Electrochemical Decomposition of Bisphenol A and Nonylphenol Using a Pt/Ti Electrode

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The electrochemical decomposition of bisphenol A and nonylphenol, which may serve as environmental endocrine disrupters, was studied by using a platinum coated titanium anode. These substances were electrochemically decomposed via a series of intermediates. The measurement of total organic carbon in a solution of bisphenol A or nonylphenol after electrochemical decomposition showed that these substances could be decomposed to CO_2.

At present, a wide variety of industrial waste chemicals are being emitted into the environments. Some of these substances may possibly serve as environmental endocrine disrupters (EDCs). In particular, bisphenol A, a material involved in the production of plastics, and nonylphenol, a biologically decomposition product of surface-active reagents have been found to be widely distributed in the environment, as well as in surface water.[1] Therefore, the development of environmental remediation techniques to decompose these pollutants is needed. Generally, wastewater, which contains organic pollutants, and cannot be easily treated by aerobic biological action, is treated by chemical oxidation. Chemical oxidation methods allow the oxidative decomposition of many organic pollutants but not complete elimination of total organic carbon (TOC) in wastewater, that is, it is difficult to decompose these compounds to carbon dioxide. In addition, these methods require large amounts of harmful reagents in many cases. On the other hand, the electrochemical decomposition of phenol using a platinum electrode has been shown to be more efficient for the removal of TOC than that of chemical oxidation.[2-5] This electrochemical method has some advantages, in that it is not necessary to use harmful reagents and that it has high efficiency for mineralization to CO_2.

In this study, the electrochemical decomposition of bisphenol A and nonylphenol using a platinum coated titanium (Pt/Ti) electrode was examined. By monitoring the amounts of TOC present, it could be confilmed that these compounds were decomposed electrochemically to CO_2.

The electrochemical decomposition was carried out by a potentiostat/galvanostat HA-501 (Hokuto Denko Ltd.) under the constant current at 0.3 A. A mesh cylinder titanium coated with platinum (4 cm diameter) was used as a working electrode, a platinum wire enclosed in a porous glass pot as a counter electrode and a Ag|AgCl electrode as a reference electrode. The electrolyte solution containing 1.0 mM bisphenol A or nonylphenol, was prepared with 0.1 M Na_2SO_4, and the pH was adjusted with 0.1 M H_2SO_4 and NaOH at pH 3 or 13, respectively. The amounts of bisphenol A or nonylphenol in the solution during electrolysis were monitored by HPLC (Hitachi L with UV detector). The decrease of TOC in the solution during the electrochemical decomposition was measured by a TOC-5000 total organic carbon analyzer (Shimadzu Co.).

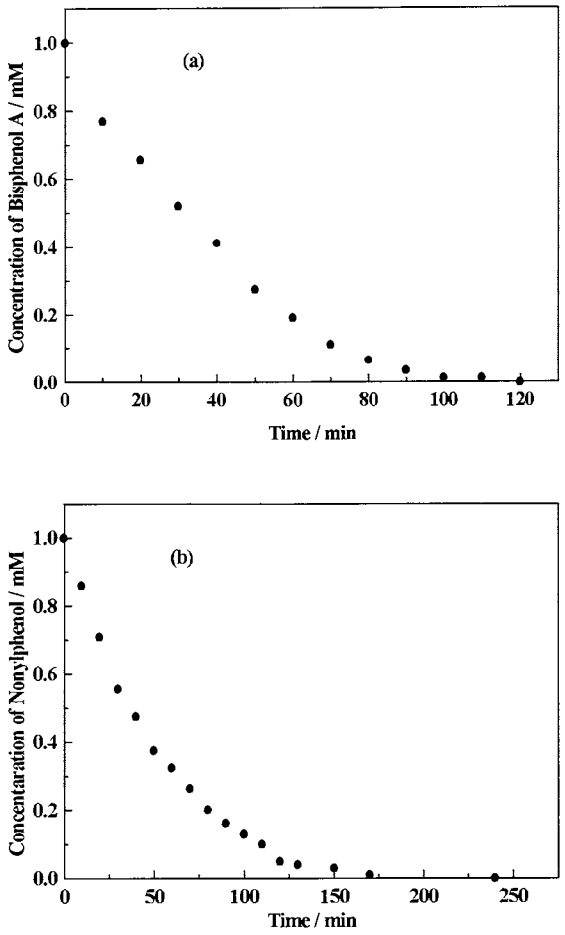

Figure 1. Electrochemical decomposition of (a) bisphenol A (1.0 mM) at pH 3.0, and (b) nonylphenol (1.0 mM) at pH 13.0 in 0.1 M Na_2SO_4 at a Pt/Ti anode as a function time (I=0.3 A).

Figure 1 shows the relationship between the concentration of bisphenol A or nonylphenol and electrochemical decomposition time. The complete elimination of 1.0 mM bisphenol A and nonylphenol was achieved by electrochemical decomposition for 120 and 240 min, respectively. UV and IR spectra at the early stages of the electrolysis indicated the formation of various aromatic intermediates such as hydroquinone, catechol, and benzoquinone derivatives, including bisphenol A. When the electrochemical decomposition of bisphenol A and nonylphenol were performed for 15 and 8 h, respectively, the presence of tartaric acid and citric acid, in addition to bisphenol A, and tartaric acid, in addition to nonylphenol could be confirmed by HPLC.

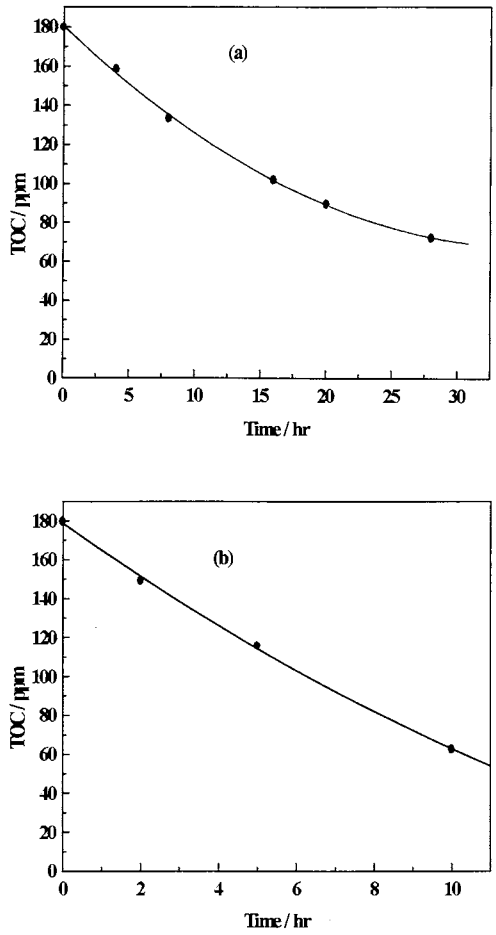

Figure 2. Electrochemical degradation of (a) bisphenol A (at pH 3.0), and (b) nonylphenol (at pH 13.0) at a Pt/Ti anode as a function of time. Both compounds present at an initial concentration of 1 mM in 0.1 M Na_2SO_4 solution.

Figure 2 shows TOC removal from the solution of bisphenol A or nonylphenol by electrochemical decomposition. In both cases, the TOC value clearly decreased with an increase in the electrolysis time. This suggests that organic carbon was electrodecomposed to CO_2 and that it was released outside the electrochemical cell.[6,7] The removal of about 50% in the bisphenol A solution and the nonylphenol solution was achieved for reaction times of 20 and 10 h, respectively. The complete decomposition of the compounds required an extended reaction time. In this method using the Pt/Ti electrode, it is shown that bisphenol A is converted to intermediates faster than nonylphenol, but that the decomposition of the intermediates to CO_2 by electrolysis is slower than that of nonylphenol. The Pt/Ti electrode did not show evidence of a decrease in activity for the electrochemical decomposition of bisphenol A and nonylphenol, even when used up to fifty times. Although the mechanism of these electrochemical decomposition reactions is very complex, it is thought to proceed mainly by two paths in a manner similar to phenol.[3,6-8] In the first path, organic pollutants such as bisphenol A and nonylphenol are directly oxidized at the electrode surface and decomposed to aliphatic acids. Second, the organic pollutants are indirectly oxidized to CO_2 by hydroxyl radicals, which are produced by the electrochemical oxidation of water at the electrode surface.

In order to achieve an effective electrochemical decomposition of bisphenol A and nonylphenol, we are now investigating the electrochemical decomposition using SnO_2 coated on a Ti electrode, as well as the detailed electrode reaction mechanism. In the case of the SnO_2 electrode, the complete decomposition of bisphenol A and nonylphenol to CO_2 was achieved in about 5 and 8 h, respectively.

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References and Notes

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