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Electrochemical waste water treatment: Electrooxidation of acetaminophen

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Abstract

Oxidation of acetaminophen at boron-doped diamond (BDD) and at Ti/SnO_2 anodes in a plug-flow divided electrochemical reactor led to electrochemical combustion, whereas at Ti/IrO_2 benzoquinone was the exclusive product except at very long electrolysis times. The difference is explicable in terms of the different mechanisms of oxidation: direct oxidation at the anode for Ti/IrO_2 vs. indirect oxidation involving electrogenerated hydroxyl radicals at BDD and Ti/SnO_2. At BDD, at which the efficiency of degradation of acetaminophen was greatest, the rate of electrolysis at constant concentration was linearly dependent on the current, and at constant current linearly dependent on the concentration. Current efficiencies for mineralization up to 26% were achieved without optimization of the cell design.

1. Introduction

Pharmaceutical compounds have recently been identified as contaminants in sewage effluents [1–5], surface and groundwater [6–13], and even drinking water [14–16]. Concern exists about the possible implications for pharmaceuticals becoming distributed in the environment on grounds both of toxicity and, in the case of antibiotics, of the development of resistant strains of microorganisms [4, 9, 15, 17–19]. Contamination can arise from many sources, including excretion of ingested pharmaceuticals, improper disposal at the consumer level, intensive animal husbandry, and inadequate treatment of manufacturing waste [18, 20].

Widespread contamination only occurs when the substances of concern are rather recalcitrant towards degradation (e.g. in secondary sewage treatment). This has led to an intensive search for methods of chemical degradation, using oxidants such as sodium hypochlorite, hydrogen peroxide, and Fenton reagent (Fe^{2+}/H_2O_2) [21, 22], as well as so-called "Advanced Oxidation Processes" using reagents such as O_3, O_3/H_2O_2, H_2O_2/UV and $H_2O_2/Fe^{2+}/UV$ [23–28].

The subject of the present investigation is acetaminophen (also known as paracetamol or *N*-(*p*-hydroxyphenyl)-acetamide), which has been found in sewage effluents at concentrations up to 6.0 $\mu g\ l^{-1}$ [1]. This compound may also enter the environment from manufacturing wastes [29]. An unusual source of contamination in Guam has been reported through its use in control of poisonous tree snakes [30].

Andreozzi et al. [31] oxidized acetaminophen using ozonation or photolysis of hydrogen peroxide, both of which achieved complete removal of the substrate as well as partial mineralization: 30% for ozonation and 40% for H_2O_2 photolysis. Ozonolysis at the aromatic ring led to the formation of hydrogen peroxide and aliphatic acids, such as glyoxylic, oxalic, and formic acids. The peroxide/UV system gave hydroquinone and 2-hydroxy-4-(*N*-acetyl)-aminophenol as intermediates; further oxidation gave several products, including (from hydroquinone) 1,2,4-trihydroxybenzene and a mixture of oxalic, malonic, and succinic acids. Vogna et al. [32] used GC-MS and ^{15}N NMR to track the nitrogenous products of UV/H_2O_2 oxidation of acetaminophen, among them 4-acetylaminocatechol and acetamide.

Sirés et al. [33] recently studied acetaminophen mineralization at pH 3, using electrochemical variants of Fenton and photo-Fenton chemistry in which hydrogen peroxide was generated by reduction of O_2 at a gas-diffusion carbon-PTFE cathode. Although hydroxyl radicals were formed to some extent at the Pt counter electrode, it was more efficient in practice to add Fe^{2+} to the solution as in conventional Fenton chemistry.

A drawback to the use of iron salts was resistance to degradation of the iron complexes of aliphatic carboxylic acids formed as intermediates, and no better than 76% mineralization, based on total organic carbon (TOC) remaining in solution, could be achieved. This limitation was overcome by using Cu^{2+} in place of, or in combination with, Fe^{2+}; the combination of electrolysis, added copper salts, and UV-A radiation afforded almost complete loss of TOC from the solution.

Our own work on electrochemical oxidation of acetaminophen has taken a different approach. Instead of producing OH radicals through catalytic breakdown of hydrogen peroxide formed at the cathode, we have relied on electrode materials that produce OH radicals at the anode by oxidation of water. These results are reported below.

2. Experimental details

2.1. *Materials*

Acetaminophen (4-acetamidophenol, 98%) was supplied by Sigma-Aldrich (Oakville, ON); sodium sulphate used as supporting electrolyte was supplied by Fisher Scientific Company (Toronto, ON). Solutions were prepared using water from a Millipore Milli-Q Reagent Water System having resistivity not less than 10 MΩ cm.

The anodes used were a boron doped diamond electrode (BDD), supplied by Swiss Center for Electronics and Microtechnology, Inc., Neuchâtel, a dimensionally stabilized anode (DSA) made of Ti coated with IrO_2, and a DSA made of Ti coated with SnO_2, both supplied by ELTECH Systems Corporation, Painesville, OH. A nickel plate (Sigma-Aldrich) was used as the cathode. DuPont Nafion-424 cation exchange membrane was purchased from Electrosynthesis Company (Lancaster, NY).

2.2. *Apparatus*

Electrolyses were performed with a home-built Plexiglas electrochemical reactor that consisted of two compartments each having dimensions 58 mm × 15 mm × 4.5 mm, separated by a Nafion-424 cation exchange membrane. The outer dimensions of all electrodes were 50×15 mm. The cell was operated with the electrodes held vertically, to allow the escape of gases evolved during electrolysis. Pieces of Pt wire (Sigma-Aldrich) were used as electrode feeders. Power to the electrochemical reactor was supplied by an EG&G Model 363 Potentiostat/Galvanostat.

2.3. *Experimental procedures*

The reactor was operated in plug flow mode, with separate solutions passed through the anode and cathode compartments at equal flow rates of 0.5–1.5 ml min^{-1}, using a Masterflex C/L peristaltic pump. The anolyte (50 ml) was a 0.5–2.0 mM solution of acetaminophen in water, with 0.025 M Na_2SO_4 as supporting electrolyte; in most experiments the anolyte was recirculated into a reservoir of capacity 100 ml. The catholyte was 0.05 M Na_2SO_4 which was passed only once through the reactor. All electrolyses were run galvanostatically in unbuffered solutions at currents of 100–800 mA. Total electrolysis times ranged from 200 to 400 min.

HPLC analyses employed a Waters 600E system, equipped with a Model 486 variable wavelength UV–Visible detector set at 254 nm and a reverse-phase Waters Spherisorb column 4.6×250 mm, equipped with a silica pre-column guard. Acetonitrile:water (30:70) filtered through a 0.2 μm filter was used as mobile phase at flow rates of 0.5–1.5 ml min^{-1}. Calibration samples and electrolysis samples were manually injected with a 25 μl syringe into a 5 μl sample loop of a Rheodyne injector. Analyses were performed in duplicate and evaluated using Millennium® Version 3.20 software. TOC was analysed with a Shimadzu TOC analyser, model TOC-VCSH.

3. Results and discussion

Figure 1 shows the disappearance of acetaminophen using the divided cell plug-flow reactor in recirculation mode with different anode materials: Ti/IrO_2, Ti/SnO_2, and BDD. During electrolysis the pH of the solution dropped from the initial value of pH 7.8, as a result of the oxidation of both substrate and water, reaching values near pH 1.4 at all three anodes at sufficiently long electrolysis times. The reaction followed pseudo-first

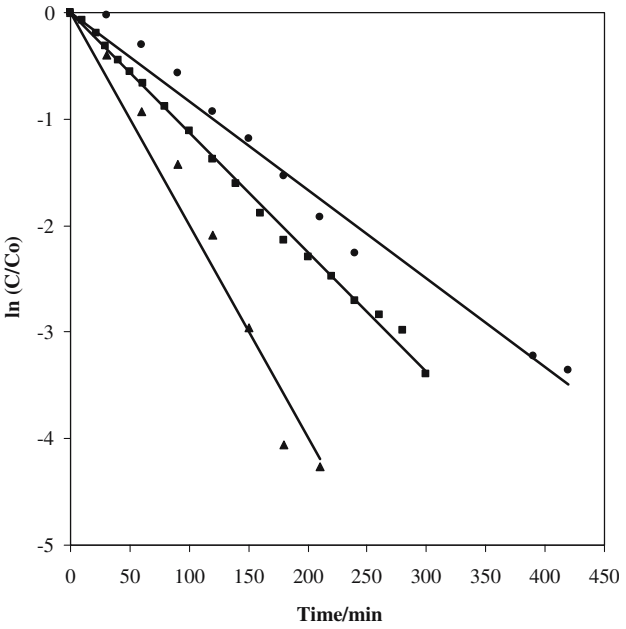


Fig. 1. Comparison of rates of degradation of acetaminophen at BDD, Ti/IrO_2, and Ti/SnO_2 anodes in a divided plug-flow reactor. Initial concentrations ~1 mM; flow rates 1 ml min^{-1}; applied current 500 mA; recirculation mode. ▲ = BDD; ■ = Ti/IrO_2; ● = Ti/SnO_2.

order kinetics at all three anodes, irrespective of flow rate, current, and substrate concentration. At a flow rate of 1 ml min^{-1} and applied current of 500 mA, the apparent first order rate constants were $k(BDD) = 0.0218 \pm 0.0013$, $k(Ti/SnO_2) = 0.0087 \pm 0.0004$ and $k(Ti/IrO_2) = 0.0112 \pm 0.0001$ min^{-1}.

The similarities in the apparent rate constants mask significant differences in behaviour, as shown by analysis of a solution initially having TOC = 116 mg l^{-1}. All TOC measurements were taken after 210 min electrolysis at a flow rate of 1 ml min^{-1}. At BDD, most of the starting material was mineralized, residual TOC = 31 mg l^{-1} at 200 mA and 20 mg l^{-1} at 500 mA. At Ti/IrO_2, almost all the TOC remained in solution after 210 min, and the corresponding TOC values were 115 and 111 mg l^{-1}. Ti/SnO_2 displayed intermediate behaviour with the corresponding TOC values 70 and 63 mg l^{-1}. Another difference was that at BDD and Ti/SnO_2, HPLC analysis showed no evidence of intermediates or products having absorption near 254 nm. In contrast, at Ti/IrO_2 the disappearance of starting material was mirrored by the appearance of a single strongly absorbing product having retention time 5.6 min. Initially it was hypothesized that this might be the hydroxylation product 4-acetylaminocatechol, but synthesis of the latter compound by the method of Vogna et al. [28] showed it to have completely different HPLC retention characteristics. The retention time and UV–Visible absorption spectrum of the product were found to be identical to those of *p*-benzoquinone. Independent experiments under the same conditions confirmed that benzoquinone, which is highly resistant to oxidation [34], disappeared with a rate constant 0.0009 min^{-1}, more than an order of magnitude less than its rate constant for formation from acetaminophen. Consequently, at Ti/IrO_2 benzoquinone is sufficiently stable to be observed as a moderately long-lived intermediate.

Figure 2 shows the disappearance of acetaminophen and the appearance of benzoquinone at a Ti/IrO_2 anode, with applied current 200 mA. These data are fitted with $k(-AP) = k(+BQ) = 0.0087$ min^{-1} and a chemical yield of benzoquinone (BQ) = 8%, consistent with the relative rate constants for loss of acetaminophen and benzoquinone. Similar curves were obtained at 500 and 800 mA: e.g., at 800 mA $k(-AP) = k(+BQ) = 0.014$ min^{-1} and the yield of benzoquinone was again 88%. At the longest times studied, the yields of benzoquinone declined on account of its further reaction, as noted above.

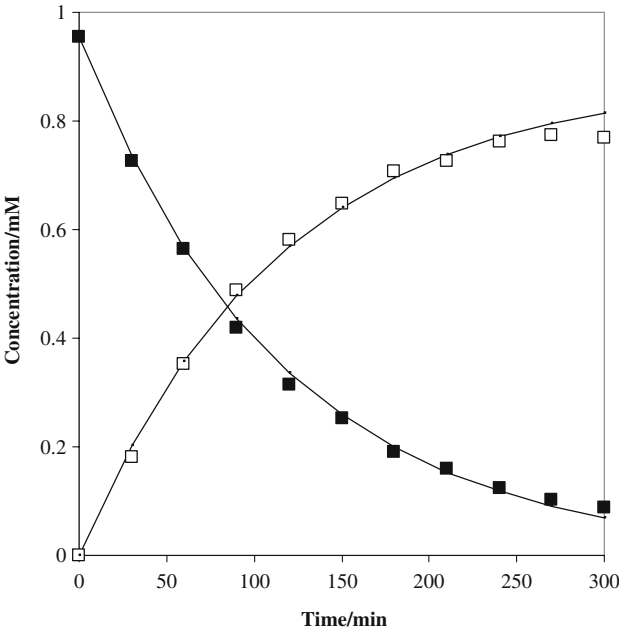
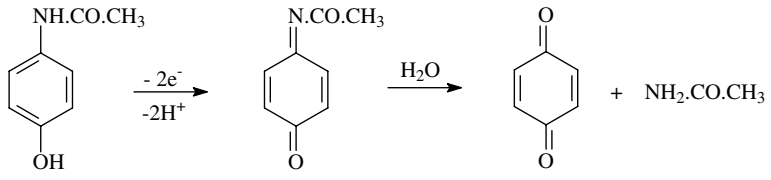


Fig. 2. Disappearance of acetaminophen and appearance of *p*-benzoquinone using a Ti/IrO_2 anode in a divided plug-flow reactor. Initial concentration 0.95 mM; flow rate 1 ml min^{-1}; applied current 200 mA; recirculation mode. ■ = Acetaminophen; □ = *p*-Benzoquinone.

The foregoing results are explicable in terms of the behaviour of the different electrodes under anodic polarization. BDD and Ti/SnO_2 are characterized as anodes at which water hydrolysis affords initially adsorbed hydroxyl radicals [35–37]. Oxidation of the substrate therefore occurs by attack of hydroxyl radicals, any intermediate products formed are themselves susceptible to oxidative attack. Consequently the ultimate outcome of the reaction is mineralization, by way of small aliphatic acids as intermediates [33]. By contrast, Ti/IrO_2 functions by the "higher oxide" mechanism, in which the substrate is oxidized at the electrode by surface-bound Ti/IrO_x species [35]. The mechanism of chemical oxidation of acetaminophen involves formation of the quinonemethide *N*-acetyl-*p*-benzoquinoneimine, which is unstable with respect to hydrolysis to benzoquinone and acetamide – the latter previously reported by Vogna et al. [28] – in the increasingly acidic environment formed as the electrolysis proceeds.



The foregoing explanation is consistent with cyclic voltammetry studies on acetaminophen at a carbon paste electrode. In a solution buffered at pH 6, acetaminophen underwent a reversible two-electron oxidation at

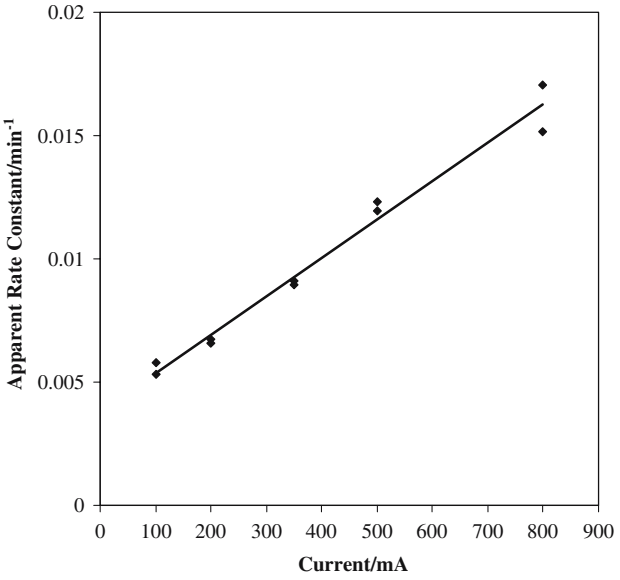


Fig. 3. Variation with current of the apparent rate constant for disappearance of acetaminophen at a BDD anode in a divided plug-flow reactor. Initial concentration 1.0 mM; flow rate 1 ml min^{-1}; recirculation mode.

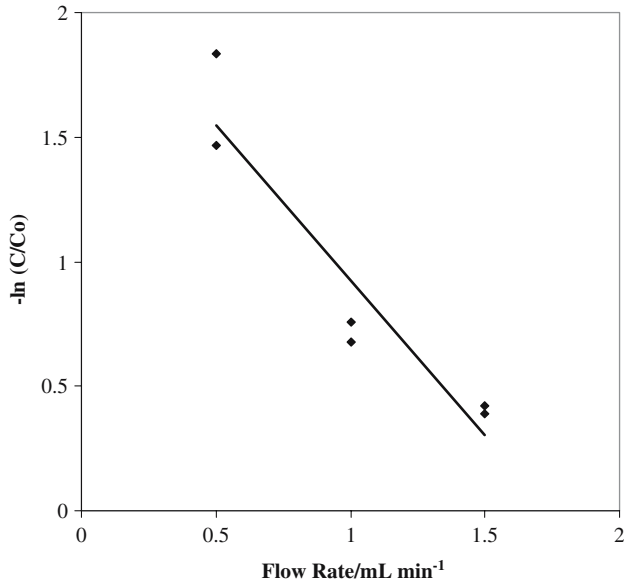


Fig. 4. Variation with flow rate of the rate of disappearance of acetaminophen at a BDD anode in a divided plug-flow reactor. Initial concentration 1.0 mM; applied current 500 mA; single-pass mode.

$\sim +0.6$ V vs. Ag/AgCl to give *N*-acetyl-*p*-benzoquinoneimine, which was stable on the time-scale of the CV experiment at pH 6, but which hydrolysed to *p*-benzoquinone at more acidic pH values [38, 39]. In our work, however, no oxidation wave was observed in a cyclic voltammetry study of acetaminophen at either BDD or Ti/IrO_2 – although Wangfuengkanaul and Chailapakul [40] did succeed in observing an oxidation peak near $+0.6$ V vs. Ag/AgCl in phosphate buffer at pH 8 using a thin-film BDD anode.

Most of our subsequent electrolyses employed the BDD anode. In recirculation mode the rate constant (as opposed to the raw rate) for loss of acetaminophen was almost independent of initial concentration, consistent with a process that is first order in acetaminophen. The value of k(obs) was 0.0203 ± 0.0023 min^{-1} over 10 experiments covering the concentration range 0.5, 1.0, 2.0 mM, at constant flow rate of 1 ml/min and applied current 500 mA. However, Figure 3 shows that the pseudo first order rate constant depends almost linearly on the applied current, at a constant flow rate of 1 ml min^{-1} and concentration of 1.0 mM. These data are consistent with a bimolecular reaction between acetaminophen and OH radicals, with the steady state concentration of OH radicals, which are formed by electrolysis of water, being approximately proportional to the applied current over the current range investigated in Figure 3.

When the plug-flow reactor was operated in recirculation mode there was almost no dependence of the apparent rate of loss of acetaminophen on flow rate (concentration 1.0 mM, current 500 mA). This is an artefact of operating the reactor in recirculation mode; the extent of reaction in a given passage through the reactor was small, and the effluent then remixed with the higher concentration of acetaminophen in the reservoir. In these experiments the residence time of the solution in the reactor (2–8 min) was short compared with the overall electrolysis time (200–300 min). The true effect of flow rate was observed when the reactor was operated in single-pass mode, as seen in Figure 4, which shows how the concentration of acetaminophen exiting the reactor varied with flow rate (initial concentration 1.0 mM, current 500 mA). As expected, the loss of acetaminophen, in terms of concentration change, upon passage through the reactor decreased with increasing flow rate and hence shorter residence time.

Calculations on current efficiency were based on the electrolysis of a 1.0 mM solution of acetaminophen. In the case of electrolysis at Ti/IrO_2 the stoichiometry is straight forward: oxidation is a two-electron change.

$$CH_3C(=O)\cdot NH\cdot C_6H_4\cdot OH \rightarrow CH_3C(=O)\cdot N{=}C_6H_4{=}O + 2H^+ + 2e^-$$

$$CH_3C(=O)\cdot N{=}C_6H_4{=}O + H_2O \rightarrow O{=}C_6H_4{=}O + CH_3C(=O)\cdot NH_2$$

At the earliest time point (10 min, $i = 500$ mA), 0.08 mmol l^{-1} (4×10^{-6} mol) of acetaminophen had been oxidized, and the current efficiency was only 0.25%.

At both BDD and Ti/SnO_2 the calculation had to be carried out on the basis of the TOC measurements, because electro-oxidation involves mineralization. If there is complete mineralization we have a 23-electron change:

$$C_8H_9NO_2 + 14H_2O \rightarrow 8CO_2 + 0.5N_2 + 23H^+ + 23e^-$$

At the time point of 210 min, essentially all the starting material had disappeared, although the solution

still had appreciable TOC. At a current of 200 mA, the loss of TOC was 46 mg l^{-1} in the case of Ti/SnO_2 and 86 mg l^{-1} in the case of BDD. Hence, the approximate current efficiencies were 14% in the case of Ti/SnO_2 and 26% in the case of BDD, in both cases assuming that the residual TOC was due to unreacted starting material. Since this is not the case – the residual TOC comprised a complex mixture of partly oxidized products rather than unreacted substrate – these values are underestimated. Presumably also, even higher current efficiencies could be attained near the beginning of the reaction, when relatively more hydroxyl radicals can react with substrate or intermediate products, compared with the situation later in the reaction when these have been depleted, and evolution of O_2 is favoured.

We note also that the foregoing current efficiencies are not exactly comparable, because the Ti/SnO_2 electrode was a grid whereas the BDD electrode was a flat plate. The Ti/SnO_2 anode therefore experienced a higher current density than the BDD; the comparison of residual TOC at 200 and 500 mA applied current given earlier shows clearly that the current efficiency decreases with increasing current density (due to more efficient combination of OH radicals to afford O_2).

The high apparent current efficiencies at Ti/SnO_2 and BDD are possible because these are radical chain reactions: the introduction of one hydroxyl radical into the solution leads to a cascade of autoxidation processes, some of which involve addition of carbon-centred radicals to the co-product O_2. The purely faradaic contribution to the current efficiency through formation of OH radicals is therefore much lower than the apparent overall current efficiency, but is not easily elucidated.

Finally, it should be noted that acetaminophen is a phenolic compound. Phenols are notoriously difficult to oxidize electrochemically, due to anode fouling caused by the deposition of insoluble polymeric material [41, 42]. However, recent work has demonstrated that mineralization of simple phenols is possible at electrodes that function mechanistically by production of hydroxyl radicals. For example, Feng and Li [43] found that phenol could be mineralized at Ti/PbO_2 but not at various doped Ti/RuO_2 anodes. Tahar and Savall [44] mineralized phenol at Bi-doped PbO_2 on a Ti-metal oxide base; Borras et al. [45] oxidized *p*-substituted phenols, also at Bi-doped PbO_2, and found that although mineralization occurred, oxidation of the intermediate benzoquinone was the slow step of the overall process, a result comparable to the present findings. Of closest relevance to the present study, phenol was shown to be oxidizable at BDD [37]; in the potential region of water stability an electrode-fouling film was formed, but in the potential region of water decomposition oxidation of the substrate occurred by way of reactive intermediates (subsequently shown to be hydroxyl radicals formed at the surface of BDD [46]) and fouling did not occur [47].

Phenols substituted with *o*- and *p*-electron-donating groups are oxidizable electrochemically even at active electrodes such as platinum [48]. This effect is especially marked in the case of the aminophenols: the *p*-isomer oxidized smoothly to hydroquinone/benzoquinone, the *o*-isomer gave a conducting polymer, and the *m*-isomer gave a non-conductive polymer that fouled the electrode [49]. As the *N*-acetyl derivative of *p*-aminophenol, acetaminophen displays behaviour intermediate between that of *p*-aminophenol and the parent compound phenol.

4. Conclusion

Acetaminophen was mineralized with high efficiency at anodes (BDD and Ti/SnO_2) that function mechanistically by generating hydroxyl radicals. Although our simple flow-through cells use planar electrodes that are not optimally configured for mass transfer, the fact that hydroxyl radical attack initiates a radical chain mechanism of oxidation alleviates the need for every substrate molecule to approach the anode surface directly. Presumably a more sophisticated cell design would improve these current efficiencies further. By contrast, at Ti/IrO_2, which functions by direct oxidation at the electrode surface, the current efficiency is low. In addition at Ti/IrO_2, acetaminophen is only partly degraded (to benzoquinone) rather than fully mineralized.

In this work, acetaminophen has been used as a model compound for the destruction of pharmaceutical industry wastes. The results make clear that high efficiency can only be anticipated by using anodes that function indirectly, by production of reactive intermediates such as hydroxyl radicals. Furthermore, since the rate of mineralization depends linearly on substrate concentration, the electrochemical method will be best suited to relatively high strength wastes, and not to the very low concentrations typical of incompletely degraded sewage effluents. At the present time, BDD, our most efficient anode material, is too expensive and probably insufficiently rugged to be considered for long-term industrial use. Further work in our laboratory is directed towards development and investigation of anode materials that surmount these limitations.

Acknowledgements

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