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Final Report to the California Department of Pesticide Regulation for Project 15-C0087
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Background: The project evaluated a novel activated carbon-based electrochemical system system to capture and destroy pesticides, such as fipronil, bifenthrin, permethrin and imidacloprid, in urban runoff. All of these pesticides, and indeed many other contaminants of concern in urban runoff, are halogenated. The ultimate goal was to have a flow-through system in which pesticides in urban runoff would sorb to the granular activated carbon (GAC)-based electrodes, and then electrons from the electric grid would promote the dehalogenation of the sorbed pesticides, liberating halides (e.g., Cl$^-$) as harmless products:

$$R\text{-}Cl + e^- \rightarrow R^* + Cl^-$$

This report summarizes the results for efforts related to Task 3 of the project. The results related to Tasks 1 and 2 have been published (Li and Mitch, 2018). Briefly, Task 1 evaluated reaction conditions to optimize the destruction of fipronil, bifenthrin and permethrin sorbed to activated carbon when a constant negative potential was applied to the activated carbon (i.e., direct current (DC) mode), such that the GAC-based electrode functioned as a cathode in an electrochemical cell. Highlights include that we were able to achieve complete dehalogenation of the 6 fluorines and 2 chlorines in fipronil when -1 V vs. S.H.E. was applied over 15 h to loose activated carbon wrapped in sheet graphite within a 2-cell electrolysis system (Figure 1), yielding fluoride and chloride as harmless products. This result is particularly important in light of the difficulty associated with degradation of C-F bonds, and indicates that the system may be able to capture and destroy perfluorinated contaminants, some of the most difficult persistent organic pollutants of concern in urban runoff. Recognizing that the resistance between GAC particles may limit the degradation kinetics, we developed a more efficient electrode in which the GAC particles were crushed to a powder and attached to carbon cloth as an efficient distributor of the electric current to the GAC. With this novel electrode >90% fipronil destruction was achieved within 2 h.
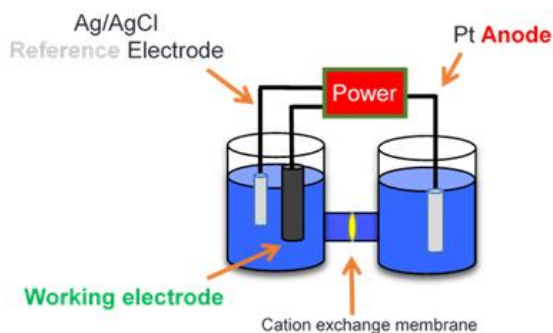

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Figure 1: DC Electrolysis in a 2-cell system

Task 2 evaluated the use of an alternating current (AC) system, in which the potential applied to parallel-plate GAC/carbon cloth electrodes was varied using a triangular waveform between -1 to +1 V vs. S.H.E (Figure 2). This configuration was advantageous in several respects. First, in the DC mode, only one electrode (the cathode) participated in electrolytic

reductive dehalogenation of pesticides. In the AC mode, two parallel-plate GAC-based electrodes would serve alternately as cathode and anode, such that both could participate in pesticide sorption and destruction. Second, in the DC mode, a cation exchange membrane between the electrodes (Figure 1), prevents passage of halides to the anode where oxidation would form chlorine and other oxidizing agents. These oxidizing agents could react with natural organic matter (NOM) to form halogenated byproducts. The formation of these byproducts has been a major hurdle to the application of electrochemical systems to natural waters. We found that we could avoid formation of oxidizing agents if the frequency of the alternating potential were sufficiently fast to avoid transport of halides to the anode. At 0.0125 Hz, we were able to achieve dehalogenation of sorbed fipronil without oxidizing chloride to chlorine. Accordingly, we would remove the ion exchange membrane, which vastly simplifies the system configuration. It would be much more difficult to scale-up a system with the ion exchange system as depicted in Figure 1. Lastly, the AC configuration was more energy-efficient than the DC system.
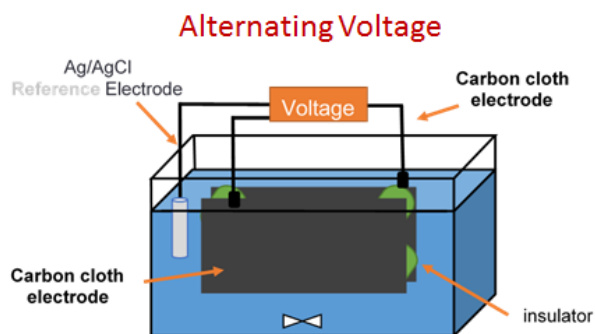

Figure 2: AC electrolysis system with parallel-plate GAC-based electrodes

Overall, the system featured three significant innovations relative to current research on electrochemical systems for environmental applications. First, most electrochemical systems focus on oxidation (i.e., anodes). Most contaminants of concern are halogenated and the electron-withdrawing nature of halogens hinders oxidation reactions. Our system focuses on reductive dehalogenation. Second, most current electrochemical systems focus on materials with negligible sorptive capacity, often with exotic materials (e.g., diamond). It is very difficult for such systems to treat water in flow-through systems, because contaminant degradation must occur over the seconds timescale relevant to contact of the chemicals with the electrodes. Our system focuses on inexpensive GAC, which can capture and sequester the pesticides in a flow-through configuration. This sorption capacity permits degradation to occur over longer timescales than the short hydraulic residence time of water in the reactor in a flow-through configuration. Third, our system is one of the few instances wherein AC electrolysis has been applied to environmental systems, and this configuration simplifies the system, along with the other advantages outlined above.

Task 3 Results Summary

Objective: The objective of Task 3 was to develop and test a small pilot-scale reactor to treat urban runoff, based upon the results of Task 2. These tasks demonstrated that we could destroy pesticides sorbed to activated carbon, releasing halides as harmless byproducts. In a pilot-scale system, we sought to evaluate both the sorption and destruction of the pesticides from water in a flow-through system.

Target Water: For another project, we have been conducting work on treating the concentrate formed by reverse osmosis treatment of a wastewater effluent as part of a pilot study for an advanced potable reuse facility. We measured 640 ng/L imidacloprid and 160 ng/L fipronil in the concentrate; bifenthrin and permethrin were not detected, concurring with expectations given the hydrophobicity of these compounds. Given the consistent flowrate and pesticide concentrations in the concentrate, along with the challenging matrix (i.e., high salt and organic matter concentrations), this field site was selected to test our small pilot-scale systems.

Pilot Results: The first pilot-scale unit configuration tested involved a scaled-up version of the AC-based parallel-plate reactor (Figure 2) tested under Task 2 (Figure 3). The reactor consisted of a long rectangular trough (~6 cm width, 0.5 m long, ~ 5 L volume) containing 2 long sheets of aluminum foil electrodes coated with powdered activated carbon. The sheets were separated by 2 cm. A stock of 0.5 mg/L fipronil dissolved in DI water was pumped through the system with a residence time of ~ 3 hours. The electrolysis system was not turned on, as we were initially testing the ability of the system to sorb and capture fipronil. However, despite the long hydraulic residence time, breakthrough of fipronil occurred (Figure 4), indicating that the sorption kinetics of the system would limit the degradation of fipronil.
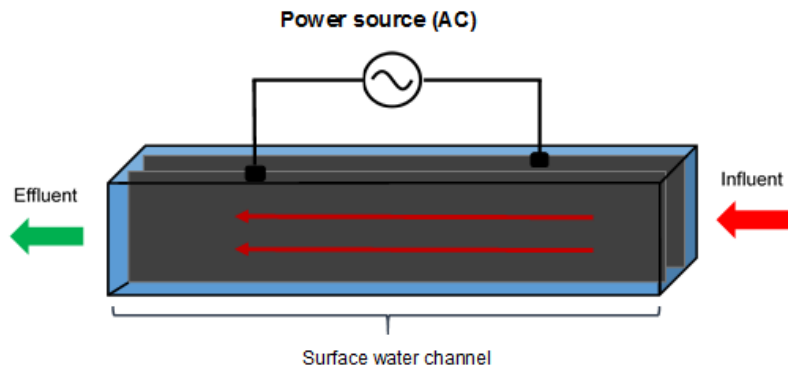

Figure 3: Scaled-up flow-through parallel-plate AC reactor
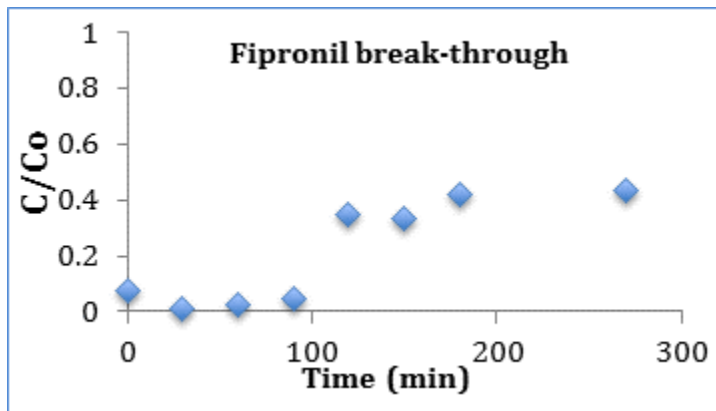

Figure 4: Fipronil concentration in the effluent of the reactor in Figure 3.

We reverted to a system involving loose activated carbon constituting nearly all of the reactor cross-section, similar to a GAC-based contactor. Such systems have been demonstrated

to retain fipronil in flow-through configurations on other projects (e.g., the UC Davis system wherein fipronil in agricultural-impacted waters is retained on GAC without degradation). The system consisted of a rectangular cross-section divided into 5 cells of approximately equal size by 4 insulating plastic vertical sheets (~0.5 cm wide); the sheets were perforated to permit passage of ions. Each channel was ~8 cm long x ~2 cm wide x ~5 cm tall. The sheets were lined with aluminum foil to serve as the current distributor and then the cells were filled with loose GAC (Figure 5).

During electrolysis, the edges of the aluminum foil were attached to titanium wires and connected to a potentiostat. Alternating current from -1 to +1 V vs. S.H.E. was applied to the electrode channels at 0.025 Hz (40 second cycle time). Neighboring channels were connected to different poles of the potentiostat, such that while one channel served as a cathode, its two neighbors would serve as anodes. Then, when the polarity of the potentiostat switched, the channel in question would serve as an anode while its neighbors would serve as cathodes. Chambers at the front and rear of the channels served to distribute water across the cross-section of the reactor. Water pumped into the front channel flowed through the reactor by gravity.
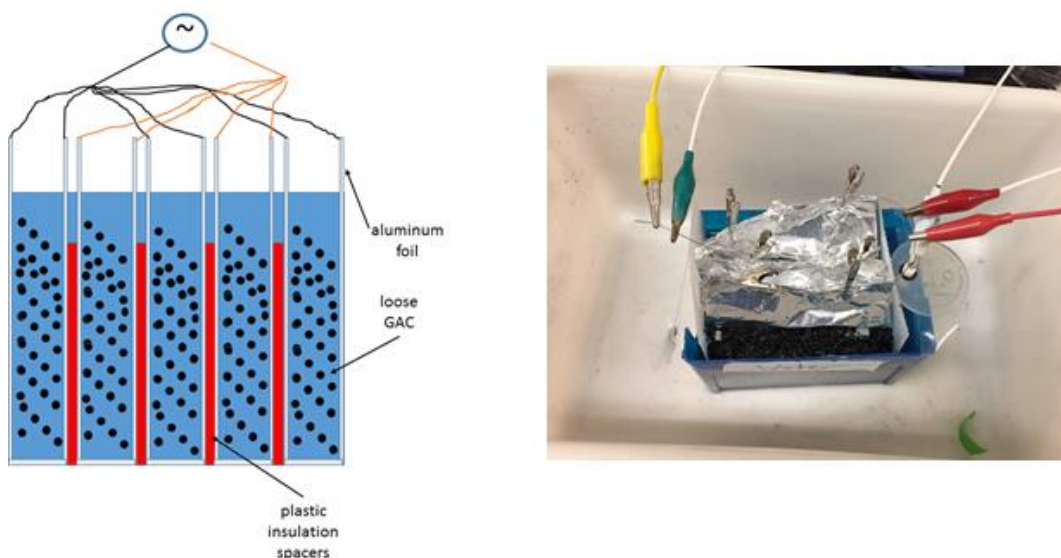

Figure 5: Cross-sectional schematic (left) and top-view picture (right) of the second flow-through pilot-scale reactor.

Adsorption experiments with the reactor were performed using the RO concentrate spiked with 0.1 mg/L fipronil and imidacloprid; spiking was done to permit decreases in concentration to be measured readily and with lower sample volumes (i.e., 500-mL sample volumes were needed to detect the ng/L concentrations measured in the native concentrate). The system flowrate was first set to a 16 min Empty Bed Contact time (EBCT); EBCT indicates the average residence time of water in the unit. At 16 min EBCT, breakthough was observed, with up to 30% of the influent imidacloprid and fipronil measured in the effluent (Figure 6). The EBCT was then set to 30 min, reducing breakthrough to ~10%. We believe that this breakthrough represents water bypassing the GAC through channels around the GAC; there were small spaces between the aluminum foil and the reactor wall, for example. Thus we believe that a 30 min EBCT would be sufficient to fully capture the fipronil and imidacloprid on the carbon for a full-scale reactor where such avenues for short-circuiting were blocked.
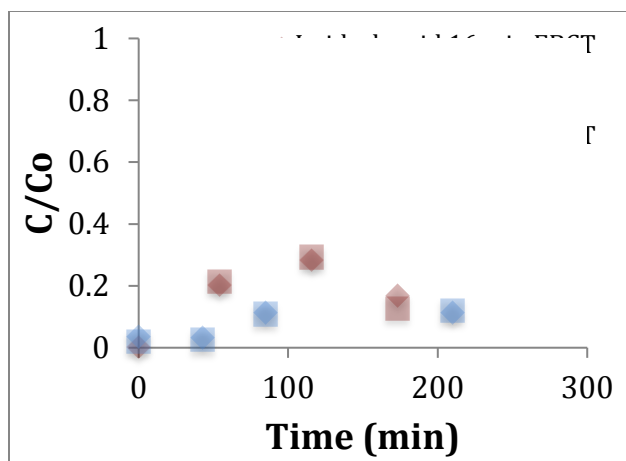
Figure 6: Breakthrough of fipronil and imidacloprid in RO concentrate for pilot-scale reactor EBCT.

After ~ 5.5 L of stock flowed through the reactor (~14 bed volumes), the flow was stopped and AC electrolysis commenced. Before electrolysis, the GAC in the middle and one of the side channels was removed from the reactor, homogenized, then underwent extraction with acetonitrile in order to measure the initial concentration of pesticides on the carbon (per g dry carbon), as well as determine the distribution of pesticides in the different channels. The concentrations were very similar between the middle and side channels (0.03 vs. 0.04 µg imidacloprid/g carbon and 0.16 vs. 0.20 µg fipronil/g carbon, respectively), indicating decent mixing across the cross section. One of the other channels was sampled near the inlet, middle and outlet of the channel for sorbed pesticides. The pesticides were concentrated near the inlet (Figure 7), as expected. These results suggest the potential to optimize the flow of current towards the front of the reactor. The homogenized mass was then placed back into the middle and side channels and electrolysis was commenced.
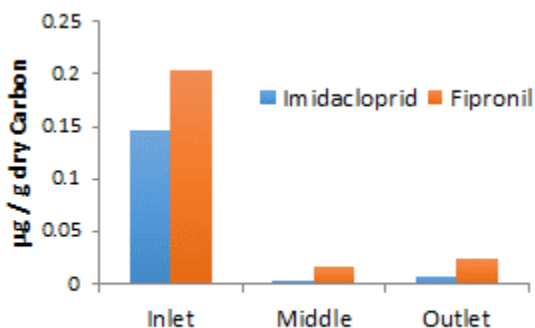

Figure 7: Concentration of pesticides measured near the inlet, middle and outlet of the pilot-scale reactor channels.

The electrolysis of the channels was conducted over the course of 145 hours (6 days). After 6 days, the GAC in the middle channel was removed, homogenized and then sampled again for sorbed pesticides. No significant decrease in the concentration of sorbed pesticides was observed (Figure 8). This negative result is not altogether surprising because the average current delivered by our potentiostat was -25 mA, comparable to that delivered in our previous work (Li

and Mitch, 2018), but the mass of carbon in our reactor (~170 g) was 425 times higher than the 0.4 g employed previously. Accordingly, the electrolysis time for the same current would be expected to take 425-fold longer. We expect that we should be able to achieve pesticide degradation over times comparable to the ~15-30 h timescale observed for loose GAC electrodes previously (Li and Mitch, 2018) if we can scale the current in accordance with the increased size of the treatment system.
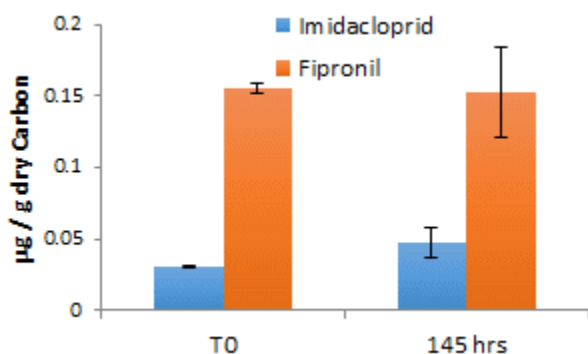

Figure 8: Concentrations of imidacloprid and fipronil measured on the GAC at the beginning (T0) and end (145 hrs) of the electrolysis.

Summary and Future Research: Our work has demonstrated that pesticides in urban runoff, including RO concentrate from advanced treatment trains for the potable reuse of municipal wastewater effluents, can be captured and concentrated on GAC if the reactor has a ~30 min EBCT, which is reasonable for full-scale process units. We have also demosntrated that application of -1 V vs. S.H.E. to loose GAC can achieve dehalogenation of the sorbed pesticides, yielding halides as harmless byproducts. Many contaminants beyond pesticides are halogenated, and halogens are likely to be important functional groups contributing to the toxicity of the contaminants. Accordingly, the capture and destruction of halogenated contaminants by this electrolysis system could represent a broad-screen treatment system for contaminants in urban runoff.

      We characterized electrolysis conditions promoting the degradation of sorbed pesticides in both the DC and AC modes, and demonstrated that the AC mode can achieve dehalogenation while simplifying the configuration (e.g., avoiding the ion exchange membrane) and reducing energy consumption.

      However, the key factor that must be further optimized is the tradeoff between capture efficiency and electrolysis efficiency. Sorption kinetics of the pesticides to the carbon could limit the process. We found that sorption could be achieved with loose GAC with a 30 min EBCT, which is reasonable for full-scale treatment process units. The sorption kinetics could be optimized by reducing the diameter of the GAC particles, but the particle diameter can not be too small or the headloss in the reactor would be too high. Since 30 min EBCT is already reasonable, it is likely that this factor would not limit full-scale implementation.

      The electrolysis system could also be optimized. In our final pilot-scale configuration, we had channels of loose GAC particles. This system could be optimized in several ways. First, we found that resistance between the GAC particles hindered the electrolysis kinetics in previous work (Task 1). We increased the electrolysis kinetics by an order of magnitude by crushing the GAC to a powder and attaching as a thin layer on the carbon cloth current distributor. The

kinetics of the pilot reactor likely could be enhanced by reducing the GAC particle diameter and reducing the channel width (i.e., the spacing between the aluminum current distributors). These alterations could reduce the overall resistance of the system and facilitate the transfer of electrons to the GAC particles, thereby increasing the kinetics while reducing the power consumption. The second modification would be to scale the current to the size of the pilot system. The current delivered by our potentiostat to the pilot reactor was roughly 425-fold smaller than that in our earlier (successful) lab-scale experiments on a per mass of carbon basis. We have initiated conversations with an electrical engineer regarding cheap power supply systems that could deliver the requisite current at the appropriate AC frequency.

References

Li, Y.; Mitch, W.A. Capture and Reductive Transformation of Halogenated Pesticides by an Activated Carbon-Based Electrolysis System for Treatment of Runoff. *Environ. Sci. Technol.,* **2018**, 1435-1443.