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Electrochemical oxidation of phenol for wastewater treatment using SnO_2 anodes

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The electrochemical oxidation of phenol for waste water treatment was studied on doped SnO_2 anodes. Analysis of reaction intermediates and a carbon balance has shown that the main reaction is oxidation of phenol to CO_2. This unexpected behaviour of the SnO_2 anode is explained by a change of the chemical structure of the electrode surface during anodic polarization.

1. Introduction

Wastewater containing organic pollutants, which cannot be easily treated by biological action, has to be treated by chemical oxidation. Chemical oxidation allows, in general, complete elimination of the principal organic pollutants but complete removal of total organic carbon (TOC) is more difficult. Thus, oxidation of phenol with a powerful oxidant such as ozone ($E^0 = 2.07$ V) allows only a 30% TOC removal [1]. Similar levels of TOC removal are obtained using H_2O_2 at room temperature (in the presence of Fe^{2+} catalyst) [2].

Electrochemical oxidation has been reported to behave in a similar way [3,4] but in previous work [5] we have demonstrated that the TOC removal obtained by the electrochemical oxidation at a platinum anode is higher than that obtained by chemical oxidation. This higher TOC removal using electrochemical oxidation has been attributed to the oxidation of adsorbed organic compounds to carbon dioxide.

In this paper, the electrochemical oxidation of phenol has been studied, using doped SnO_2 coated titanium anodes to elucidate the mechanism of the electrochemical oxidation to CO_2. Recently Stucki and co-workers [6,7] have shown that doped SnO_2 anodes oxidize a wide range of organic compounds with an efficiency about five times higher than with platinum anodes.

2. Experimental details

2.1. *Determination of the current efficiency, EOI, EOD and X*

Two methods have been used for the determination of the current efficiency during the electrochemical oxidation of phenol. The oxygen flow rate method and the chemical oxygen demand (COD) method. Details concerning these methods are given in a previous paper [5].

From the instantaneous current efficiency–time (*ICE–t*) curves the electrochemical oxidation index (*EOI*), the electrochemical oxygen demand (*EOD*) and the degree of organic oxidation (*X*) can be calculated using the relations:

$$EOI = \frac{\int_0^\tau ICE \cdot \mathrm{d}t}{\tau}$$

$$EOD = \frac{8(EOI \times I\tau)}{F[\mathrm{PhOH}]} \quad [(\mathrm{g\,O_2}\,(\mathrm{g\,phenol})^{-1}]$$

$$X = \frac{EOD}{(COD)_0} \times 100$$

where

τ = time of electrolysis at which *ICE* is almost zero (h)
I = current (A)
F = Faraday constant (26.8 Ah)
[PhOH] = amount of phenol in the electrolyte (g)
$(COD)_0$ = initial *COD* value expressed in g O_2 (g phenol)$^{-1}$

2.2. *Electrode material, electrochemical cell and analysis*

The SnO_2 film electrodes doped with antimony were prepared on titanium base metal by Stucki by the standard spray hydrolysis method; the best composition of the spray solution was 10 g $SnCl_4 \times 5H_2O$, 0.1 g $SbCl_3$ in 100 ml of ethanol. Preparation details are given in [6].

A two compartment cell of 150 ml capacity was used; the anode was made of SnO_2-coated titanium and the cathode was a platinum spiral enclosed in a 10 ml porous porcelain pot; stirring was provided by a magnetic bar.

The disappearance of phenol and the appearance of its oxidation products were monitored by HPLC (Shimazu 8 A). The progress of the electrochemical oxidation was monitored by measuring the total organic carbon (TOC, XERTEX, Dohrman) and the chemical oxygen demand (COD, Hach Dr 2000).

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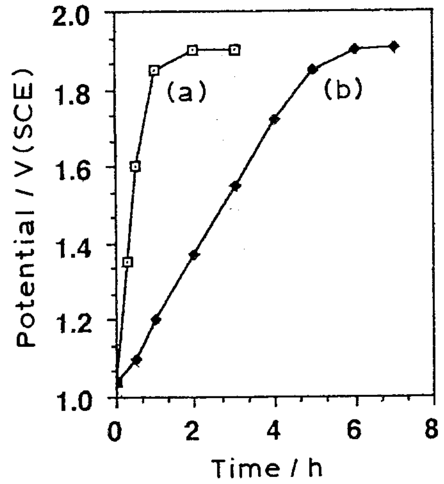

Fig. 1. Potential-time curves obtained at constant current density ($12\,mA\,cm^{-2}$), $T = 25°C$. (a) New SnO_2 anode; (b) pretreated SnO_2 anode by anodic polarization at $12\,mA\,cm^{-2}$ for 5 h. Electrolyte: $50\,g\,dm^{-3}$ Na_2SO_4 + $4\,g\,dm^{-3}$ NaOH.

The oxygen formed in the anolyte during electrolysis was measured by a gas burette and analysed by gas chromatography.

3. Results and discussion

3.1. *Electrochemical measurements*

The SnO_2 anode potential at a given current density depends strongly on the polarization time and on the previous history of the anode. Figure 1 shows typical potential–time (*V–t*) curves obtained at constant current density ($12\,mA\,cm^{-2}$) with two anodes, one untreated (new anode) and the other pretreated by anodic polarization at $12\,mA\,cm^{-2}$ for 5 h (pretreated). Both anodes give an initial electrode potential of about 1.05 V/SCE and show an increase of potential with time, to achieve a final value of about 1.90 V/SCE. The rate of increase of anode potential with time depends on the anode history. Thus, for a new electrode the rate of increase is about $0.2\,V\,h^{-1}$ compared to $1\,V\,h^{-1}$ for a pretreated electrode.

The reversible deactivation of the SnO_2 anode toward oxygen evolution is probably due to electrode hydration [8] or/and due to the formation of a non stoichiometric oxides (SnO_{2+x} or/and Sb_2O_{5+x}). The long time necessary for deactivation of a new electrode is probably due to the existence of less accessible surface regions which become progressively accessible after electrode pretreatment. Electrode deactivation after pretreatment is also observed in the current–potential curves (Fig. 2).

3.2. *Electrochemical oxidation of phenol*

3.2.1. Electrode pretreatment. The current efficiency for the electrochemical oxidation of phenol at an SnO_2 anode depends strongly on the previous history of the anode. Thus, using new anodes, low *EOI* were obtained (*EOI* = 0.10–0.12) in contrast to pretreated anodes, where high *EOI* values were achieved (0.3–0.4).

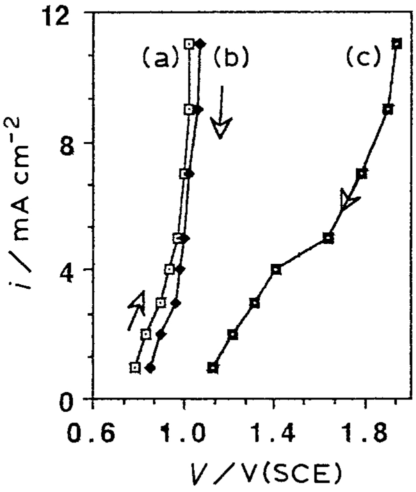

Fig. 2. Current–potential curves for the SnO_2 anode. (a) Forward scan (new electrode); (b) backward scan (new electrode); and (c) backward scan (pretreated at $12\,mA\,cm^{-2}$ for 5 h). Electrolyte as in Fig. 1.

The *ICE–t* curves for a pretreated anode show a maximum after 1.0–1.5 h (8–12 $Ah\,dm^{-3}$) of electrolysis; this corresponds to the time necessary for hydration of the anode resulting in a high overpotential for oxygen evolution.

3.2.2. Comparison of SnO_2 and Pt anodes. Figure 3 shows a trend of *ICE* during the electrochemical oxidation of phenol at a platinum and a SnO_2 anode; from this figure the *EOI*, *EOD* and *X* values were calculated. *EOI* values obtained with the SnO_2 anode (0.25) are much higher than those obtained with the platinum anode (0.10) and *X* values obtained with SnO_2 ($X = 90\%$) indicate a high degree of phenol oxidation in comparison to platinum ($X = 40\%$).

Figure 4 compares the rate of phenol and *TOC* removal obtained with SnO_2 and platinum. The rate of phenol elimination is almost the same for both anodes (complete elimination of phenol after 25–30 $Ah\,dm^{-3}$) but the rate of *TOC* removal is much higher for the

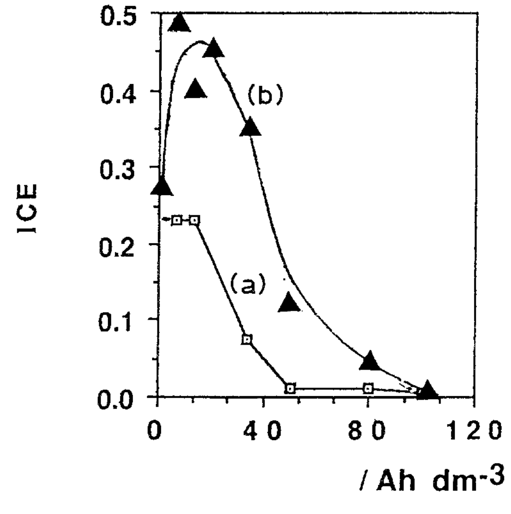

Fig. 3. *ICE* variation with the specific electrical charge passed ($Ah\,dm^{-3}$ of the electrolyte) during the electrochemical oxidation of phenol. (a) Platinum anode; (b) SnO_2 anode. Current density, $i = 50\,mA\,cm^{-2}$; temperature, $T = 70°C$; pH 2 (constant). Initial phenol concentration: 21 mM.

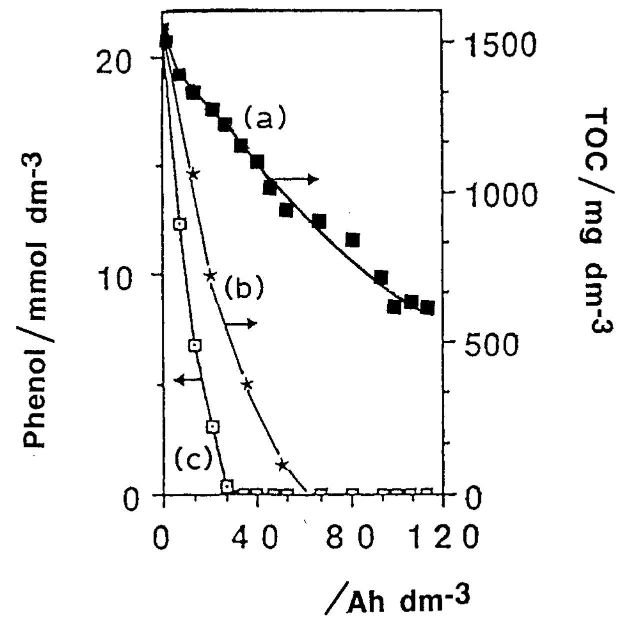

Fig. 4. Rate of phenol and *TOC* removal. (a) Platinum anode (*TOC*); (b) SnO_2 anode (*TOC*); (c) platinum and SnO_2 anodes (phenol). Conditions as in Fig. 3.

SnO_2 electrode. Thus, using the SnO_2 anode 90% *TOC* removal can be achieved after the passage of 50 Ah dm^{-3} in comparison to 38% *TOC* removal obtained with platinum.

The trend of the oxidation products during the electrolysis of phenol at platinum and SnO_2 anodes are given in Fig. 5. The concentration of the other non identified intermediates (curve 7 in Fig. 5) has been calculated from the relation

$$\begin{bmatrix}\text{Non identified}\\ \text{intermediates}\end{bmatrix} = \begin{bmatrix}\text{Initial}\\ \text{phenol}\end{bmatrix} - \begin{bmatrix}\text{Mass balance}\\ \text{identified intermediates}\end{bmatrix}$$

The mass balance of the identified reaction intermediates (or product) has been calculated using the relation

$$\begin{pmatrix}\text{Phenol}\\ \text{hydroquinone}\\ \text{catechol}\\ \text{benzoquinone}\end{pmatrix} + \begin{pmatrix}\text{Maleic}\\ \text{fumaric}\end{pmatrix} + \frac{1}{3}\begin{pmatrix}\text{Oxalic}\end{pmatrix} + \frac{1}{6}\left[\begin{pmatrix}CO_2\end{pmatrix} - 2\begin{pmatrix}\text{Maleic}\\ \text{fumaric}\end{pmatrix}\right]$$

Comparison of the oxidation products obtained with platinum and SnO_2 shows two main differences:

(i) At the SnO_2 anode there are only very small amounts of aromatic intermediates (hydroquinone, catechol, benzoquinone); these intermediates are formed in large amounts on the platinum anode.
(ii) Aliphatic acids (fumaric acids (fumaric, maleic, oxalic) are rapidly oxidized at the SnO_2 anode and are practically electrochemically inactive at the platinum anode.

3.3. *Comparison of electrochemical with chemical oxidation*

To understand better the mechanisms of the electrochemical oxidation of phenol a comparative study was undertaken between electrochemical (with Pt and SnO_2 anodes) and chemical oxidation of phenol with H_2O_2 in the presence of Fe^{2+} catalyst (Fenton's reagent) which is well known to occur by electrophilic attack of hydroxyl radicals on the organic compound [9].

There are two techniques for the oxidation with Fenton's reagent: (i) room temperature oxidation, in which oxidation is effected at room temperature (25° C) by mixing phenol with excess H_2O_2 [9]; and (ii) high temperature oxidation, in which oxidation is effected at high temperature (140° C) and pressure (5 bar) by continuous introduction of H_2O_2 to the reaction medium [10].

In the case of room temperature oxidation, large amounts of aromatic intermediates (hydroquinone, catechol, benzoquinone) are formed initially and these are further oxidized to aliphatic acids (maleic, fumaric, oxalic). These acids are stable toward further oxidation.

This reaction scheme is similar to that observed with platinum (Fig. 5(a)). The main difference between room temperature Fenton's reagent oxidation and electrochemical oxidation with a platinum anode is that the level of *TOC* elimination is higher for the electrochemical oxidation (60% *TOC* elimination) than the chemical oxidation (30% *TOC* elimination) [5]. For the oxidation at high temperature and pressure (140° C, 5 bar) with Fenton's reagent, only small amounts of aromatic intermediates are formed. The principal intermediates are aliphatic acids which are further oxidized to carbon dioxide. This reaction scheme is similar to that observed with SnO_2 anodes (Fig. 5(b)). For both oxidations the level of *TOC* elimination is higher than 90%.

It is well known that Fenton's reagent generates hydroxyl radicals in solution [9]:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\cdot$$

These oxidize the organic compound (phenol or its oxidation intermediates) by electrophilic attack.

$$[\text{PhOH}] \xrightarrow[k_1]{OH^\cdot} \begin{bmatrix}\text{Aromatic}\\ \text{intermediates}\end{bmatrix} \xrightarrow[k_2]{OH^\cdot} \begin{bmatrix}\text{Aliphatic}\\ \text{acids}\end{bmatrix} \xrightarrow[k_3]{OH^\cdot} CO_2$$

The rate constant k_1 for phenol hydroxylation is very high ($k_1 = 10^{10}\,dm^3 mol^{-1} s^{-1}$ [11]) and this reaction can be considered as instantaneous (molecular diffusion will determine the rate of the reaction). Rate constants k_2 and k_3 are relatively low at room temperature ($k_2 = 10^8\,dm^3 mol^{-1} s^{-1}$, $k_3 = 10^5\,dm^3\,mol^{-1} s^{-1}$ [11]). But as these reactions have high activation energies [10] the rate constants increase considerably with temperature and probably at 140° C

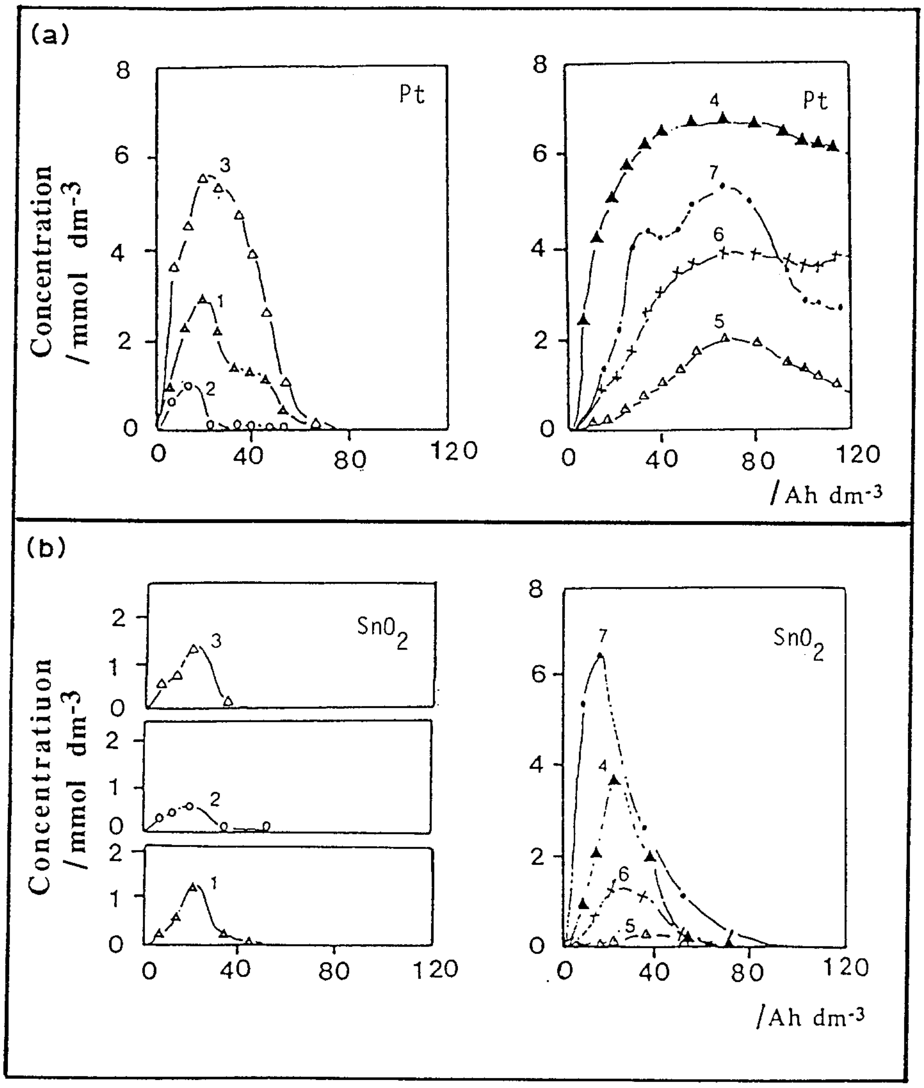

Fig. 5. Variation of oxidation products with the specific electrical charge passed (Ah dm^{-3} of the electrolyte) during electrolysis of phenol (conditions as in Fig. 3). (a) Platinum anode; (b) SnO_2 anode. (1) Hydroquinone, (2) catechol, (3) benzoquinone, (4) maleic acid, (5) fumaric acid, (6) oxalic acid, and (7) other intermediates (Δ).

(high temperature, Fenton's reagent) all three reactions are instantaneous.

A similar model can be proposed for the electrochemical oxidation of phenol at platinum and SnO_2 anodes. Thus for the electrochemical oxidation at a platinum anode the rate constants k_2 and k_3 are relatively low in contrast with the SnO_2 anode where all three reactions are instantaneous.

3.4. *Mechanism of the electrochemical oxidation of phenol for waste water treatment at a SnO_2 anode*

The reaction mechanism of the electrochemical oxidation of phenol is complex and takes place in a number of steps. We present here a simplified reaction sequence similar to those given previously for the oxidation of phenol at a platinum anode [5]. In the first stage hydroxyl radicals are produced by the electrochemical oxidation of water:

$$2H_2O \xrightarrow{r_1} 2OH^{\cdot}_{ads} + 2H^+ + 2e^- \quad (1)$$

The hydroxyl radicals thus formed oxidize phenol at the electrode surface to CO_2 (Equation 2) or subsequently react giving O_2 (Equation 3):

$$C_6H_5OH + 28(OH^{\cdot}_{ads}) \xrightarrow{r_2} 6CO_2 + 17H_2O \quad (2)$$

$$2OH^{\cdot}_{ads} \xrightarrow{r_3} H_2O + \tfrac{1}{2}O_2 \quad (3)$$

The experimental results obtained in this paper have shown that pretreatment of the SnO_2 electrode by anodic polarization causes an increase in the overpotential for oxygen evolution i.e. a decrease in the rate of oxygen evolution (Equation 3) and an increase in the rate of phenol oxidation (Equation 2).

This unexpected behaviour of the SnO_2 electrode after anodic polarization is due to the change in the chemical structure of the electrode surface, which is known to play a major role in electrocatalysis [12]. A possible change in the chemical structure of the SnO_2 electrode proposed previously by Watanabe [8] is hydration of the $-Sn{=}O$ bond, or/and formation of non stoichiometric oxides (SnO_{2+x} or/and Sb_2O_{5+x}).

The increase in the rate of oxidation (Equation 2) can be explained by a preferential adsorption of phenol at the hydrated electrode surface. Thus the electrochemical oxidation of phenol at a SnO_2 anode can be presented as a two step process; adsorption on the surface then oxidation to carbon dioxide:

$$\mathrm{PhOH} \longrightarrow (\mathrm{PhOH})_{\mathrm{ads}} \xrightarrow{28(\mathrm{OH}^{\bullet}_{\mathrm{ads}})} 6\mathrm{CO_2} + 17\mathrm{H_2O}$$

Further investigations are in progress to obtain more specific information on the mechanism of electrochemical oxidation at SnO_2 electrodes.

4. Conclusion

The oxidation of phenol for wastewater treatment has been effected using Pt and SnO_2 anodes. Comparison of the oxidation product obtained with these anodes show two main differences:

(i) At the SnO_2 anode there are only very small amounts of aromatic intermediates; these intermediates are formed in large amount on Pt anode.
(ii) Aliphatic acids are rapidly oxidized at the SnO_2 anode and are practically electrochemically inactive at the Pt anode.

The electrochemical oxidation (using Pt and SnO_2 anodes) was compared with the chemical oxidation (using H_2O_2 at room and high temperature) and a mechanism for the electrochemical oxidation is proposed.

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