathrm{C_{14}H_{20}NO_2^{\bullet} + e^- \rightleftharpoons C_{14}H_{20}NO_2^-} \quad (2)$$

$$\mathrm{C_{14}H_{20}NO_2^- + H^+ \rightarrow C_{14}H_{21}NO_2} \quad (3)$$

Scheme 2. Detailed mechanism for acetochlor reduction, proposed in previous work.[29]

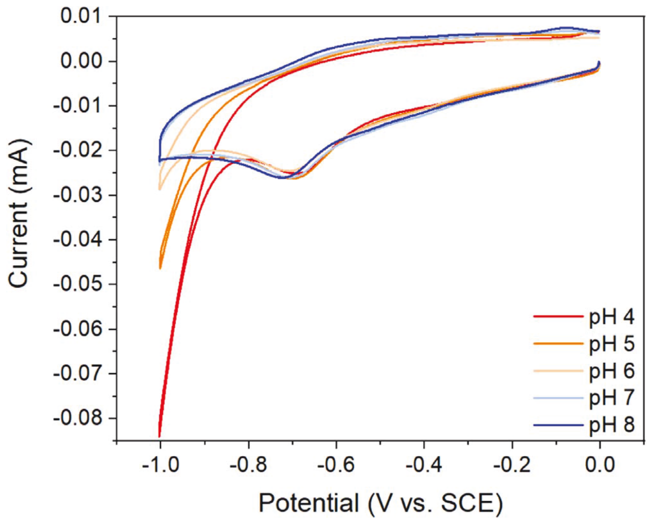

Figure 1. Cyclic voltammograms for 0.1 mM acetochlor at silver cathodes (area = 0.071 cm^2) at 100 mV s^{-1} in oxygen-free water containing phosphate salts (H_3PO_4–K_2HPO_4). Phosphoric acid and potassium phosphate dibasic ratios were adjusted to yield the desired pH in the range of 4–8. Potential was scanned from 0.0 to –1.0 to 0.0 V.

Separation, identification, and quantitation of products.—As detailed in a previous publication,[29] reaction mixture components were extracted with ethyl acetate followed by separation and identification via gas chromatography-mass spectrometry (GC-MS, Agilent 6130 GC coupled with Agilent 5973 MS detector). For batch electrolysis, quantitation was achieved by means of the method of internal standards (*N*-phenylacetamide). For flow electrolysis, relative product yields were obtained via analysis of the relative abundance of compounds (area normalization method). The area normalization method has been used by other groups,[38–40] but should only be used if all products can be detected. To verify that discrepancies in ionization and partition efficiencies of products and analyte would not lead to gross error, a standard mixture was prepared and analyzed via this method.

Results and Discussion

Cyclic voltammetry.—To understand the voltammetric response of the solvent-electrolyte system and to evaluate possible interference from the hydrogen evolution reaction (HER), separate CVs were collected of the background at various pH conditions (SI, Fig. S1 (available online at stacks.iop.org/JES/168/075502/mmedia)). On the basis of these voltammograms, the potential range of study of acetochlor was limited to 0.0 to –1.0 V to avoid HER. Depicted in Fig. 1 are cyclic voltammograms (CVs) for 0.1 mM acetochlor (**1**) at silver cathodes in water containing phosphate salts (H_3PO_4–K_2HPO_4, pH range 4–8) at 100 mV s^{-1}. Reduction of 0.1 mM acetochlor is observed at ca. –0.7 V vs SCE, with no significant peak shift as a function of pH.

In consideration of the overall reaction proposed in our previous work,[29] a potential shift of approximately –120 mV would be expected as the pH increases from 4 to 8, assuming Nernstian behavior. However, concerted electron transfer (Scheme 2, Eq. 1) results in irreversible C–Cl bond cleavage; consequently, the chemical reaction that follows (Scheme 2, Eq. 3) should cause no change in the reduction potential of **1**.[41]

Bulk electrolysis (Batch Mode).—Large scale electrochemical degradation of pollutants can be achieved via bulk electrolysis with controlled-current or controlled-potential techniques. Traditionally, CPE is the preferred method in our laboratory because of the ability to selectively drive a particular reaction through control of the working electrode potential, which has proven useful for mechanistic analysis.

Coulometric *n* values and product distributions from CPE of 1.0 mM acetochlor in water containing phosphate salts, at pH 4–8, are shown in Table I, with total (or near total) conversion of **1** to deschloroacetochlor (**2**) achieved in acidic and neutral conditions (pH 4–7). However, incomplete reduction is observed at pH 8, with ca. 10% starting material unreduced. Additionally, complete reduction of **1** was achieved in approximately 1 h at pH 4, however, electrolysis time lengthened to over 3 h as pH increased. In acidic and neutral media, coulometric *n* values correlate well with the two-electron reduction mechanism proposed previously. At pH 8, *n* appears to be slightly lower than the expected 1.8 for 90% conversion. However, statistical analysis (see SI) shows the sample mean does not differ from the expected (population) mean. Further evidence of a two-electron reduction mechanism is observed via a pH increase during electrolysis, which results from consumption of H^+ in the cathode compartment. Use of a divided cell prevents replenishment of H^+ by water oxidation at the anode. This pH change is most apparent in experiments at pH 4, where $\Delta pH = 1.4$. At pH 6–8, changes in pH were not as evident, likely due to buffering from phosphate salts.

Complex instrumentation and cell setup (i.e., potentiostat and three-electrode arrangement needed) combined with long electrolysis times caused by low average current, make CPE unattractive for large-scale or industrial applications. In recent years, CCE has grown in popularity for synthesis of organic compounds, as reaction times can be lowered significantly through application of higher current densities. In addition, a simple two-electrode system coupled to a power source suffices since potential is not regulated, which eliminates need of a reference electrode. For these reasons, CCE of 1.0 mM acetochlor in water containing phosphate salts (pH 4–8) were performed; results are shown in Table II.

Unlike CPE, total (or near total) conversion of **1** to **2** is achieved in all pH conditions. Reduction of **1** via CCE results in similar product yields when compared to CPE, but in shorter times. However, a single-compartment (undivided) cell was used for CCE. To determine the effect of cell design, CCE was also conducted in a divided cell (Table II, Entry 6). Electrolyses in a divided cell result in lower conversion, which was found to be significant through statistical analysis (see SI). A possible explanation for improved performance in an undivided cell involves reduction assisted by water oxidation at the anode. This process produces H^+, which facilitates protonation of the carbanion intermediate (2^-) through convergent paired electrolysis,[42] as illustrated by Fig. 2. To emphasize this point further, complete conversion of **1** to **2** in basic conditions was obtained with an undivided cell, which results from freely moving H^+ produced at the anode reacting with the carbanion intermediate, a pathway was unattainable in a divided cell. Anodic production of H^+ also allows for stabilization of pH, which is observed through little to no change in pH post electrolysis. We should emphasize that water oxidation is more favorable than chloride oxidation, and that Cl_2 formation is unlikely to occur.

Though results from CCE are encouraging, a reviewer kindly pointed out that experiments discussed herein were conducted under optimal conditions, i.e., in the absence of O_2. It seems, therefore, pertinent to clarify that dissolved O_2 in solution presents a competing reactant, and that electroreduction of oxygen is more facile than that of acetochlor. To illustrate this point, CCE conducted in conditions similar to Table II entry 5, but without the continuous stream of argon, resulted in 42%–55% yield of **2**. This 40%–50% decrease in conversion of **1** to **2** is indicative that formation of O_2 from water oxidation can negatively impact the efficiency of acetochlor reduction.

Furthermore, a significant disadvantage associated with CCE is possible loss of selectivity that can occur for the synthesis of a desired compound. This is most apparent in Fig. 3, as the relative yield of **2**, decreases as current density increases. Note that a fixed amount of charge (9 C) was passed for each experiment. For example, electrolysis at –5 mA was conducted for 30 min, whereas electrolysis at –30 mA lasted 5 min At higher applied currents, the working electrode potential increases (SI, Fig. S2), eventually reaching a value where HER occurs. This presents a competitive reaction, which leads to decreased selectivity, and therefore decreased efficiency, for the reduction of acetochlor. It should be said that **2** is the only reduction product observed, and that the remainder yield is accounted for in unreduced **1**. Finally, we should point out that CCE resulted in decreased current efficiency even at lower applied currents. For example, at pH 6 (Table II, entry 3, –5 mA), 9 C was employed to electrolyze 0.02 mmol acetochlor (20 ml of 1 mM acetochlor electrolyzed in batch experiments) which corresponds to 43% current efficiency.

Flow electrolysis.—As discussed previously, flow electrochemistry presents many advantages over batch methods, including improved mass transfer and surface-to-volume ratio, which can lead to increased reaction rates.[31–33] To test the feasibility of flow systems for the reduction of acetochlor, we conducted CCE in an undivided, parallel-plate flow cell in single pass mode. Optimization of reaction conditions followed similar procedures described by Waldvogel and co-workers.[38,43] The effect of applied current, flow rate, and gap between electrodes were analyzed. Current optimization was investigated first to maximize cell productivity and minimize selectivity loss. Figure 4 shows the relationship between applied current and cell productivity; product yield increased as a function of applied current (30–60 mA), but reached a maximum at 60 mA. Currents higher than 60 mA resulted in lower yields of **2**, likely due to HER.

Effects of flow rate and electrode spacing were then investigated. Contained in Table III are product yields for CCE at –60 mA at flow rates of 0.25, 0.50, and 1.00 ml min^{-1} (entries 1–3). As shown,

Table I. Coulometric *n* values and relative product distributions for electroreduction of acetochlor via controlled-potential electrolysis (E = –1.0 V vs SCE, divided cell) at silver cathodes in oxygen-free phosphate–water.

				Product Distribution (%)[b)]		
Initial pH	Final pH	Electrolysis time (min)	n[a)]	1	2	Total
4.0	5.4	70	1.9 ± 0.1	ND	95 ± 7	95
5.0	5.4	100	1.9 ± 0.2	ND	99 ± 3	99
6.0	6.2	140	1.8 ± 0.3	ND	94 ± 2	94
7.0	7.1	170	1.9 ± 0.2	TR	97 ± 3	97
8.0	8.1	200	1.5 ± 0.3	12 ± 4	89 ± 3	101

1 = acetochlor; **2** = deschloroacetochlor; **ND** = not detected; **TR** = trace amounts. a) Average number of electrons per molecule of substrate. b) Yield expressed as percentage of substrate converted to product.

Table II. Relative product yield for electroreduction of acetochlor via controlled-current electrolysis (undivided cell, unless otherwise noted) at silver cathodes in oxygen-free phosphate–water. Total charge passed 9 C.

		30 min (i = –5 mA)		15 min (i = –10 mA)	
Entry	Initial pH	Final pH	2[b)]	Final pH	2[b)]
1	4.0	3.9	98 ± 3	3.8	94 ± 2
2	5.0	4.9	99 ± 1	4.9	95 ± 2
3	6.0	6.1	100 ± 0.1	6.0	96 ± 1
4	7.0	7.0	100 ± 1	7.0	95 ± 2
5	8.0	8.0	95 ± 4	8.0	94 ± 2
6	8.0[a)]	—	—	8.1	80 ± 6

2 = deschloroacetochlor. a) CCE performed in a divided (Klein) cell. b) Yield expressed as percentage of substrate converted to product.

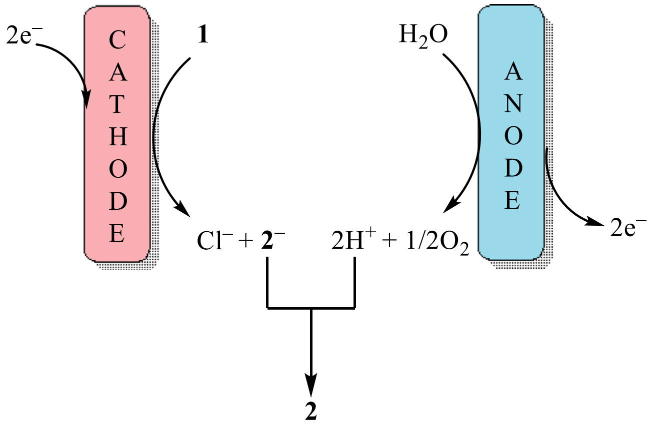

Figure 2. Schematic of convergent paired electrolysis of acetochlor (**1**) reduction and water oxidation to form deschloroacetochlor (**2**) in an undivided cell.

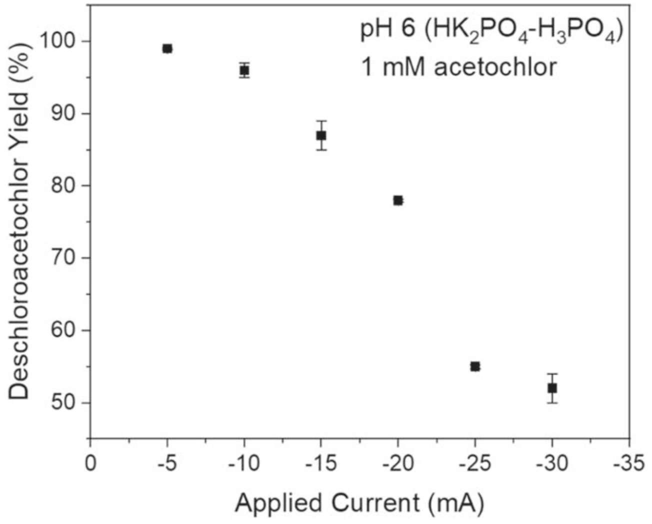

Figure 3. Relative product yield (%) as a function of applied current. Results from batch constant-current electrolyses of 1.0 mM acetochlor in water containing phosphate salts (at pH 6). Electrolyses were performed in an undivided cell and a fixed charge of 9 C was passed for each experiment.

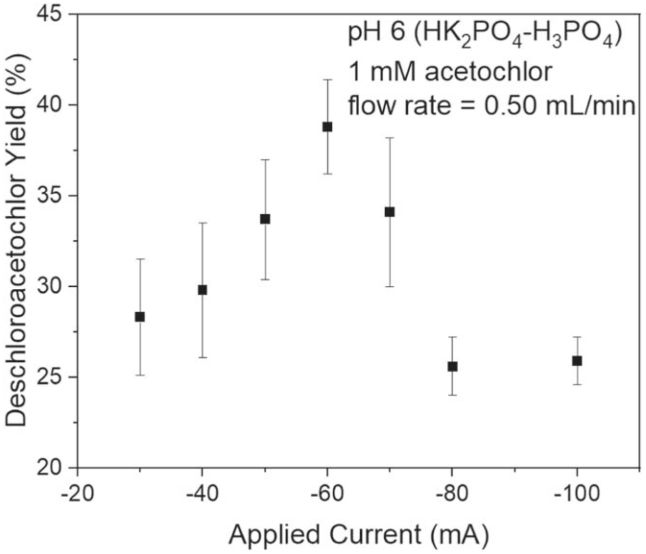

Figure 4. Relative product yield (%) as a function of applied current. Results from constant-current electrolyses of 1.0 mM acetochlor in water containing phosphate salts (at pH 6). Electrolyses were performed under flow conditions (0.50 ml min^{-1}), single pass, in an undivided cell.

product yield decreases as flow rate increases. This can be rationalized by the lower charge passed due to the lowered residence time in the cell. For example, collection of 10 ml of solution at 0.25 ml min^{-1} takes 40 min, whereas 10 ml can be collected in 10 min at 1.00 ml min^{-1}. Because the current was held constant (–60 mA), 144 C of charge was passed in entry 1, but only 36 C in entry 3. However, lower flow rates worsen the mass transfer regime, thereby decreasing the rate of chemical change.[44] Higher product conversion does not signify higher efficiency in terms of acetochlor removed per hour. Electrolysis of 1.0 mM acetochlor at 0.25 ml min^{-1} with a 55% dechlorination yield leads to a dechlorination rate of 2.2 mg h^{-1}. The highest dechlorination rate is achieved at 0.50 ml min^{-1} (3.2 mg h^{-1}).

Entries 2 and 4 of Table III show CCE results (i = –60 mA, flow rate = 0.50 ml min^{-1}) at electrode gaps of 4 and 2 mm, which causes cell volume to decrease from 4.8 to 2.4 ml. With the narrower electrode gap, a slight increase in % yield is observed, however this increase is not shown to be statistically significant (see SI for details). Generally, other studies have shown an improved perfomance with narrower interelectrode gaps.[38,43] The main advantage of narrower gaps between electrodes are decreased ohmic drop and use of minimal electrolyte.[31,34,45] In the case of acetochlor reduction in an undivided cell, a smaller electrode spacing allows for quick contact between the **1**$^-$ (formed at the cathode) and H$^+$ (formed at the anode). However, other issues may arise with a smaller gaps, such as HER, which may lead to production of bubbles and cause conductivity challenges. Furthermore, the solution residence time is also decreased with the narrower electrode gap.

Conclusions

In summary, this study demonstrated dechlorination of acetochlor via electroreduction in aqueous media. Cyclic voltammograms of acetochlor in water containing phosphate salts (pH 4–8) revealed a

Table III. Optimization of flow parameters for electroreduction of acetochlor via controlled-current electrolysis (i = –60 mA, undivided cell) at silver cathodes in oxygen-free phosphate–water (pH 6).

Entry	Flow Rate (ml min^{-1})	Spacer (mm)	Electrolysis time (min)[a)]	**2**[b)]
1	0.25	4	40	55 ± 1
2	0.50	4	20	39 ± 3
3	1.00	4	10	18 ± 3
4	0.50	2	20	43 ± 3

2 = deschloroacetochlor. a) Electrolysis time for 10 ml of solution collected. b) Yield expressed as percentage of substrate converted to product.

single cathodic peak, E_{pc} = –0.7 V vs SCE. Reduction potentials were shown to be independent of pH, likely due to the concerted nature of electron transfer, leading to fast and irreversible cleavage of C–Cl. Bulk electrolysis was conducted in batch under constant-potential and constant-current modes. Under constant potential, total (or near total) dechlorination of acetochlor is achieved in acidic and neutral conditions (pH 4–7), but incomplete reduction is observed at pH 8. CPE results provide evidence in support of the two-electron mechanism proposed previously.[29] Furthermore, high selectivity is obtained via CPE, but long electrolysis times are required for complete reduction. On the other hand, CCE is a viable alternative for fast and complete reduction of acetochlor, independent of pH. Care must be taken at higher current densities, as selectivity may be lost due to competing HER at the cathode. Additionaly, the effect of cell configuration (divided vs undivided) was considered. Electrolyses conducted in undivided cells led to higher product yields and stable pH during electrolysis. We attributed these results to convergent paired electrolysis, in which protons produced at the anode (water oxidation) combine with reduction intermediate, $\mathbf{2}^{-}$, to form deschloroacetochlor (**2**).

Flow electrolyses were conducted under constant current in an undivided parallel-plate flow cell, in single pass. The effects of flow rate and applied current were considered and optimized for this system. Analogous to batch electrolysis, higher applied currents aid in faster electrolysis, however selectivity could be lost due to competing reactions. With regards to flow rate, lower values leads to higher conversion per pass in a single pass, but it comes at the cost of improving the rate of product formation. Additionally, two different interelectrode gaps were compared, however no conclusive determination was reached. Typically, a narrower spacing is preferred as it results in a lower ohmic drop and allows for low amounts of electrolyte to be used.[31,34]

To conclude, this work presents beginning steps towards electrochemical reduction of halogenated pollutants in aqueous systems. For improved results with the flow system, an electrode with a higher surface area (e.g., porous electrode) or a reservoir with solution recycle could be implemented. Overall, this electrochemical flow system provides a viable opportunity for large-scale electroreduction and dehalogenation of organic pollutants. It would be beneficial to expand upon this work and investigate further under non-optimal conditions, including in the presence of other species (electroactive and non-electroactive).

Acknowledgments

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