Electrochemical waste water treatment: Electrooxidation of acetaminophen

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Received 30 November 2004; accepted in revised form 24 August 2005

Key words: acetaminophen (paracetamol), benzoquinone, boron-doped diamond anode, dimensionally stable anodes, electrochemical combustion

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$_2$O$_2$) [21, 22], as well as so-called “Advanced Oxidation Processes” using reagents such as O$_3$, O$_3$/H$_2$O$_2$, H$_2$O$_2$/UV and H$_2$O$_2$/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$_2$O$_2$ 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$_2$O$_2$ 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 M\(\Omega\) 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 \(\times\) 15 mm \(\times\) 4.5 mm, separated by a Nafion-424 cation exchange membrane. The outer dimensions of all electrodes were 50 \(\times\) 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\(_2\)SO\(_4\) as supporting electrolyte; in most experiments the anolyte was recirculated into a reservoir of capacity 100 ml. The catholyte was 0.05 M Na\(_2\)SO\(_4\) 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 \(\mu\)m 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 \(\mu\)l syringe into a 5 \(\mu\)l sample loop of a Rheodyne injector. Analyses were performed in duplicate and evaluated using Millennium\textsuperscript{\copyright} Version 3.20 software.

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