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Electrochemical decomposition of bisphenol A using Pt/Ti and SnO_2/Ti anodes

S. TANAKA[1]*, Y. NAKATA[1], T. KIMURA[1], YUSTIAWATI[1], M. KAWASAKI[2] and H. KURAMITZ[1]
[1]*Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, Hokkaido, 060-0810, Japan*
[2]*National Institute of Advanced Industrial Science and Technology (AIST), Onogawa, Tsukuba, 305-8569, Japan*
*(*author for correspondence, fax: +81 11 706 2219, e-mail: shunitz@ees.hokudai.ac.jp)*

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Abstract

Methodology for the electrochemical decomposition of bisphenol A is described. The electrochemical behaviour of bisphenol A at a Pt electrode was investigated by means of cyclic voltammetric techniques. The electrochemical oxidation of bisphenol A led to the deactivation of the electrode as a result of the deposition of an electropolymerized film. However the electrochemical decomposition of bisphenol A could be achieved by the use of a platinum coated titanium (Pt/Ti) electrode and a tin dioxide coated (SnO_2/Ti) electrode. The electrolysis was carried out galvanostatically at a constant current of 0.3 A. The mineralization of bisphenol A was monitored by determining the amount of total organic carbon. Furthermore, the generation and nature of intermediates produced in the electrochemical reactions was investigated. Although large amounts of aliphatic acids were generated by electrolysis with the Pt/Ti anode, they were produced only to a small extent in at the SnO_2/Ti anode. In the case of the SnO_2/Ti anode, bisphenol A is rapidly oxidized to carbon dioxide and water, compared to the Pt/Ti anode.

1. Introduction

It is well-known that 2,2′-bis(4′-hydroxyphenyl) propane (bisphenol A) has estrogenic activity [1], that is, it serves as an endocrine disrupting chemical. However, bisphenol A continues to be used as a raw material in the production of polycarbonate and epoxy resins. The purification of wastewater containing phenolic compounds is a longstanding problem owing to the low rate of biodegradation and high toxicity of such phenol derivatives. Therefore, a variety of treatment techniques for wastewater which contains phenol or chlorinated phenols have been considered, using chemical [2, 3], biological [4], photochemical [5, 6], or electrochemical [7–11] procedures. However, only a few reports have appeared on the treatment of wastewater containing bisphenol A [12–15].

The application of electrochemical methods to the removal of organic pollutants has certain advantages compared with chemical or biological procedures. Biological methods are frequently subject to inhibition by highly toxic pollutants and are temperature dependent. Furthermore, it is difficult to completely eliminate total organic carbon (TOC) in wastewater, that is, pollutants cannot be decomposed to carbon dioxide and water. Chemical and electrochemical methods can achieve the mineralization of organic compounds. However, chemical oxidation and its hybrid methods require large amounts of reactive chemicals, for example, hydrogen peroxide, chlorine dioxide or ozone. Electrochemical methods have little or no harmful effects to the environment, because they do not require such harmful reagents. Moreover, electrochemical reactions are more or less independent of conditions such as toxicity or temperature, and can proceed so long as electrical current is supplied to the electrode.

Platinum and dimensionally stable anodes (DSA), which are typically prepared by the thermal deposition of a thin layer of a metal oxide (e.g., SnO_2, PbO_2 or IrO_2) on a base metal, have been used for the oxidation of various organic pollutants, notably phenol [8–11]. The goal of these methods is the efficient mineralization of organic pollutants by taking advantage of the reactivity of hydroxyl radicals, which are generated by the electrochemical oxidation of water on the electrode surface. In a previous study, we reported the electrochemical decomposition of bisphenol A and *p*-nonylphenol using a Pt/Ti anode [13].

This paper reports an investigation of the electrochemical behaviour of bisphenol A on a Pt electrode by voltammetric techniques in order to better understand the electrochemical oxidation of bisphenol A. The electrochemical decomposition of bisphenol A was demonstrated using a SnO_2/Ti electrode and a Pt/Ti anode. The nature of the oxidation intermediates during the electrolysis was investigated. The extent of electrochemical mineralization of bisphenol A was evaluated by monitoring the amounts of TOC present.

2. Experimental details

Voltammetric measurements were performed in unstirred solutions using a CV-50W Voltammetric Analyzer (Bioanalytical Systems Inc. (BAS)). A platinum disc electrode (1.6 mm dia., BAS) was used as working electrode. Prior to the measurements, the electrode was polished with 0.3, 0.05 μm alumina powder, and then cleaned ultrasonically for 3 min. A platinum wire was used as counter electrode and all potentials were recorded against an Ag/AgCl electrode (BAS). 1.0 mM bisphenol A in 0.1 M Na_2SO_4 was used as a stock solution, the concentration of bisphenol A was determined from the TOC value (TOC-5000, Shimadzu). A sodium sulfate electrolyte solution was prepared with 0.1 M Na_2SO_4 and pH adjustment was carried out using H_2SO_4 or NaOH.

A 0.1 M sodium sulfate solution (50 cm^3) containing 0.1 M bisphenol A was treated galvanostatically under a constant current at 0.3 A (potentiostat/galvanostat HA-501, Hokuto Denko). The cell was equipped with a magnetic stirrer and a water bath to maintain the mixing and a constant temperature at 20 °C. The mesh cylinder type Pt/Ti and SnO_2/Ti electrode with diameter of 3 cm, height of 4 cm was used as a working electrode. The Pt/Ti and titanium electrode were purchased from Tanaka Kikinzoku Kogyo. The SnO_2/Ti electrode was prepared as follows. A potential of −0.5 V was applied to the mesh cylinder titanium electrode for 10 min in 0.1 M hydrochloride solution containing 10 mM stannous sulfate, in order to deposit the tin electrochemically. After drying at room temperature, the electrode was annealed at 600 °C for 4 h in air in a muffle furnace (Isuzu Seisakusho, AT S-13). A coiled platinum wire, as a counter electrode, was inserted in a Vicor glass tube, which was isolated from the anodic sample solution. An Ag/AgCl electrode was used as a reference electrode.

The progress of the electrochemical decomposition of bisphenol A was monitored by HPLC; L-6000 Pump and L-4200 UV-VIS Detector (225 nm, u.v. wavelength, Hitachi) with an Inertsil PH column (150 mm × 4.6 mm i.d., GL Science). The mobile phase was methanol-water (7:3) and the flow rate was 1.0 ml min^{-1}. Analysis of organic acids, which were produced as intermediates was carried using the same HPLC system (210 nm u.v. wavelength) with a RSpak DE-413 column (150 mm × 4.6 mm i.d., Shodex) and a RSpak DE-G guard column (4.6 mm i.d., Shodex). 10 mM phosphoric acid was used as the eluent and the flow rate was 1.0 ml min^{-1}. Aromatic electrolysis intermediates were identified by GC-MS (GC-17A and GCMS-QP5050A, Shimadzu) with a DB-5MS column (30 m × 0.25 mm i.d., J&W Scientific). The electrochemical mineralization of bisphenol A was monitored by measuring the TOC values.

3. Results and discussion

3.1. *Electrochemical behaviour of bisphenol A on the Pt electrode*

Figure 1 shows linear sweep voltammograms for the oxidation of 1.0 mM bisphenol A at the Pt electrode in the pH range 2–12. The oxidation peak corresponding to bisphenol A at pH 2.0 appears at 0.82 V. The oxidation peak potential of bisphenol A shifted to lower potentials with increasing pH, especially at pH 10.0, where two peaks were observed. Since the pK_a of bisphenol A is 9.8 [16], the two peaks likely correspond to the oxidation of two species, that is, neutral bisphenol A and the phenolate ion. This indicates that the phenolate is oxidized more easily than the neutral bisphenol A at the Pt electrode.

Figure 2 shows progressive cyclic voltammograms of 1.0 mM bisphenol A in 0.1 M sodium sulfate solution (pH 12.0) by repeated potential scanning five times within the range −0.1 to 1.0 V. The electrode response of bisphenol A is typical of an irreversible electrode reaction such as other phenolic compounds. In the first cycle, a well-defined oxidation peak corresponding to bisphenol A, which disappears in subsequent cycles can be seen. This indicates that, after the original oxidation of bisphenol A, the resulting polymer film formed blocks further access of the bisphenol A monomer to the electrode surface, or an interference in the electrode reaction by the adsorption of bisphenol A. Similar behaviour has been observed for other phenolic compounds [17–19]. It is well-known that noble metal electrodes exhibit short-lived activity for the oxidation of phenolic compounds, as a consequence of surface fouling.

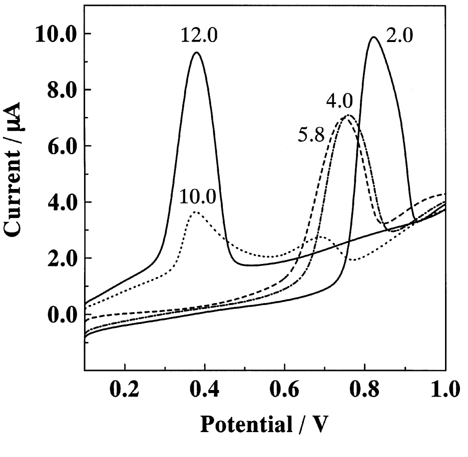

Fig. 1. Linear sweep voltammograms for the oxidation of 1.0 mM bisphenol A at the Pt electrode in 0.1 M sodium sulfate solution of different pH values. All voltammograms are first scan. Scan rate 0.05 V s^{-1}.

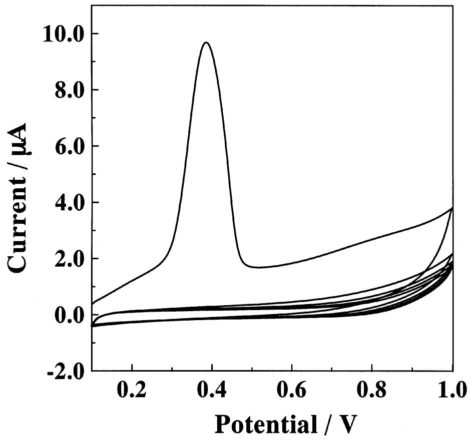

Fig. 2. Progressive cyclic voltammograms for 1.0 mM bisphenol A in 0.1 M sodium sulfate solution (pH 12.0). Scan rate 0.05 V s^{-1}.

The adsorption behaviour of bisphenol A on the Pt electrode surface was investigated by means of cyclic voltammetry. Figure 3 shows the relationship between the peak currents for the oxidation of 1.0 mM bisphenol A at different solution pH values (pH 2.0, 5.8, 12.0) with various scan rates. Prior to each measurement, the electrode was cleaned to remove the electropolymerized film from the electrode surface. The peak currents for bisphenol A at pH 2.0 and 12.0 are directly proportional to the square root of the scan rate (Figure 3(a), (c)). Hence, the electrode process for bisphenol A at the Pt electrode is controlled by diffusion at both pH 2.0 and 12.0. However, the peak currents of bisphenol A at pH 5.8 are not proportional to the square root of scan rate (Figure 3(b)). These results suggest that bisphenol A in a solution at neutral pH is easily absorbed to the Pt electrode surface, compared to acidic or alkaline media. Since electrode fouling by the adsorption of bisphenol A and the formation of the electropolymerized film is a significant practical issue in accomplishing the effective electrochemical decomposition of bisphenol A, the electrochemical treatments should be performed under conditions where this problem is minimized. In general, alkaline media, a low current density, a high temperature and high phenol concentrations favoured film formation on the noble metal electrode surface [7]. Therefore, subsequent investigations of the electrochemical decomposition of bisphenol A were carried out in acidic media (pH 2.0).

3.2. *Electrochemical decomposition of bisphenol A using Pt/Ti and SnO_2/Ti electrode*

The electrochemical decomposition of bisphenol A was performed galvanostatically under a constant current at 0.3 A using a Pt/Ti and SnO_2/Ti anode. The potential during the electrochemical decomposition at the Pt/Ti and the SnO_2/Ti anode was about 0.8–1.0 V and 3.0–4.0 V, respectively. Figure 4 shows the relationship between the concentration of bisphenol A and electrochemical decomposition time. The complete degradation of 1.0 mM bisphenol A was achieved at the Pt/Ti and the SnO_2/Ti anode in 2 and 1 h, respectively. The SnO_2/Ti electrode was more effective in terms of the electrochemical decomposition of bisphenol A than the Pt/Ti electrode. The electrochemical mineralization of bisphe-

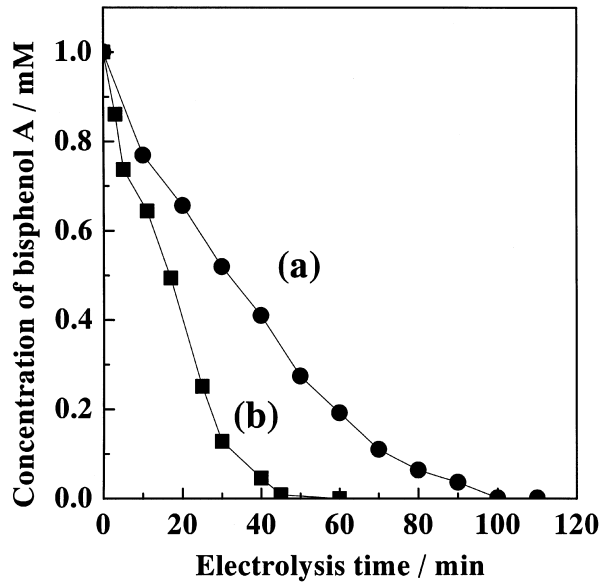

Fig. 4. Relationship between the concentration of bisphenol A and the electrochemical decomposition time. (a) Pt/Ti anode, (b) SnO_2/Ti anode.

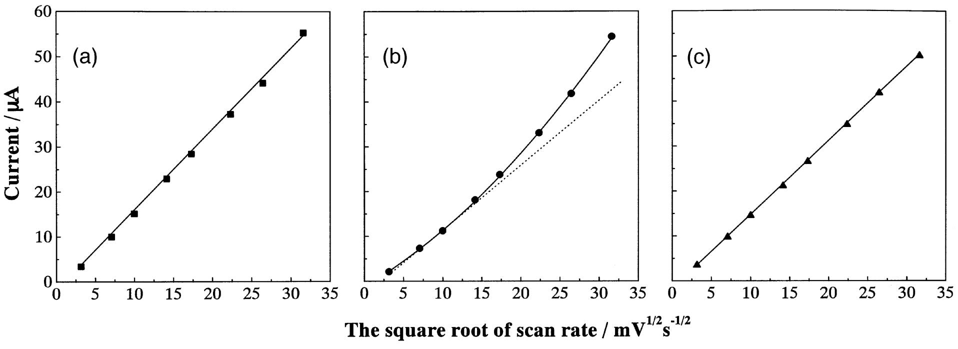

Fig. 3. Relationship between the oxidation peak current and square root of scan rate in the different pH of solution. (a) pH 2.0, (b) pH 5.8, (c) pH 12.0.

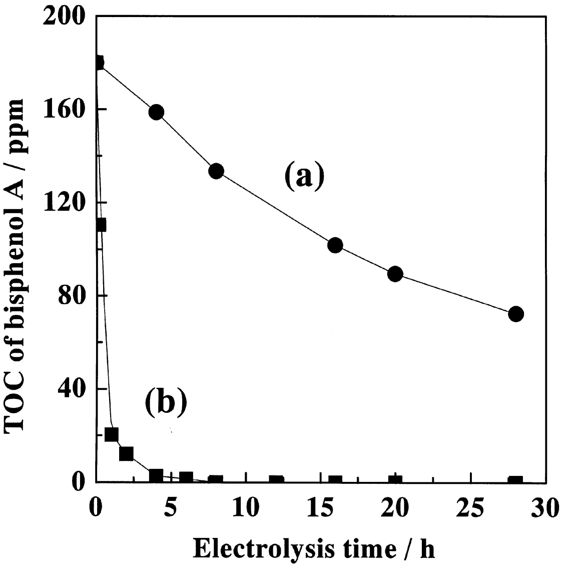

Fig. 5. Rate of TOC removal. (a) Pt/Ti anode, (b) SnO_2/Ti anode. Initial bisphenol A concentration: 1.0 mM.

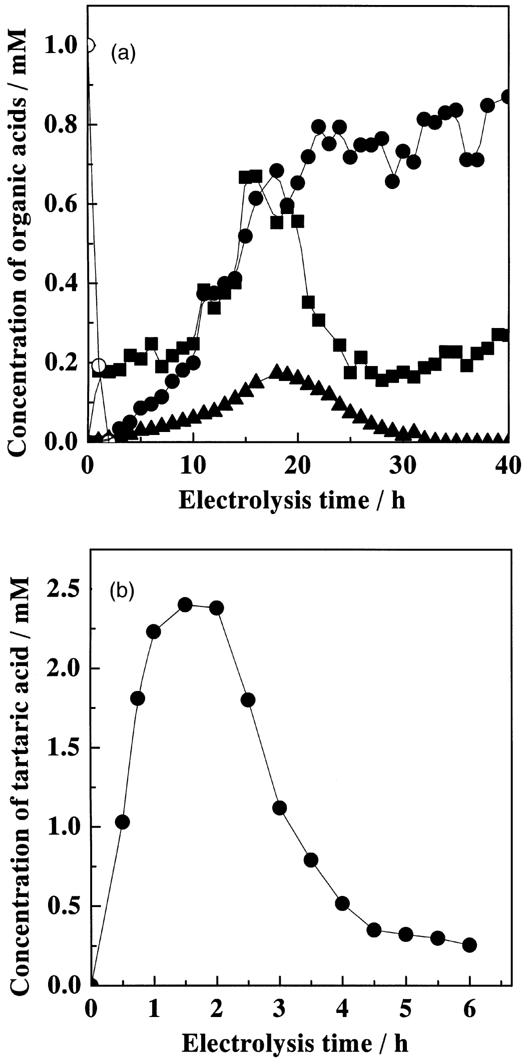

Fig. 6. Relationships between concentration of aliphatic acids and electrolysis time by use of; (a) Pt/Ti anode, (b) SnO_2/Ti anode. (○) bisphenol A, (●) tartaric acid, (■) citric acid, (▲) maleic acid. Initial bisphenol A concentration: 1.0 mM.

nol A was monitored by measuring TOC values. Figure 5 shows changes in the TOC value of a bisphenol A solution during electrochemical decomposition using the Pt/Ti or the SnO_2/Ti anode. In both cases, the TOC value clearly decreased with increasing electrolysis time. This indicates that bisphenol A is decomposed electrochemically to carbon dioxide and water. Although about 50% of the TOC in the bisphenol A solution was removed after 20 h when the Pt/Ti electrode was used, the complete removal of TOC was achieved in only 6 h with the SnO_2/Ti electrode. Therefore, bisphenol A is converted to intermediates faster for both anodes, but the decomposition efficiency of the intermediates to carbon dioxide and water is much higher for the SnO_2/Ti electrode than for the Pt/Ti electrode.

It is known that phenol is mineralized electrochemically via the generation of quinone derivatives and organic acids as intermediates [7–9]. It is thought that the electrochemical decomposition of bisphenol A involves the production of similar intermediates. The generation and destruction of intermediates during the electrochemical decomposition of bisphenol A was monitored by GC-MS and HPLC. Aromatic intermediates in the bisphenol A solution after electrochemical decomposition for 2 h were identified by GC-MS. In the case of the Pt/Ti electrode, the production of *p*-benzoquinone hydroquinone, and 2,6-bis(1,1-dimethylethyl)-4-methylphenol were observed. However, these intermediates were barely detectable, in the case of the SnO_2/Ti electrode. This suggests that aromatic intermediates are rapidly oxidized to organic acids by electrophilic attack of hydroxyl radicals at the SnO_2/Ti electrode. An analysis of organic acids generated during the electrochemical decomposition of bisphenol A was carried out by HPLC. Aliphatic acids as intermediaries are formed by the further oxidation of quinone derivatives. The changes in the concentration of some organic acids during the electrochemical decomposition of bisphenol A are shown in Figure 6. In the case of electrochemical decomposition using the Pt/Ti anode, three organic acids (maleic, citric and tartaric acid) were detected. These organic acids are stable toward further oxidation at the Pt/Ti anode and did not disappear even when the period of electrochemical decomposition was extended to 35 h (Figure 6(a)). On the other hand, tartaric acid was the major product during the electrolysis at the SnO_2/Ti electrode (Figure 6(b)). The concentration of tartaric acid generated from the electrochemical decomposition of bisphenol reached a maximum within 3 h. These results indicate that bisphenol A is rapidly oxidized to organic acids and further oxidation to carbon dioxide and water is also rapid for the SnO_2/Ti, compared with the Pt/Ti electrode.

Although the mechanism for the electrochemical decomposition of bisphenol A is complex, it is thought that the electrochemical decomposition of bisphenol A proceeds via two pathways. In the first path, bisphenol

A is decomposed to organic acids via the generation of aromatic intermediates by direct oxidization at the electrode surface. Second, bisphenol A and its intermediates are indirectly oxidized to carbon dioxide and water by hydroxyl radicals, which are powerful oxidants. The evolution of oxygen on the anode surface by oxidation of water can be described by

$$2\,H_2O \rightarrow 2\,OH^{\bullet} + 2\,H^+ + 2e^- \quad (1)$$

$$2\,OH^{\bullet} \rightarrow 2\,H^+ + O_2 + 2\,e^- \quad (2)$$

If the electrode material presents an overpotential, which is low for Equation 1 but high for Equation 2 of the oxygen evolution, $OH^{\bullet}$ can be effectively generated [11]. The overpotential of SnO_2/Ti for oxygen evolution is high, that is, the rate of oxygen evolution is low [8]. Therefore, the effective mineralization for bisphenol A solution by use of the SnO_2/Ti electrode is probably due to the effective generation of hydroxyl radicals on the SnO_2/Ti electrode.

4. Conclusions

The electrochemical behavior of bisphenol A at a Pt electrode was investigated by voltammetry at several pH values and sweep rates. It was apparent that the electrochemical oxidation of bisphenol A was the source of the electropolymerized film on the electrode surface. Bisphenol A in a solution at neutral pH is easily absorbed at the Pt electrode surface, compared to its behavior in acidic or alkaline media. The electrode and a SnO_2/Ti electrode. Both anodes effectively decomposed bisphenol A to other intermediates. However, effective mineralization, as evaluated from TOC values, was much higher for the SnO_2/Ti anode than for the Pt/Ti anode. Although the production of aromatic intermediates (*p*-benzoquinone hydroquinone, 2,6-bis(1,1-dimethylethyl)-4-methylphenol) and organic acids (maleic, citric, tartaric acid) was observed in the electrolysis solution of bisphenol A using the Pt/Ti electrode, tartaric acid was the major product for electrolysis using the SnO_2/Ti electrode.

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References

1. A.V. Krishnan, P. Stathis, S.F. Permuth, L. Tokes and D. Freldman, *Endocrinology* **132** (1993) 2279.
2. F. Wajon, D.H. Rosenblatt and E.P. Burrous, *Environ. Sci. Technol.* **16** (1982) 396.
3. O. Koyama, Y. Kamagata and K. Nakamura, *Water. Res.* **28** (1994) 895.
4. P.M. Armenante, D. Kafkewitz, G.A. Lewandowski and C.J. Jou, *Water. Res.* **33** (1999) 681.
5. D.W. Chen and A.K. Ray, *Water. Res.* **32** (1998) 3223.
6. T. Krutzler and R. Baner, *Chemosphere* **38** (1999) 2517.
7. Ch. Comninellis and C. Pulgarin, *J. Appl. Electrochem.* **21** (1991) 703.
8. Ch. Comninellis and C. Pulgarin, *J. Appl. Electrochem.* **23** (1993) 108.
9. Ch. Comninellis and A. Nerini, *J. Appl. Electrochem.* **25** (1995) 23.
10. J.D. Rodgers, W. Jedral and N. Bunce, *Environ. Sci. Technol.* **33** (1999) 1453.
11. A.M. Polcaro, S. Palmas, F. Renoldi and M. Mascia, *Electrochim. Acta* **46** (2000) 389.
12. A.B. Boscoletto, F. Gottardi, L. Milan, P. Pannocchia, V. Tartari and M. Tavan, *J. Appl. Electrochem.* **24** (1994) 1052.
13. S. Tanaka, Y. Nakata, H. Kuramitz and M. Kawasaki, *Chem. Lett.* (1999) 943.
14. Y. Ohko, I. Ando, C. Niwa, T. Tatsuma, T. Yamamura, T. Nakashima, Y. Kubota and A. Fujishima, *Environ. Sci. Technol.* **35** (2001) 2365.
15. H. Kuramitz, Y. Nakata, M. Kawasaki and S. Tanaka, *Chemosphere* **45** (2001) 37.
16. M. del Olmo, A. Zafra, A.G. Casado and J.L. Vilchez, *Intern. J. Environ. Anal. Chem.* **69** (1997) 99.
17. E. Ekinci, A.A. Karagozler and A.E. Karagozler, *Electroanalysis* **8** (1996) 571.
18. P.I. Iotov and S.V. Kalcheva, *J. Electroanal. Chem.* **442** (1998) 19.
19. A. Ciszewski and G. Milczarek, *Anal. Chem.* **71** (1999) 1055.