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RESEARCH ARTICLE

Aqueous Degradation of Imidacloprid and Fenothiocarb using Contact Glow Discharge Electrolysis: Degradation Behavior and Kinetics

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Abstract Degradation of the pesticides fenothiocarb and imidacloprid in water using contact glow discharge electrolysis (CGDE) achieved rates of 57.8 and 43.2% respectively. Degradation was enhanced using citric or hydrochloric acid to lower the pH to 3.0. Both acids enhanced both the degradation rate and the amount. Fenothiocarb degradation was 77.14% at pH 3 with citric acid, and 100% with HCl. Degradation of imidacloprid at pH 3 was 70.18% with citric acid and 93.02% with HCl. Acidic conditions favor either production of $^{\bullet}OH$ radicals or enhancement of the degradation of organic compounds by $^{\bullet}OH$. Both the degradation rates and amounts for fenothiocarb and imidacloprid were reduced in the presence of methanol due to competition between pesticides and MeOH for $^{\bullet}OH$. Degradation of pesticides was not completely inhibited by MeOH. Degradation of both fenothiocarb and imidacloprid using CGDE obeys a first-order rate law with high regression coefficient values (R^2>0.99).

Keywords: CGDE, fenothiocarb, imidacloprid, degradation, pesticide

Introduction

Pesticides are widely used in modern agriculture in order to produce more food for both humans and animals. The role of pesticides in agriculture and their contribution to crop protection is increasing. However, with increasing pesticide use, concern over adverse effects on non-target organisms, including human beings, has increased. As a result, consumers are becoming aware of food quality and safety issues, and are realizing the need to be selective about the foods they consume. Therefore, governments have taken legislative action to ensure that only safe food of acceptable quality is sold, and that the risk of food-borne health hazards is minimized. To ensure the safety of foods, most governments regulate the maximum acceptable levels of pesticide residues (MRLs). Even though the use of pesticides has been controlled due to more rigorous regulations and innovative pesticide application methods, pesticides continue to be detected in foods, primarily fruits and vegetables (1). Therefore, removal of pesticide residues from foods has become an important issue with respect to food safety.

The presence of pesticides in food is a concern for human exposure to pesticides. On the other hand, recently emerging technologies, such as advanced oxidation processes (AOPs) and zerovalent iron (ZVI) for removal of pesticide residues are mainly focused on residues in soil and water (2-7), and are unsuitable for application to removal of pesticides from fresh fruits and vegetables as both would require addition of external elements to a reaction medium. Moreover, chemical oxidation also often results in incomplete destruction of pesticide molecules and tends to form undesirable by-products (8). Among the current methods, ozonation may be the best way to remove residual pesticides from fruits and vegetables since it has a long history of use and study for aqueous pesticide degradation (9,10). However, the removal efficiency of ozonation for certain pesticides is relatively low, compared to other AOPs, such as O_3/H_2O_2 (8,11,12). The high energy requirement

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for generating ozone and large investment for UV lamps make the technology expensive to use. The frequent use of catalysts to increase reaction rates also raises concerns over the environmental friendliness of this technology. It is important to develop new technologies with high a destruction efficiency and an environmentally benign application that can operate at room temperature and atmospheric pressure to minimize the risk of pesticide pollution.

Recently, a novel electrochemical process named contact glow discharge electrolysis (CGDE) has attracted the interest of many scientists due to its effectiveness for removal of contaminants, and environmental friendliness. In the CGDE process, a high voltage causes a sheath of vapor to form around an electrode through which current flows as a glow discharge (11). Plasma is generated and sustained by DC glow discharges between the electrode and the surface of a liquid solution. In the plasma, water vapor molecules are ionized or activated resulting in production of free OH radicals. Water molecules also disassociate into H_2, H_2O_2, and H_2O^+ gas. These active species diffuse into the solution where they interact with any active substrate present (12). To date, few studies have been conducted addressing the efficiency of CGDE for removal of pesticides and, therefore, further research is needed to address the potential of CGDE. Degradation of aqueous carbofuran induced by CGDE was reported by Pu *et al.* (15). Chen *et al.* (16) reported degradation of both methamidophos and chlorpyrifos in apple juice treated with pulsed electric fields, which is a similar to CGDE. However, to the best of our knowledge, there is no report about degradation of other pesticides by CGDE. Therefore, the highly water soluble pesticides fenothiocarb and imidacloprid (30 and 514 ppm, respectively), which are not organophosphates, were selected for analysis.

Degrading pesticides in foods by CGDE should be done in water. This is best suited to fruits and vegetables. The objectives of this study were to investigate the applicability of CGDE for degrading fenothiocarb and imidacloprid in water, and to investigate the reaction kinetics and behaviors of pesticide degradation induced by CGDE. The effect of low pH and the presence of methanol were also investigated.

Materials and Methods

Chemicals Pesticides were purchased from Dr. Ehrenstorfer, GmbH (Augsburg, Germany). Chemical structures and the physicochemical properties of pesticides are shown in Table 1. Acetonitrile and methanol solvents were products of Merck, KGaA (Darmstadt, Germany). Distilled water was generated using a Milli-Q Gradient, R105-5, Millipore (Bedford, MA, USA). Monohydrate citric acid was purchased from Sigma Chemical Co. (St. Louis, MO, USA) and 35% HCl was provided by Junsei Chemical Co., Ltd. (Tokyo, Japan).

Preparing stock and working solutions Calculated amount of standards were dissolved in acetonitrile to achieve a 1,000 ppm stock solution. For working solutions, stock solutions were diluted with appropriate amounts of distilled water.

CGDE instrument Glow discharge electrolysis equipment (CLEAZ) was purchased from a private household goods company (Hann Co., Seoul, Korea). The equipment was designed to control microorganisms in contaminated fruits and vegetables at 220 V and 60 Hz.

CGDE treatment A series of 2 ppm standard working solutions were prepared in 2 L beakers and reactors. Electolytic discharge part of the CGDE was dipped in the standard working aqueous pesticide solutions, the volume of which was 1.4 L, measured using a volumetric flask. The reaction vessel (2 L beaker) was put into a water bath to maintain a constant temperature under ambient conditions, and 1 mL sample aliquots were withdrawn at 0, 5, 10, 15, 30, 60, and 120 min. The standard working aqueous pesticide solution was mechanically stirred at each sampling time. An amount of 0.5 mL of 1% formic acid was added to 1 mL of sample and vortex mixed. It was

Table 1. Chemical structure and physicochemical properties of selected pesticides

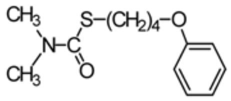
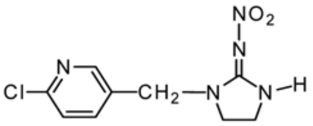
No.	Name	Type	Group	Structure	Formula	Water solubility (g/L)
1	Fenothiocarb	Acaricide	Carbamate		$C_{13}H_{19}NO_2S$	0.03
2	Imidacloprid	Insecticide	Neonicotanoid		$C_9H_{10}ClN_5O_2$	0.61

Table 2. LC-MS/MS set-up conditions for fenothiocarb and imidacloprid

No.	Name	Precursor	Fragmentor voltage	Product ion 1	CE (1)	Product ion 2	CE (2)	Ret. time (min)
1	Fenothiocarb	254.1	85	160.1	4	72.1	12	11.52
2	Imidacloprid	256.1	80	209.1	10	175.0	10	7.02

then filtered through a 0.2 μm GHP filter (Pall, Port Washington, NY, USA) and the concentration of pesticide in the sample was determined using HPLC-MS/MS.

For experiments with methanol, 20% methanol was used for preparation of working solutions instead of distilled water. A final 1.5 mL sample was further diluted with distilled water to 5 orders of magnitude due to the high content of methanol that made the detector response unstable.

For pH controlled experiments, 0.5 M citric acid or 0.5 M hydrochloric acid (HCl) was added to the solution to prepare a 2 ppm standard working solution. The initial pH value of the pesticide solution was adjusted to 3.0. Control samples were also adjusted to pH 3.0, but not exposed to CGDE treatment, then allowed to stand under ambient conditions during the experiments.

LC-MS/MS condition LC-MS/MS analysis was performed using an Agilent Technologies (Palo Alto, CA, USA) model 1200 series HPLC coupled to an Agilent 6410 triple-quadrupole mass spectrometer. Precursor and product ions were analyzed in scan mode. The fragmentor voltage and collision energy that produced the most intense peak of selected ions for pesticides were used (Table 2). Instrument parameters were a gas temp of 350°C, a gas flow rate of 10 L/min, and a nebulizer psi of 50 using N_2 gas. Ionization was achieved using electrospray ionization at the positive mode. Analyte separation was achieved using a YMC-Pack Pro C18 RS, 3 μm, 100×3 mm i.d., (YMC Co., Ltd., Kyoto, Japan). The column temperature was 40°C. The mobile phase consisted of water buffered with 10 mM ammonium formate (solvent A), and acetonitrile (solvent B). The LC gradient for the separation was a linear increase in B from 5 to 70% from 0 to 5 min; a linear increase of B from 70 to 90% from 5 to 10 min; A linear increase of B from 90 to 95% from 10 to 12 min; followed by an isocratic at 95% B from 12 to 15 min. Initial conditions were re-established in 6 s and were maintained for 54 s. The post-running time was 4 min, resulting in a total run time of 20 min. The flow rate of the mobile phase was 0.2 mL/min. The sample injection volume was 10 μL. Data processing was performed using MassHunter Workstation data acquisition software (Agilent Technologies, USA) in MRM mode. The dwell time was 200 s for both pesticides. Peak areas of each pesticide were used directly as signals for quantitative analysis.

Degradation amount and kinetic calculation The pesticide concentration was calculated from the detector response to injected samples using a stand calibration curve in an Excel spreadsheet (MS Office 2007; Microsoft, USA). Pesticide degradation was calculated based on the initial concentration of pesticide using the following equation:

$$\text{Degradation (\%)} = (1 - C_t/C_0) \times 100 \tag{1}$$

where C_t=the concentration of the pesticide at time (t), and C_0=the initial concentration of the pesticide. To calculate the degradation kinetics and half-life, the following integral 1st order kinetic equation was used:

$$\ln (C_t/C_0) = -kt \tag{2}$$

where k=the reaction rate constant, and t=the reaction time.

The slope of the linear regression line of ln (C_t/C_0) against time gives the reaction rate constant. The half-life was calculated from

$$T_{1/2} = \ln 2/k \tag{3}$$

Statistical analysis Data were input into SigmaPlot 10.0, Systat Software, Inc. (San Jose, CA, USA) for statistical analysis. A two-tailed student's *t*-test was carried out to compare results.

Results and Discussion

Pesticide degradation analysis using CGDE When a sufficiently high voltage is applied in CGDE, current flows through vapors around an electrode as a glow discharge by generation of plasma between the electrode and the surface of a liquid solution. In the plasma, water vapor molecules are ionized or activated and bombarded with liquid water molecules, resulting in the production of free OH radicals, hydrogen atoms, hydronium ions, and hydrogen peroxide (11). The reactions are as follows:

$$H_2O^+ + nH_2O \rightarrow H_3O^+ + n^{\bullet}OH + (n-1)^{\bullet}H \tag{4}$$
$$^{\bullet}OH + ^{\bullet}H \rightarrow H_2O \tag{5}$$
$$^{\bullet}OH + ^{\bullet}OH \rightarrow H_2O_2 \tag{6}$$
$$^{\bullet}H + ^{\bullet}H \rightarrow H_2\uparrow \tag{7}$$

In Eq. 4, "n" represents the number of water molecules decomposed per H_2O^+ ion. The value of n is estimated to

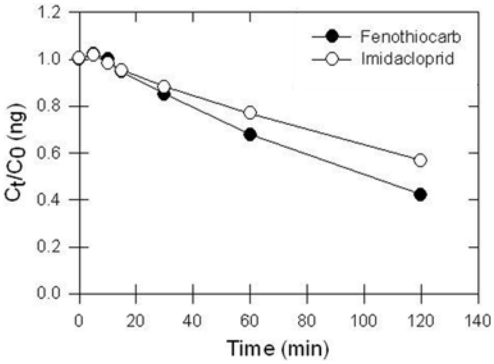


Fig. 1. Changes in concentrations of fenothiocarb and imidacloprid during CGDE treatment. C_0=2 ppm

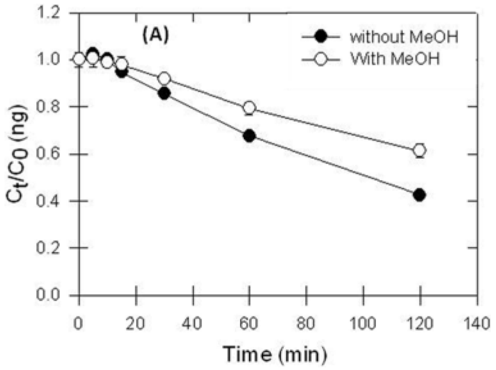


Fig. 2. Plots of regression analysis for first-order kinetics of degradation of fenothiocarb and imidacloprid using CGDE.

be as high as 12 (12). Thus, one exited or ionized H_2O molecule can produce 12 $^{\bullet}$OH ions. The hydroxyl radical ($^{\bullet}$OH) is one of the strongest oxidants and is non-selective, so it oxidizes any type of organic substance. Degradation of fenothiocarb and imidacloprid are probably induced by $^{\bullet}$OH.

Degradation values for fenothiocarb and imidacloprid were 57.8% and 43.2%, respectively, in water using CGDE. Changes in the amount of pesticide degradation with time are presented in Fig. 1. The amount of degradation was significant for treatment times from 30 to 120 min (p<0.001), indicating that pesticide degradation depends on the chemical nature of the pesticide. To characterize the kinetics of pesticide degradation, data were analyzed using an integral first order kinetic equation (Eq. 2). The resulting regression lines had high coefficient values (R^2) of 0.9941 for fenothiocarb and 0.9963 for imidacloprid, indicating good linearity (Fig. 2). Therefore, the degradation of both pesticides can be considered to obey a first order rate law. Degradation of dyes in water using CGDE also obeyed a first order rate law (15). Reaction rate constant (k) values were obtained from the slopes of the regression lines. The half-life values of the pesticides were obtained via application of k values to Eq. 3. Results and kinetic equations are shown in Table 3.

Effect of methanol on pesticide degradation using CGDE The effect of MeOH on the degradation of fenotiocarb and imidacloprid using CGDE was analyzed to determine whether the $^{\bullet}$OH ion is involved in the pesticide degradation process. MeOH was used for this purpose because it is a well known radical scavenger. Degradation of both pesticides was decreased in the present of 20% MeOH (Fig. 3A, 3B) because of competition between the pesticides and MeOH for $^{\bullet}$OH. Previous research also reported the inhibitory effect of methanol on oxidative degradation of organic compounds (16,17). Due to the non-selective behavior of $^{\bullet}$OH, degradation of pesticides is not completely inhibited in the presence of MeOH, however, the results clearly reveal that $^{\bullet}$OH is the active species that degrades pesticides in water using CGDE.

The effect of low pH and types of acids To adjust the reaction solution to pH 3.0, either 0.5 M citric acid or 0.5 M hydrochloric acid was used. The effects of low pH conditions on degradation of fenothiocarb and imidacloprid using CGDE are presented in Fig. 4 and 5. No degradation was observed at pH 3.0 within the experimental time frame for control samples of both pesticides. Degradation of both pesticides was significantly enhanced with both types of acids at pH 3.0, compared to no pH adjusted treatment

Table 3. Reaction rate constants (k), half-life values, and regression coefficients of pesticide degradation data fitted to a first order kinetic equation

No.	Name	CGDE treatment	Regression equation	Constant value	k Value (1/min)	Regression coefficient	Half-life (min)
1	Fenothiocarb	In water	Y= –0.0075X	+0.0511	7.5×10^{-3}	0.9941	92.42
		With MeOH	Y= –0.0043X	+0.0273	4.3×10^{-3}	0.9937	161.20
		With C/A	Y= –0.0121X	–0.0265	12.1×10^{-3}	0.9985	57.28
		With HCl	-	-	-	-	<5
2	Imidacloprid	In water	Y= –0.0048X	+0.0213	4.8×10^{-3}	0.9963	144.41
		With MeOH	Y= –0.0026X	+0.0062	2.6×10^{-3}	0.9932	266.60
		With C/A	Y= –0.0102X	+0.0217	10.2×10^{-3}	0.9987	67.96
		With HCl	Y= –0.0224X	+0.0447	22.4×10^{-3}	0.9991	30.94

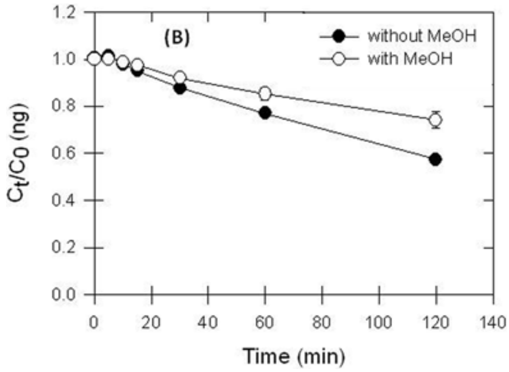


Fig. 3. The effect of the presence of MeOH on degradation of (A) fenothiocarb and (B) imidacloprid using CGDE. C_0=2 ppm, C_{MeOH}=20%

(p<0.001). Acidic conditions are either favorable for production of $^{\bullet}$OH radicals or favorable for degradation of organic compounds by $^{\bullet}$OH. On the other hand, the activity of $^{\bullet}$OH is stronger at pH 3.0 with an oxidation potential of 2.70 V. At pH 9.0 the potential is 2.34 V. A similar result was reported by Pu *et al.* (15) where carbofuran degradation using low temperature plasma was enhanced at pH 2.0 compared to pH values of 4.0 and 6.0. Fenothiocarb with citric acid achieved 77.14% degradation, and since fenothiocarb was not detected in samples treated using CGDE with HCl, degradation of fenothiocarb with HCl was probably 100%. A similar degradation trend for imidacloprid was observed. Up to 70.18% imidacloprid degradation was achieved with citric acid and 93.02% with HCl. The fact that lower pesticide degradation rates are achieved with citric acid (compared with HCL) may be due to the competitive effect of citrate against $^{\bullet}$OH. The degradation kinetics and half-life of pesticides at pH 3.0 are shown in Table 3. The reaction kinetics for degradation of fenothiocarb at pH 3.0 with HCl are not available because 100% of the pesticide was degraded within the first data collection interval (<5 min). Therefore, data could not be applied to the kinetic equation. The reaction kinetics of both pesticides at pH 3.0 with citric acid were two orders of magnitude faster than with no pH adjusted treatment. Reaction kinetics for degradation of imidacloprid at pH 3.0 with HCl were 4 orders of magnitude faster than with no pH adjusted treatment, and 2 orders of magnitude faster when adjusted to pH 3 using citric acid. The reaction kinetics at pH 3.0 are a better fit to the first-order rate law than the kinetics with no adjustment of pH.

CGDE is an effective tool for degrading pesticides in water, even at a relatively low applied voltage (220 V). Approximately half of the initial concentration of pesticide was degraded using CGDE without any modification of the reaction solution or conditions. CGDE is a promising method for removal of pesticide residues from fruits and vegetables using water as a reaction medium. Degradation is probably due to $^{\bullet}$OH ions produced from liquid water molecules bombarded with $H_2O^+_{gas}$ that are activated during the CGDE process. Further degradation of both the tested pesticides was achieved by acidifying the reaction solution to pH 3.0. For fenothiocarb, 100% degradation was achieved at pH 3.0 using HCl. The degradation rate and amount were reduced in the presence of methanol. Pesticide degradation using CGDE in all cases obeys a first order rate law. There are few applications of glow discharge electrolysis for removal of pesticide residues, but the technique is effective. Reagents in water serve as electron mediators to enhance redox reaction rates and improve pesticide degradation. Further studies are needed to determine applicability of CGDE to commercial produce using a wider range of pesticides.

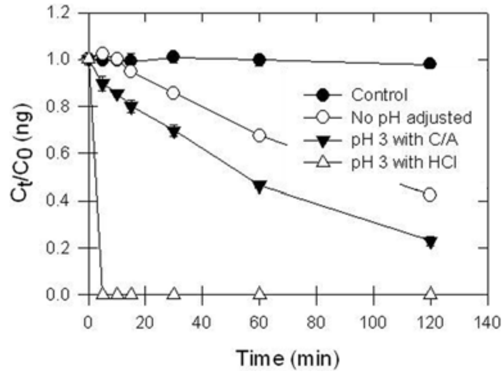


Fig. 4. The effect of low pH and acids on degradation of fenothiocarb using CGDE. C_0=2 ppm

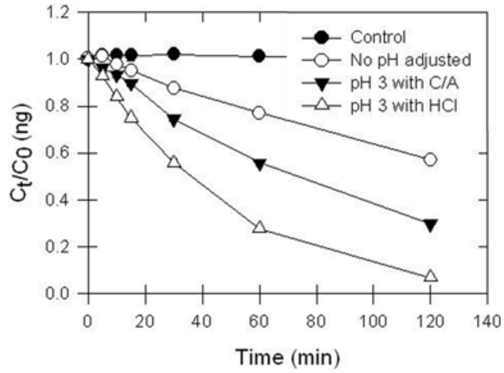


Fig. 5. The effect of low pH and acids on degradation of imidacloprid using CGDE. C_0=2 ppm

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