Electrocatalytic dechlorination of atrazine

Naomi L. Stock and Nigel J. Bunce

Abstract: Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine), a photosynthetic inhibitor that is used in large quantities for weed control in corn and sorghum, is dechlorinated in aqueous solution upon electrolysis at a reticulated vitreous carbon cathode in the presence of noble-metal catalysts. Electrocatalytic hydrogenolysis to 2-ethylamino-4-isopropylamino-*s*-triazine occurs in quantitative yield, and is most efficient with palladium-based catalysts. Current efficiency increases with atrazine and catalyst concentration, and decreasing current density. A previously unobserved phenomenon with Pd catalysts is that current must be passed for a certain time before dechlorination commences. This lag time is explained in terms of the palladium lattice absorbing a finite amount of hydrogen before catalytically active hydrogen atoms appear on the catalyst surface.

Key words: electrocatalytic hydrogenoloysis, dechlorination, atrazine, palladium catalysts.

Résumé : Soumise à une électrolyse en solution aqueuse, au niveau d'une cathode de carbone vitreuse et réticulée et en présence de catalyseurs de métaux nobles, l'atrazine (la 2-chloro-4-éthylamino-6-isopropylamino-*s*-triazine), un inhibiteur de la photosynthèse utilisé en grandes quantités pour contrôler les mauvaises herbes dans le maïs et dans le shorgo, subit une déchloration. L'hydrogénolyse électrocatalytique en 2-éthylamino-4-isopropylamino-*s*-triazine se produit avec un rendement quantitatif et les catalyseurs à base de palladium sont les plus efficaces. L'efficacité de courant augmente avec les concentrations d'atrazine et de catalyseur et elle diminue avec la densité du courant. Avec les catalyseurs de Pd, il se produit un phénomène qui n'a pas été observé antérieurement; on doit faire passer le courant pour un certain temps avant que la déchloration ne débute. On explique ce décalage dans le temps en fonction d'une absorption dans un premier temps d'une quantité finie d'hydrogène par le réseau du palladium qui précéderait l'apparition d'atomes d'hydrogène catalytiquement actifs à la surface du catalyseur.

Mots clés : hydrogénolyse électrocatalytique; déchloration; atrazine; catalyseurs de palladium.

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Introduction

Reactions involving electrochemically generated hydrogen adsorbed to a metal catalyst surface (M) have been known since the beginning of the twentieth century (1, 2). Two classes of these reactions are known: electrocatalytic hydrogenation and electrocatalytic hydrogenolysis (both abbreviated ECH). The former involves the addition of hydrogen to π bonds (3–6), whereas the latter involves the reductive cleavage of σ bonds, as in dechlorination reactions (7–11). Both types of ECH reactions involve the electrochemical reduction of a protic solvent to produce adsorbed hydrogen atoms (H_{ads}, eq. [1]) that react chemically with an adsorbed organic substrate $(R\text{-}X)_{ads}$, eq. [3]): see below, which is adapted from ref. 6.

$$[1] \quad 2H_2O(\text{or } H_3O^+) + 2e^- + M \rightarrow 2H_{ads}M + 2OH^- \ (\text{or } H_2O)$$

$$[2] \quad R\text{-}X + M \rightarrow (R\text{-}X)_{ads}M$$

$$[3] \quad (R\text{-}X)_{ads}M + 2H_{ads}M \rightarrow (R\text{-}H)_{ads}M + HX$$

$$[4] \quad (R\text{-}H)_{ads}M \rightarrow R\text{-}H + M$$

ECH always competes with the hydrogen evolution reaction (HER), which proceeds via the Volmer-Heyrovsky-Tafel mechanism (6).

$$[5] \quad H_2O + e^- + M \rightarrow H_{ads}M + OH^- \quad \text{(Volmer reaction)}$$

$$[6] \quad H_{ads}M + H_2O + e^- \rightarrow H_2 + M + OH^- \quad \text{(Heyrovsky reaction)}$$

$$[7] \quad H_{ads}M + H_{ads}M \rightarrow H_2 + 2M \quad \text{(Tafel reaction)}$$

The use of ECH for the remediation of chloroaromatic compounds is potentially advantageous compared with traditional techniques such as adsorption on granular activated carbon (GAC) or incineration. As with other electrochemical technologies, ECH is useful as a "front-end" technology for dechlorinating toxic organic compounds prior to biological treatment (12). Comparing ECH with GAC adsorption, the chloro compounds are dechlorinated rather than simply transferred to a different phase; while in comparison with incineration, ECH avoids the possible formation of toxic byproducts such as chlorinated dibenzodioxins and dibenzofurans. As an

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N.L. Stock and N.J. Bunce.[1] Electrochemical Technology Centre, Department of Chemistry and Biochemistry, University of Guelph, Guelph, ON N1G 2W1, Canada.

[1] Corresponding author (e-mail: bunce@chembio.uoguelph.ca).

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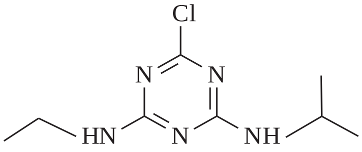
electrochemical process, ECH is a “green” technology, which employs ambient temperatures, aqueous media, and electrons rather than chemical additives to promote chemical change. Provided that high current efficiencies can be achieved, ECH is also cost and energy efficient, technically flexible, and readily allows for the selective dechlorination of many different organic compounds (7).

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) is used in large quantities in North America to control broadleaf and grassy weeds, primarily in corn and sorghum, and as a result has become a common contaminant in ground and surface water (13). This is of particular concern, since this herbicide has been identified as a possible carcinogen (14) and endocrine disruptor (15).



In this work we studied electrocatalytic hydrogenolysis (ECH) as a possible remediation method for the dechlorination of atrazine, using various noble-metal catalysts at a reticulated vitreous carbon (RVC) electrode in aqueous solutions. In particular, we examined the influence of substrate concentration, catalyst concentration and reusability, and current density on dechlorination efficiency.

Experimental

Materials

Analytical grade atrazine (99% pure) was purchased from Supelco (Oakville, Ontario). Technical grade atrazine (Aatrex-Nine-O, 90% pure) was generously donated by Peter Smith (Plant Agriculture Department, University of Guelph), and was purified by hot filtration and recrystallization from methanol. An analytical standard of dechlorinated atrazine (DCA) was generously donated by Dr. Nelson Johnson (Novartis, Jonesboro, North Carolina). All catalyst powders were 5% by weight and were obtained from Aldrich (Oakville, Ontario). Sulphuric acid (H_2SO_4), lithium perchlorate ($LiClO_4$), sodium sulphate (Na_2SO_4), and HPLC grade acetonitrile and methanol were obtained from Fisher Scientific (Toronto, Ontario). Nafion-417 membranes and RVC (80 ppi) were obtained from the Electrosynthesis Company (Lancaster, New York). Platinum foil (99.95% pure), platinum wire (99.95% pure, 0.368 mm diameter), and copper wire (99.9% pure, 1.0 mm diameter) were purchased from Alfa Aesar (Ward Hill, Massachusetts). Water used in all experiments was purified using a Millipore Milli-Q Reagent Water System and had a resistivity of not less than 10 MΩ cm.

Apparatus and procedures

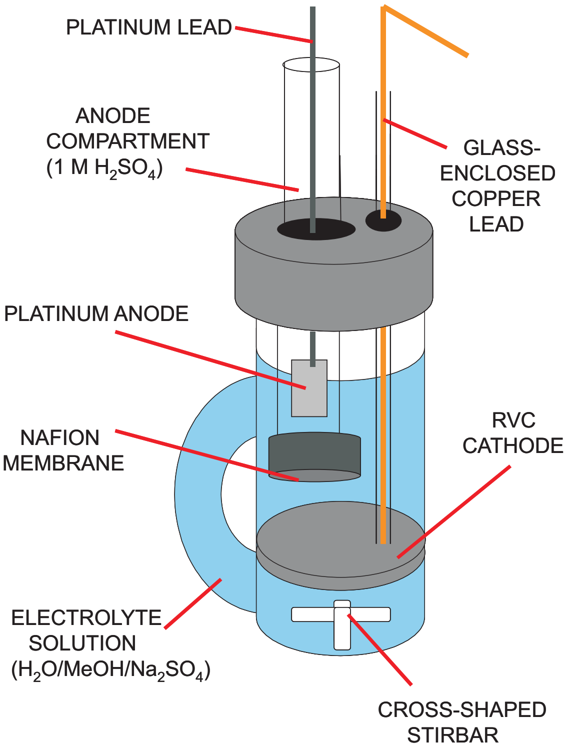
Cyclic voltammetry was conducted on unstirred atrazine–acetonitrile solutions (200 ppm) in a 20 mL open-top glass cell. Both the working and counter electrodes were platinum (0.94 and 1.26 cm^2, respectively). In all experiments, 0.15 M lithium chloride was used as the supporting electrolyte and a sweep rate of 200 mV s^{-1} was employed. All CV experiments were conducted on a computer-controlled EG&G Princeton Applied Research Potentiostat (Model 273). Data were acquired using Model 270/250 Research Electrochemistry Software (version 4.10), converted to ASCII-text format and plotted in Microsoft Excel 2000 (version 9.0.2720). A saturated silver–silver chloride electrode, which was calibrated to 200 mV, was used as a reference electrode. Reference potentials were calculated against a standard hydrogen electrode (SHE).

All electrocatalytic hydrogenations were carried out in a flow-through batch cell (Fig. 1) designed by Patrick Dubé (University of Sherbrooke) and fabricated by Yves Savoret (University of Guelph). In this cell, the anode and cathode compartments were separated with a Nafion 417 membrane. In all experiments the cathode was RVC (80 ppi, 5 mm thick and 36 mm in diameter) with a copper wire lead (enclosed in glass tubing for stability) and the anode was platinum foil (16 mm × 12 mm and 0.1 mm thick) with a platinum wire lead. The anolyte solution was 20 mL of sulphuric acid (1 M) and the catholyte solution was water–methanol (75:5 mL), and contained sodium sulphate as supporting electrolyte to a concentration of 0.15 M. Atrazine was dissolved in the methanol aliquot and catalyst powder was added to the cathode compartment. A cross-shaped stir bar was placed in the cathode compartment and upon stirring, the catholyte solution and catalyst powder were forced through the RVC cathode, resulting in the impregnation of catalyst powder in the cathode. The catalyst remained impregnated in the RVC cathode throughout the experiment. When the charge was removed and the magnetic stirrer turned off, the catalyst powder returned to solution. An Amel Instrument General Purpose Potentiostat/Galvanostat (Model 2049) was used for experiments carried out at constant current. A computer controlled EG&G Princeton Applied Research Potentiostat (Model 273), equipped with Model 270/250 Research Electrochemistry Software (version 4.10) was used for experiments carried out at constant potential. A saturated silver – silver chloride electrode, which was calibrated to 200 mV, was used as a reference electrode. All potentials were calculated against a standard hydrogen electrode (SHE). Samples of the pesticide solutions were removed for HPLC analysis at appropriate time intervals during all experiments.

Degradation of the atrazine solutions was monitored using a Waters Model 600 HPLC unit, equipped with a Waters Model 486 variable UV–vis detector, a reverse phase Genesis C_{18} column (4.6 × 250 mm) and a Waters silica precolumn guard. For all analyses, the detector was set at λ = 220 nm and a methanol–water (80:20) mobile phase (1 mL min^{-1} flow rate) was used. Prior to use, solvents were filtered using Supelco Nylon 66 membranes (0.2 μm × 47 mm) to remove microparticles. All injections were done manually using a Rheodyne syringe (Waters), which injected 25 μL of sample into a 5 μL sample loop. Chromatogram generation and peak integration was carried out with Waters Millennium software (version 1.10).

Identification of the dechlorinated product was determined by Perry Martos (University of Guelph) via LC–MS–MS analyses on a VG Quattro II equipped with a quadrapole MS detector and MassLynx software (version 3.5). The samples were ionized using Atmospheric Pressure Chemical Ioniza-

Fig. 1. Schematic of cell used for ECH.



tion (APCI). APCI probe temperatures ranged from 200 to 300°C and cone voltages ranged from 25 to 50 V. Since the samples analyzed by LC–MS contained only single compounds, a column was not required. The mobile phase employed was acetronitrile–water (75:25) (0.6 mL min^{-1} flow rate). The water portion of the mobile phase was spiked with 0.1% formic acid to facilitate ionization of the sample. Prior to use, solvents were filtered to remove microparticles.

Calculations

The apparent current efficiencies for the dechlorination of atrazine were calculated from the number of moles of substrate reacted and the charge passed assuming that two electrons were required for the removal of one chlorine. Changes in volume were taken into consideration due to the removal of samples for analysis.

Results and discussion

The ECH of a 25 ppm solution of atrazine at 50 mA, using as catalyst 50 mg Pd/Al_2O_3, resulted in the rapid production of dechlorinated atrazine (DCA) (2-ethylamino-4-isopropylamino-1,3,5-triazine). The identity of the product was established as DCA by showing that it had the same HPLC retention time and mass spectral properties as authentic material. Following 30 min of ECH treatment, greater than 95% of the atrazine was dechlorinated, and a complete mass balance was obtained (Fig. 2).

Is it really ECH?

Cyclic voltammetry was employed to determine whether the dechlorination of atrazine proceeded via ECH or by direct electroreduction followed by protonation. Ideally the $E_{1/2}$ value for atrazine would have been obtained in the water–methanol solution used for electrolyses, but the reduction of the solvent masked the reduction of atrazine, and so the aprotic solvent acetonitrile was employed instead. In acetonitrile at a platinum cathode, a cyclic voltammogram of 200 ppm atrazine indicated an irreversible reduction process with $E_{1/2} = -1.3$ V vs. SHE. Upon electrolysis in water–methanol, no reduction was observed at $E = -0.5$ V, and the rate of atrazine reduction was essentially independent of potential at $E \leq -0.8$ V (Fig. 3). Since these potentials are much less negative than $E_{1/2}$ for reduction of atrazine (albeit in acetonitrile) and in the same range as for the reduction of water (−0.83 V (16)), the observed dechlorination of atrazine cannot be as a result of direct electroreduction.

Dechlorination efficiency (Table 1)

The influences of current density, catalyst concentration, variation of the noble-metal catalyst, and initial substrate concentration on the dechlorination efficiency of atrazine were examined. In order to study the effect of current density, a series of 25 ppm atrazine solutions were electrolyzed in the presence of 50 mg Pd/Al_2O_3 at 5, 10, 20, 50, 100, and 200 mA. Applied currents ≥20 mA led to ≥93% loss of the initial atrazine within 30 min (Table 1, entries 1–6). At 10 mA, ECH treatment led to ~65% dechlorination, but at 5 mA dechlorination was negligible. Except for the case of the 5 mA electrolysis, the current efficiency decreased as the applied current increased, and was greatest (16%) at 10 mA (Table 1, entry 2). A decrease in current efficiency with increasing current density was also observed by Yusem and Pintauro (4) upon ECH of soybean oil. The explanation of this effect is that eq. [3], namely electrocatalytic hydrogenation or hydrogenolysis, is in competition with hydrogen evolution, eq. [6]. At high-current densities, the rate of the electrochemical generation of adsorbed hydrogen becomes faster than the rate at which the substrate can migrate to the surface and become adsorbed, eq. [2]. Consequently, a greater proportion of H_{ads} is lost to the unproductive reaction of hydrogen gas evolution, eq. [6].

The influence of catalyst concentration on the dechlorination of atrazine was investigated by employing 0, 25, 50, 100, 200, 400, and 600 mg of Pd/Al_2O_3 catalyst powder in the ECH treatment of 80 mL of a 25 ppm atrazine solution at 50 mA (Table 1, entries 4, 7–13). Catalyst concentrations of 50 mg resulted in the dechlorination of ≥96% of the initial atrazine within 30 min. The control experiment (atrazine without Pd/Al_2O_3) gave negligible reaction, further supporting ECH over the electronation–protonation mechanism. Current efficiency increased with catalyst concentration, with the exception of 600 mg, the maximum catalyst concentration investigated, and the best efficiency (7%) was obtained with a catalyst concentration of 400 mg. We suggest that increasing the amount of catalyst increases the production of *adsorbed* hydrogen (note that at constant current the overall production of hydrogen is independent of the amount of catalyst), thereby promoting hydrogenolysis. At some point, we would expect a further increase in the amount of catalyst to be unproductive, due to clogging the pores of the RVC cathode; this is presumably the explanation for the lower current efficiency observed with 600 mg of catalyst.

Fig. 2. Kinetic curves for the ECH (50 mA, 50 mg Pd/Al_2O_3) of atrazine (25 ppm).

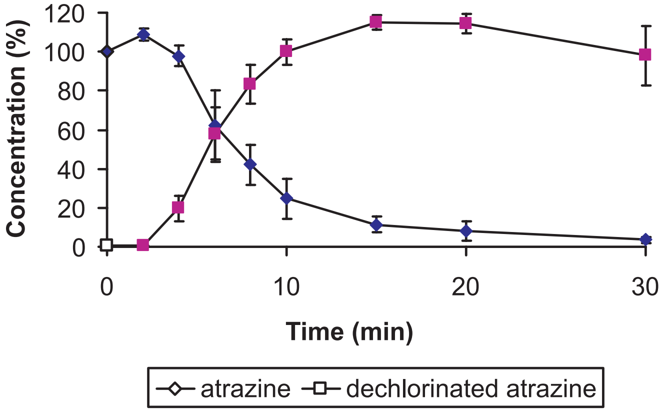


Fig. 3. Influence of constant potential on the degradation of atrazine (25 ppm) using ECH (50 mg Pd/Al_2O_3).

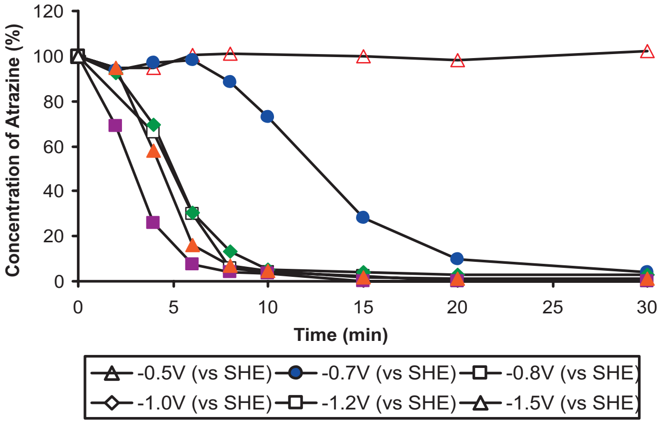


Table 1. Influence of current density, catalyst concentration, various noble-metal catalysts, and initial substrate concentration on the ECH of atrazine.

Entry	Current (mA)	Catalyst	Catalyst concentration (mg)	Initial atrazine concentration (ppm)	Current efficiency (%)[a]	Atrazine dechlorinated (%)[b]
1	5	Pd/Al_2O_3	50	25	5	7
2	10	Pd/Al_2O_3	50	25	16	64
3	20	Pd/Al_2O_3	50	25	6	93
4	50	Pd/Al_2O_3	50	25	4	97
5	100	Pd/Al_2O_3	50	25	4	98
6	200	Pd/Al_2O_3	50	25	4	100
7	50	Pd/Al_2O_3	0	25	0	0
8	50	Pd/Al_2O_3	25	25	1	62
9	50	Pd/Al_2O_3	50	25	3	97
10	50	Pd/Al_2O_3	100	25	4	96
11	50	Pd/Al_2O_3	200	25	5	100
12	50	Pd/Al_2O_3	400	25	7	100
13	50	Pd/Al_2O_3	600	25	6	100
14	20	Rh/Al_2O_3	400	25	2	28
15	20	Pt/Al_2O_3	400	25	4	31
16	20	Raney Ni	400	25	2	31
17	20	Ru/Al_2O_3	400	25	2	35
18	20	Pd/Al_2O_3	400	25	6	97
19	20	$Pd/CaCO_3$	400	25	11	97
20	20	Pd/Al_2O_3	400	4	1	98
21	20	Pd/Al_2O_3	400	83	14	85

[a] Representative experiments were run in triplicate. In these experiments, the average standard deviation was ±0.4%.
[b] Representative experiments were run in triplicate. In these experiments, the average standard deviation was ±6.3%.

The electrocatalytic properties of various noble-metal catalysts — Raney nickel; palladium, platinum, ruthenium, and rhodium on aluminia; and palladium on calcium carbonate — were investigated (Table 1, entries 14–19). Catalysts on carbon powder supports were not included in the study because atrazine rapidly and strongly adsorbed to carbon powder resulting in its removal from solution without a chemical change. Palladium was the most active ECH catalyst (Fig. 4), and current efficiencies of 11 and 6% were achieved with palladium on calcium carbonate and alumina, respectively. This result can be attributed to palladium's ability to both adsorb and absorb hydrogen (17). Similarly, Dabo et al. (18) observed that palladium catalysts offered maximum current efficiencies in the ECH of 4-phenoxyphenol. Palladized carbon felt was found to be an efficient catalyst for the dechlorination of 4-chlorophenol (19) and 2,4-dichlorophenoxyacetic acid (7–9); in the latter studies, current efficiencies for dechlorination reaction followed the sequence Pd > Rh > Ru catalysts.

The influence of the initial substrate concentration on the dechlorination of atrazine was examined using initial atrazine concentrations of 4, 25, and 83 ppm; 50 mA; and 400 mg Pd/Al_2O_3 (Table 1, entries 18, 20, 21). Within 30 min, >80% of the initial atrazine was dechlorinated. Current efficiency increased with increasing initial substrate concentration, a result that can be explained in terms of in-

Fig. 4. Influence of various noble-metal catalysts on the ECH of atrazine (400 mg of catalyst, 20 mA).

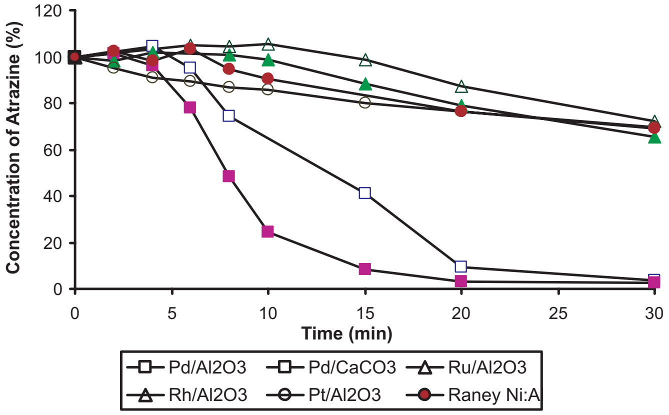
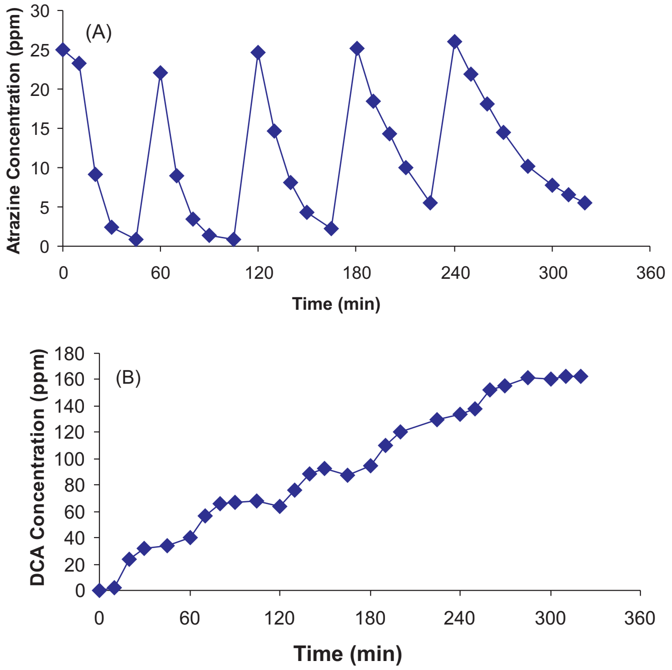


Fig. 5. Concentration of atrazine (A) and dechlorinated atrazine (B) during long-term ECH treatment (20 mA, 50 mg Pd/Al_2O_3) periodically spiked with concentrated atrazine solution.



creased adsorption of the substrate on the catalyst (eq. [2]), allowing dechlorination (eq. [3]) to compete more effectively with hydrogen evolution. Previously, Mahdavi et al. (20) found that the current efficiency for the electrocatalytic hydrogenation of cyclohexenone increased with increasing substrate concentration.

Catalyst reusability

Longevity of the catalyst is a critical parameter in any catalytic process. We investigated the reusability of Pd/A_2O_3 for the ECH of atrazine in two different experiments. In the first of these, the Pd/A_2O_3 catalyst (200 mg) was removed by filtration using glass fiber paper after an ECH experiment with 25 ppm of atrazine at 50 mA (catalyst recovery 98 ± 3%). After drying at 80°C, the recycled Pd/A_2O_3 catalyst was used for a second similar ECH experiment; 30 min of electrolysis at 50 mA gave almost complete dechlorination of the starting material, with very similar current efficiency (10% in run 2 compared with 8% in run 1).

Table 2. Current efficiencies and first-order rate constants for the loss of atrazine during long-term ECH treatments (50 mg Pd/Al_2O_3, 20 mA) periodically spiked with concentrated atrazine solution.

Hour	Maximum current efficiency (%)	Rate constant (k) (s^{-1})
1st	5	—
2nd	8	1.23
3rd	6	0.87
4th	4	0.53
5th	3	0.30

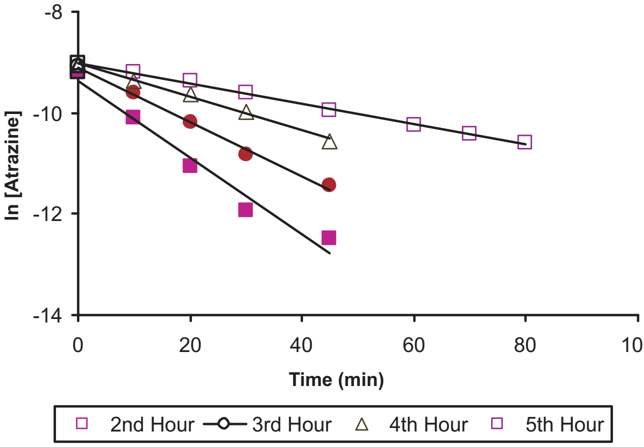
In the second experiment, involving Pd/Al_2O_3 catalyst (50 mg), the atrazine solution was electrolyzed continuously at 20 mA, but every 60 min sufficient atrazine was added to restore its concentration to the original value of 25 ppm. The small amount of catalyst for this experiment was chosen so that all of it was trapped in the pores of the RVC and none was inadvertently removed when sampling the solution for analysis. As illustrated in Fig. 5A, the concentration of atrazine rapidly decreased after each addition, although gradual loss of catalyst activity was evident. Figure 5B shows that DCA continuously accumulated in solution during the experiment, eventually reaching a concentration > 160 ppm. Maximum current efficiencies and apparent first-order rate constants for loss of atrazine are listed in Table 2. A first-order plot is illustrated in Fig. 6.

Lag time in dechlorination

The ECH reaction of atrazine, catalyzed by Pd/Al_2O_3, was characterized by a lag time that decreased with an increase of both current density and catalyst concentration (Fig. 7). The lag time (t) was inversely proportional to current density (i) for a fixed catalyst concentration, suggesting that a fixed amount of charge (Q) must pass through the solution before dechlorination of atrazine begins, i.e., $Q = it$. In support of this hypothesis, when atrazine (50 mA, 50 mg Pd/Al_2O_3) was electrolyzed with preactivation of the cathode for 5 min (the lag time observed in Fig. 7A under these conditions) before the introduction of atrazine, the lag time disappeared and the degradation of atrazine was immediate. Furthermore, the maximum current efficiency increased from 4 to 26%. Likewise, in the experiment on long-term catalyst use (Fig. 5A), a lag time was observed only with the initial solution; subsequent additions of atrazine were followed by immediate dechlorination.

We interpret the decreased lag time with higher catalyst concentration in terms of the proportion of the RVC surface that is in contact with catalyst. Since current was constant in the experiments shown in Fig. 7B, the total rate of hydrogen production was the same, but only that produced at Pd was catalytically useful. As noted already, the behaviour of Pd catalysts was unique: no lag time was observed with the other noble metals studied (although it was difficult to determine whether or not a lag time occured with Rh or Ru, because dechlorination was so slow). We therefore hypothesize

Fig. 6. Superimposed first-order kinetic curves for the degradation of atrazine each hour during long-term ECH treatment (20 mg, 50 mg Pd/Al_2O_3) periodically spiked with concentrated atrazine solution.



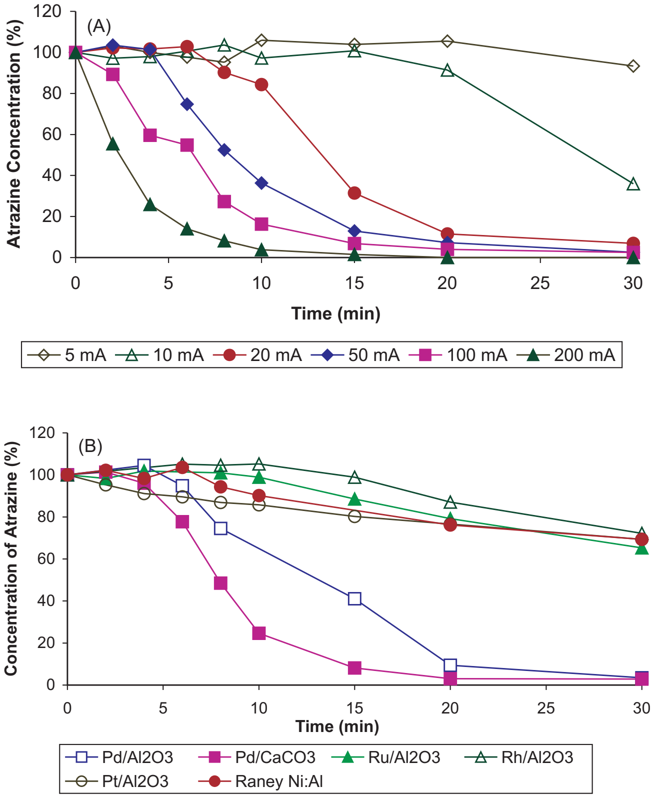
that the unique ability of palladium to both adsorb and adsorb hydrogen (17) accounts for both its superior electrocatalytic properties and the observed lag time. By analogy to a bucket filling with water and then overflowing, we propose that the palladium must first absorb the electrochemically produced hydrogen; once the palladium lattice is "full," hydrogen can be adsorbed at the palladium surface, allowing dechlorination to begin. The following calculation supports the foregoing concept. Consider the experiments in Fig. 7B involving 400 mg of catalyst. We assume that under these conditions the RVC pores are filled with catalyst and hence all the electrolytic hydrogen is formed at a Pd surface. The lag time is 3 min, which at 50 mA corresponds to Q = 9 C, or 9 × 10^{-5} mol H. The mass of Pd (5% on alumina) is 20 mg = 2 × 10^{-4} mol, i.e., mol H ~ mol Pd. This is consistent with H occupying the interstices of the Pd lattice, but not with Pd merely covering the surface of Pd particles.

In considering why the lag phenomenon had not previously been reported, we noted that most ECH reactions are characterized by reaction times on the order of several hours with samples taken every hour (8) or only at the beginning and end of the experiment (4). In our experiments, complete dechlorination was observed in 30 min and samples were taken every 2 min, making the lag effect easy to observe. Related observations have been reported by Tsyganok et al. (7), in whose dechlorination of 2,4-dichlorophenoxyacetic acid (2,4-D), the electrocatalytic activity of carbon-supported palladium was dramatically enhanced 2 h into the ECH treatment. These authors, who had also noted that preactivation of the cathode resulted in accelerated dechlorination, suggested that preactivation led to the formation of a hydrogen-saturated palladium phase and a change in spatial distribution of the supported Pd-clusters.

Conclusion

We found that electrocatalytic hydrogenolysis is an effective method of dechlorinating atrazine solutions at ppm concentrations. The method may have application to remediation, particularly of waste water streams, though it is not clear whether it has sufficient efficiency to be useful for contaminated ground water. The reaction product, DCA, is formed in quantitative yield. The DCA molecule still retains the *s*-triazine moiety, and it is not clear whether this reaction product will be a photosynthesis inhibitor like the parent molecule. Plant bioassays on the electrolyzed solutions of atrazine are in progress and will be reported separately.

Fig. 7. Occurrence of lag time in the degradation of atrazine. Influence of current density (50 mg Pd/Al_2O_3) (A) and catalyst concentration (50 mA) (B).



Acknowledgments

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