

Microwave activation of electrochemical processes: High temperature phenol and triclosan electro-oxidation at carbon and diamond electrodes

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Abstract

The electrochemical oxidation of phenolic compounds in aqueous media is known to be affected by the formation of electro-polymerized organic layers which lead to partial or complete electrode blocking. In this study the effect of high intensity microwave radiation applied locally at the electrode surface is investigated for the oxidation of phenol and triclosan in alkaline solution at a 500 μm diameter glassy carbon or at a 500 μm \times 500 μm boron-doped diamond electrode. The temperature at the electrode surface and mass transport enhancement are determined by calibration with the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system in aqueous 0.3 M NaOH and 0.2 NaCl (pH 12) solution. The calibration shows that strong thermal and mass transport effects occur at both glassy carbon and boron-doped diamond electrodes. The average electrode temperature reaches up to 390 K and mass transport enhancements of more than 20-fold are possible. For the phenol electro-oxidation at glassy carbon electrodes and at a concentration below 2 mM a multi-electron oxidation (ca. 4 electrons) occurs in the presence of microwave radiation. For the electro-oxidation of the more hydrophobic triclosan only the one-electron oxidation occurs. Although currents are enhanced in presence of microwave radiation, rapid blocking of the electrode surface in particular at high phenol concentrations still occurs.

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1. Introduction

Microwave radiation has been applied as an alternative heating method in a wide range of organic syntheses [1], inorganic syntheses [2], analytical processes [3], and many other chemical processes [4]. The ability of microwave radiation to interact with the dielectric and not (or to a lesser extent) with the metal or container walls produces new types of processes where heat is delivered rapidly and the rate limiting heat transfer across the solid–liquid interface [5] can be avoided. Under these conditions

entirely new processes are possible and new physical effects are observed.

Temperature in electrochemistry is generally regarded as an important parameter and a range of techniques based on “hot wires” [6], electromagnetically heated microelectrodes [7] and channel flow electrodes [8], as well as laser pulse heated electrodes [9,10] have been developed. In all of these processes thermal activation is limited by the transfer of heat from the electrode surface into the solution phase. Recently, activation of electrochemical processes has also been achieved by focusing microwave radiation at the tip of a micro-electrode in a newly developed electrochemical cell [11,12]. Focused microwave radiation offers an in situ thermal activation technique where the flow of heat is not limited by the electrode|liquid interface and this novel methodology may be applied for a wide range of

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electrochemical processes, for electroanalytical processes, and for quantitative studies of microwave effects at solid|solution interfaces.

The microwave activation effect at metal micro-electrodes is highly localized at the tip of micro-electrode and this induces fast temperature transients within a small zone at the electrode surface|solution interface [13]. Mass transport is enhanced up to three orders of magnitude by the temperature effect on the rate of diffusion and by forced convection or “jet-boiling” in the presence of temperature gradients [14–16]. Using this technique, electrochemical processes in the presence of microwave radiation have been studied in aqueous media [17], organic solutions [18], micellar solutions [19], and in ionic liquids [20]. Both metal [15] and carbon or boron-doped diamond electrode materials have been employed [21].

The analytical determination of phenolic compounds has received considerable attention because their importance in food, environmental, and industrial processes. Also, these compounds are important synthetic intermediates in the chemical industry used as components in resins, preservatives, and pesticides [22]. Generally, the electro-oxidation of phenolic compounds at electrode surfaces produces active phenoxy radicals that can be further oxidized to soluble quinones or that can react to form dimers and polyaramotic compounds [23–26]. The formation of these insoluble polyphenols results in the deactivation and fouling of the electrode surface. The relative rate of these two oxidation pathways (forming quinone intermediates or insoluble polymers) depends on the type and concentration of the phenolic compound. At higher phenolic compound concentrations occurs enhanced polymerization and electrode blocking, and lower concentrations multi-electron oxidation to quinones [26,27]. Moreover, the phenolic compound electro-oxidation pathway depends also on the nature of the electrode, pH, solvent, additives, electrode potential, and current density [28,29]. The electrochemical oxidation of phenolic compounds has been widely studied at different metal electrodes [30], but metal oxide, carbon, and boron-doped diamond electrodes have been shown to result in less electrode fouling [31]. Qiu et al. have demonstrated that laser-pulse activation allows well-defined responses for phenol oxidation to be obtained [32].

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol) is an anti-fungal and anti-bacterial reagent active against both gram-negative and -positive bacteria and used as anti-microbial agent in a wide range of consumer products such as preservative, disinfectant, and hygiene formulations. Only a few studies have been reported on the direct electrochemical oxidation of triclosan at glassy carbon and boron-doped diamond electrodes [33,34]. Cyclic voltammetry experiments showed that the direct oxidation of triclosan occurs to give a phenoxy radical intermediate and a second oxidation response was tentatively assigned to an oxidation of the ether moiety. Under all conditions a passivating poly-oxyphenylene polymer film is rapidly formed at the electrode surface.

Here, high temperature–high mass transport conditions induced by focused microwaves at glassy carbon and at boron-doped diamond electrode surfaces are employed to enhance the electrochemical oxidation of phenol and triclosan in aqueous

NaOH and NaCl solutions. A calibration procedure allows temperature and mass transport conditions to be defined and the substantial current enhancements for both phenol oxidations to be quantified. Whereas triclosan remains a one-electron process, phenol is observed to switch to a four-electron pathway at sufficiently low concentrations.

2. Experimental

2.1. Chemical reagents

Reagents such as NaOH, NaCl, $K_4(Fe(CN)_6)$, $K_3Fe(CN)_6$, and phenol were obtained in analytical grade purity from Aldrich and used without further purification. Triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol) was supplied by Professor Eleftheria Psillakis. De-ionized and filtered water of 18 M Ω cm resistivity was taken from an Elga water purification system. Argon (BOC, UK) was employed for de-aeration of the electrolyte solutions. Prior to experiments, the solution was degassed with argon for at least 1 h.

2.2. Instrumentation

A conventional three-electrode micro-Autolab potentiostat system (Eco Chemie, NL) was employed to conduct electrochemical measurements. A 500 μ m diameter (2 cm long) glassy carbon rod (type 1, Goodfellow, UK) and a 500 μ m \times 500 μ m (1 cm long) diamond rod (Element Six Ltd., UK) mounted in epoxy were used as working electrodes. The electrodes were made by back contacting to copper wire with silver epoxy (RS Components, UK), then coating with a thin layer of TorrsealTM ceramic epoxy (Varian vacuum products, USA), followed by sealing into a heat and chemically resistant two-component epoxy E14A and E14B (Bondmaster, UK), and mounting into a 5 mm outer diameter borosilicate glass tubes. Electrodes prepared in this way are readily renewed by polishing and stable over many experiments even at relatively high microwave intensities. A saturated calomel electrode (SCE, Radiometer) was used as the electrode and ca. 1 cm² platinum gauze as the counter electrode in a flow through configuration cell [12]. Only the working electrode placed in a small volume Teflon cell is exposed to microwave radiation. Details of the cell design, vacuum degassing (porous tubing supplied by W.L. Gore & Associates Ltd., UK), and application of microwaves have been reported previously [12]. The flow rate of liquid through the cell was typically 0.65 cm³ min⁻¹. Prior to each experiment the working electrode was polished with aqueous slurries of 1 μ m alumina on polishing cloth (Buehler, UK) followed by thorough rinsing with de-ionized water. In order to remove any alumina particles left on the surface, the electrode was further polished on a clean, wet polishing cloth and again rinsed with water. In addition, before each scan the electrode was electrochemically treated by holding the potential at +3 V versus SCE for 10 s to electrochemically clean and pre-condition the electrode surface. A Panasonic multi-mode microwave oven (NN-3456, 2.45 GHz, 800 W) with modified power supply, a water energy sink, and a port for the electrochemical cell was

employed [12]. The microwave intensity was controlled by controlling the magnetron anode current and the nominal output power was approximately 3.7 W for each mA magnetron anode current. Special care is required when metal objects are placed into a microwave cavity. Before and during operation, the system was tested for leaking microwave radiation with a radiation meter.

3. Results and discussion

3.1. Temperature and mass transport calibration in the presence of microwaves for glassy carbon or boron-doped diamond electrodes employing the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system in alkaline aqueous media

The effect of microwaves on electrochemical processes at metal and carbon microelectrodes [12] and microelectrode arrays [35] has been reported previously. Due to the frequency in the GHz range, microwave activation allows considerable amounts of energy to be delivered (focused) directly into a small volume of solution at the electrode surface. There is no limitation of heat flow from the solid to the liquid phase and therefore novel effects due to localised heating can be observed. In this study, glassy carbon and boron-doped diamond electrodes of 500 μm size are employed in order to explore the possibility of using microwave effects at conventional macro-sized carbon electrodes and for important processes such as phenol and phenol derivative oxidation. Initially, a calibration process is required in order to assess the temperature and mass transport conditions at these electrodes as a function of microwave power. The $\text{Fe}(\text{CN})_6^{3-/4-}$ one-electron redox system [11] is used to quantify the effects of microwave radiation.

Fig. 1A shows a set of typical voltammograms recorded at a 500 μm diameter glassy carbon disc electrode immersed in an aqueous solution containing 0.3 M NaOH, 5.0 mM $\text{Fe}(\text{CN})_6^{4-}$, and 5.0 mM $\text{Fe}(\text{CN})_6^{3-}$. In the absence of microwave activation (Fig. 1A, curve i) the equilibrium potential for oxidation and reduction peaks is observed at ca. 0.195 V versus SCE. The peak currents for oxidation and reduction are ca. 3.5 and $-3.2 \mu\text{A}$, respectively. In the presence of microwave radiation a gradual increase of both the anodic and cathodic limiting currents (see Fig. 1A) is observed. The limiting currents are readily enhanced by a factor of more than 20 due to thermally enhanced convection and faster diffusion. This effect is possible due to the degassing process which allows only transient vapour bubble formation and which leads to considerable convection effects. Noise and current fluctuation at elevated microwave power indicate solution boiling at the electrode|solution interface (see Fig. 1A, curve iii). The midpoint potential of the voltammograms (or the reversible potential for the $\text{Fe}(\text{CN})_6^{3-/4-}$ system measured under zero current conditions) is shifted linearly to more negative values as the temperature increases. Therefore, the temperature induced equilibrium potential shift for the $\text{Fe}(\text{CN})_6^{3-/4-}$ system in 0.3 M NaOH solution can be employed to obtain an estimate of the temperature at the electrode surface ($T_{\text{electrode}}$) in presence of microwave radiation. The temperature coefficient, $dE_{\text{equilibrium}}/dT = -1.3 \pm 0.05 \text{ mV K}^{-1}$, has

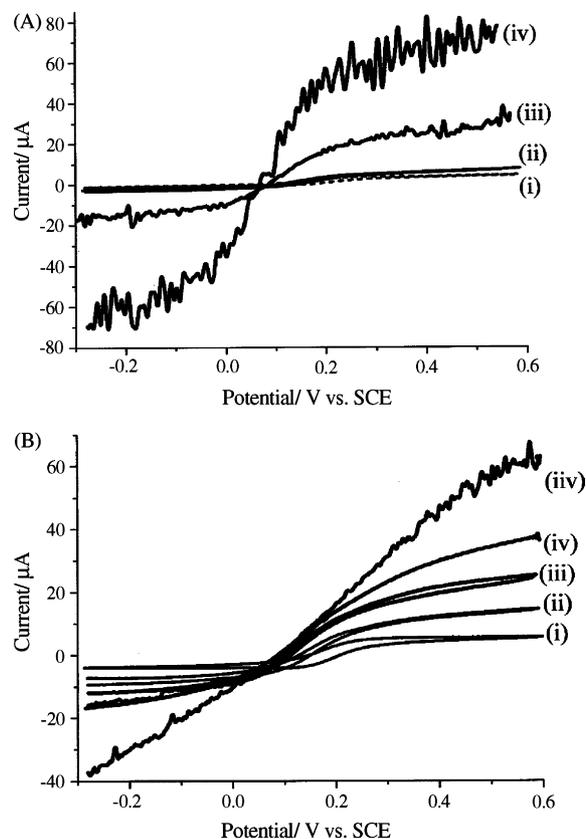


Fig. 1. (A) Cyclic voltammograms (scan rate 50 mV s^{-1}) for the oxidation and reduction of 5 mM $\text{Fe}(\text{CN})_6^{4-}$ /5 mM $\text{Fe}(\text{CN})_6^{3-}$ in aqueous 0.3 M NaOH obtained at a 500 μm diameter glassy carbon disc electrode in the presence of microwave radiation (magnetron currents (i) 0 mA, (ii) 5 mA, (iii) 10 mA, and (iv) 20 mA). (B) Cyclic voltammograms (scan rate 50 mV s^{-1}) for the oxidation and reduction of 5 mM $\text{Fe}(\text{CN})_6^{4-}$ /5 mM $\text{Fe}(\text{CN})_6^{3-}$ in aqueous 0.3 M NaOH obtained at a 500 $\mu\text{m} \times 500 \mu\text{m}$ boron-doped diamond electrode in the presence of microwave radiation (magnetron currents (i) 0 mA, (ii) 10 mA, (iii) 15 mA, and (iv) 20 mA).

been determined independently in a conventionally heated non-isothermal electrochemical cell using a 500 μm diameter glassy carbon disc electrode in a solution containing 0.3 M NaOH, 5.0 mM $\text{Fe}(\text{CN})_6^{4-}$, and 5.0 mM $\text{Fe}(\text{CN})_6^{3-}$. Fig. 2A shows the corresponding plot of the temperature versus microwave power (given here as magnetron anode current). It can be seen that as the average electrode surface temperature reaches the boiling point of water no further increase in temperature and current fluctuations due to boiling are observed. Perhaps surprisingly, in spite of the constant temperature the mass transport at the electrode continues to increase further with microwave power (vide infra).

Fig. 1B shows voltammetric responses obtained at a 500 $\mu\text{m} \times 500 \mu\text{m}$ boron-doped diamond electrode immersed in 0.3 M NaOH, 5.0 mM $\text{Fe}(\text{CN})_6^{4-}$, and 5.0 mM $\text{Fe}(\text{CN})_6^{3-}$. Similar potential shift and mass transport effects are observed. However, at higher microwave power a distorted voltammetric response showing resistivity effects is obtained. These resistivity effects are believed to be due at least in part to the interaction of vapour bubbles with the electrode surface and the reduced amount of electrolyte in the vicinity of the vapour bubble coated

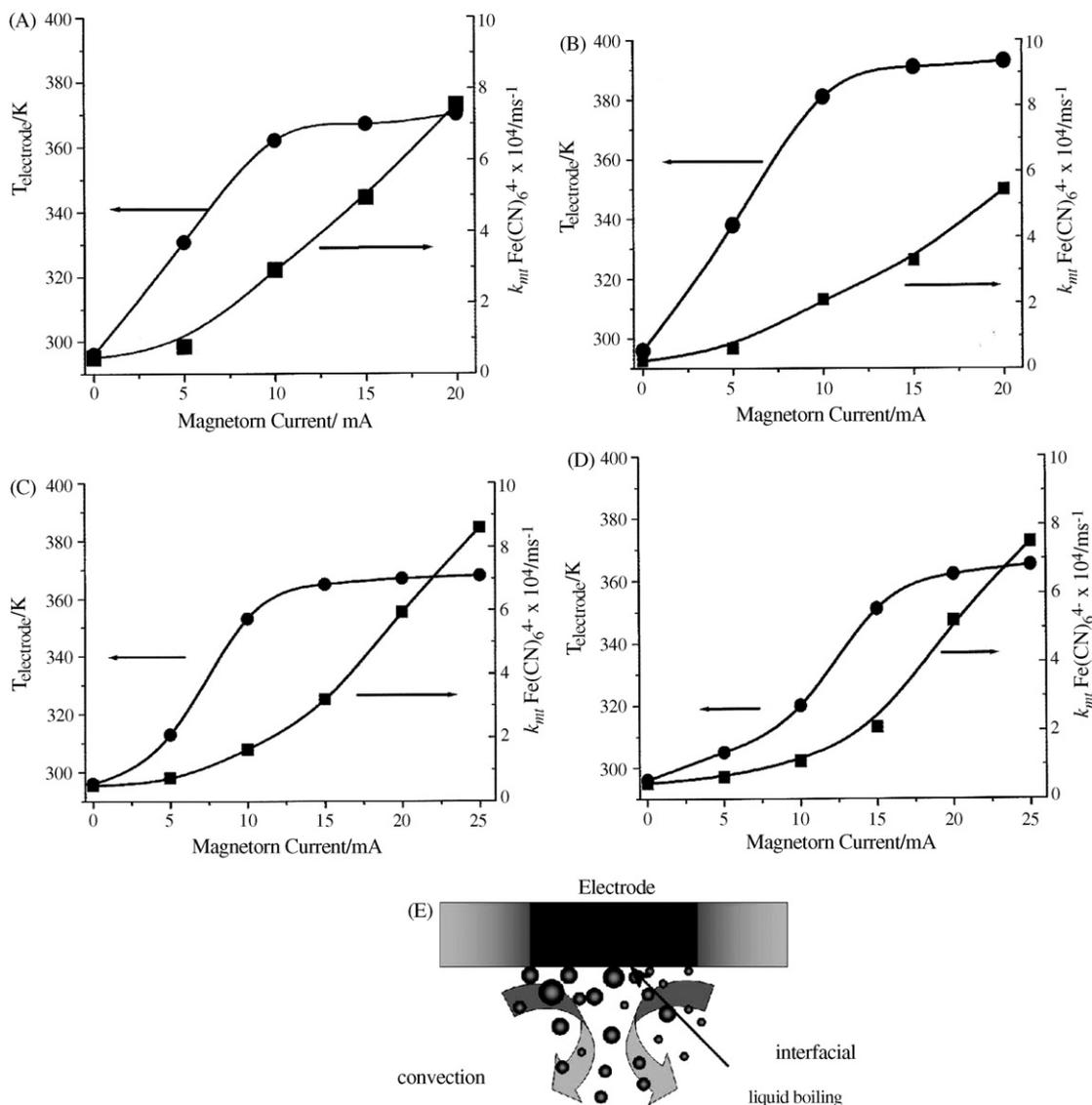


Fig. 2. Plots of the variation of $T_{\text{electrode}}$ and mass transports $k_{\text{mt}}^{\text{Fe(CN)}_6^{4-}}$ as a function of microwave intensity in aqueous solution of 5 mM Fe(CN)_6^{4-} /5 mM Fe(CN)_6^{3-} at a 500 μm diameter glassy carbon electrode in (A) 0.3 M NaOH and (B) 0.2 M NaCl (pH 12). Also shown are calibration plots for a 500 $\mu\text{m} \times 500 \mu\text{m}$ boron-doped diamond electrode in (C) 0.3 M NaOH and (D) 0.2 M NaCl (pH 12). The drawing (E) shows an artist impression of the interfacial boiling process causing increased convection.

electrode. Fig. 2C shows a plot of the electrode temperature, $T_{\text{electrode}}$, at the boron-doped diamond electrode as a function of the applied microwave power in aqueous 0.3 M NaOH. The data show that with gradual increase in microwave power, the temperature at the electrode|solution interface increases. A temperature limit consistent with the boiling point of water is again reached.

The mass transport coefficient, $k_{\text{mt}}^{\text{Fe(CN)}_6^{4-}}$, is a measure of the combined rate of diffusion and convection towards the electrode and was calculated using the following expression Eq. (1) [36]

$$k_{\text{mt}}^{\text{Fe(CN)}_6^{4-}} = \frac{I_{\text{lim}}}{nFAc} \quad (1)$$

In this equation I_{lim} denotes the mass transport limited current plateau (average), $n = 1$, the number of electrons transferred per

molecule diffusing to the electrode, $F = 96,487 \text{ C mol}^{-1}$, A is the electrode area (1.96×10^{-7} and $2.5 \times 10^{-7} \text{ m}^2$ for a 500 μm diameter glassy carbon and a 500 $\mu\text{m} \times 500 \mu\text{m}$ boron-doped diamond electrode, respectively) and $c = 5 \text{ mol m}^{-3}$, the bulk concentration. Fig. 2C and D shows the effect of microwave radiation on the mass transport coefficient for the oxidation of Fe(CN)_6^{4-} in aqueous 0.3 M NaOH and in 0.2 M NaCl (pH 12) solutions. The data clearly demonstrate that upon application of microwave radiation, $k_{\text{mt}}^{\text{Fe(CN)}_6^{4-}}$ is enhanced by more than one order of magnitude at both glassy carbon and boron-doped diamond electrodes. Further increases are possible at higher microwave power.

It is possible to compare the magnitude of this effect with the mass transport conditions reached at a rotating disc electrode under uniform temperature conditions. The variation in diffusion

coefficient due to temperature is accounted for by Eq. (2). In this expression $D_{293} = 7.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $E_a = 13 \text{ kJ mol}^{-1}$ is the diffusion coefficient at 293 K and the activation energy [37], respectively

$$D_T = D_{293} \exp\left(\frac{E_a}{8.31} \left(\frac{1}{293} - \frac{1}{T}\right)\right) \quad (2)$$

The increase in current density corresponds to a substantially increased mass transport parameter $k_{\text{mt}}^{\text{Fe(CN)}_6^{4-}}$ which can be expressed for the case of a rotating disc electrode [38] Eq. (3)

$$k_{\text{mt}}^{\text{Fe(CN)}_6^{4-}} = 0.62\omega^{1/2} D^{2/3} \nu^{-1/6} \quad (3)$$

In this equation the mass transport parameter $k_{\text{mt}}^{\text{Fe(CN)}_6^{4-}}$ is given by the rate of electrode rotation, ω the diffusion coefficient D ($2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 373 K), and the viscosity ν ($0.28 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ at 373 K). The equivalent rate of rotation to achieve mass transport conditions similar to those observed in the presence of microwaves is 14 kHz (for a 25 mA magnetron current) which is beyond the range of conventional rotation rates.

This is indicative for very fast mass transport conditions due to vigorous boiling (see Fig. 2E) and from the calibration plots it can be seen that further increases are still possible at higher microwave power.

3.2. Microwave activation effects for the phenol oxidation at glassy carbon and boron-doped diamond electrodes in alkaline aqueous media

The electro-oxidation of phenol has been widely studied [39] and the beneficial effects of power ultrasound [40] and of laser pulse electrode activation [32] have been considered. Here, the effects of microwave activation are reported and the phenol oxidation has been chosen as a model system to allow comparison with the more complex oxidation of triclosan. Fig. 3A shows typical cyclic voltammograms recorded in the absence of microwave radiation for oxidation of 0 mM (curve i), 1.0 mM (curve ii), and for 12.0 mM (curve iii) phenol solution in 0.3 M NaOH at polished 500 μm diameter glassy carbon electrode. An anodic peak can be seen at a potential of 0.45 V

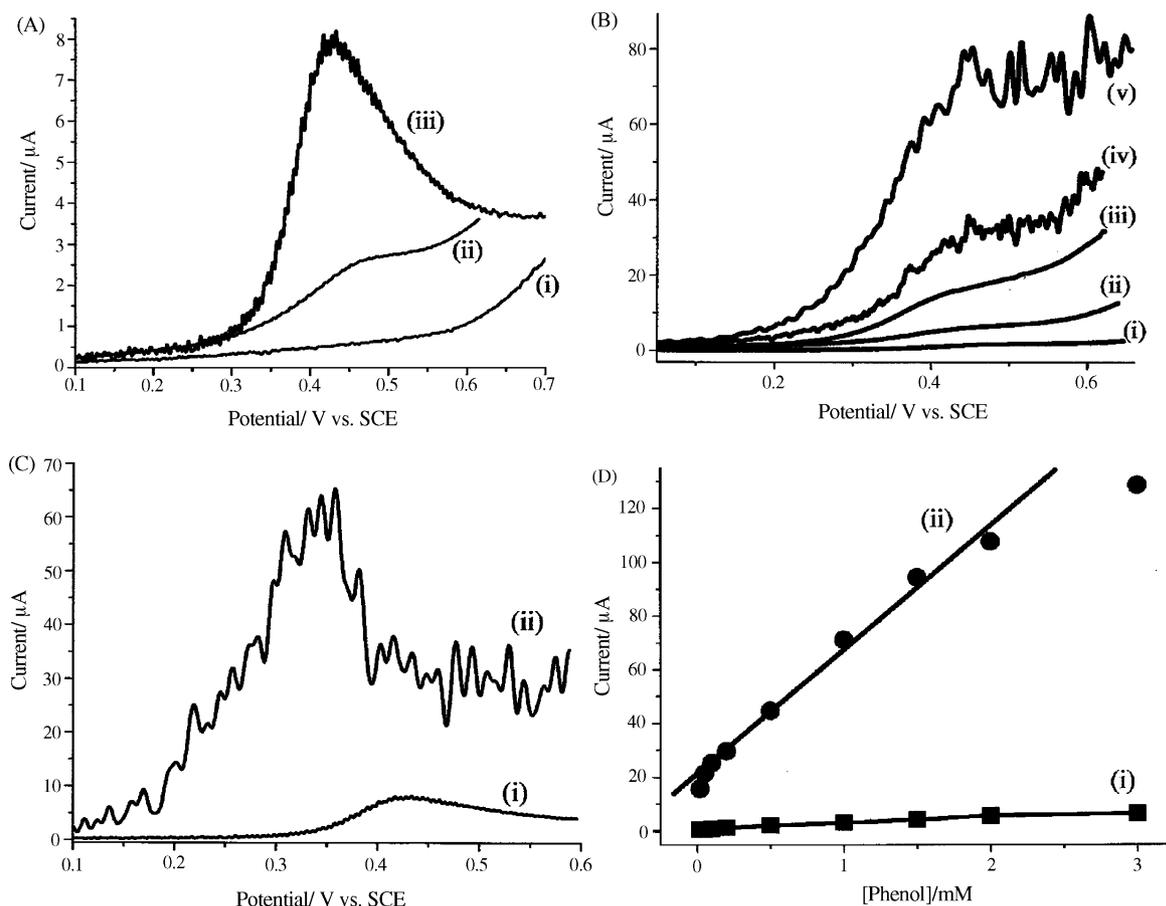


Fig. 3. (A) Cyclic voltammograms (scan rate 50 mV s^{-1}) for the phenol oxidation at a 500 μm diameter carbon disk electrode immersed in aqueous 0.3 M NaOH in the presence of (i) 0 mM, (ii) 1.0 mM, and (iii) 12.0 mM phenol in absence of microwave radiation. (B) Cyclic voltammograms (scan rate 50 mV s^{-1}) for the oxidation of 1.0 mM phenol in aqueous 0.3 M NaOH obtained at a 500 μm diameter glassy carbon disk electrode in the presence of microwave radiation (magnetron currents (i) 0 mA, (ii) 5 mA, (iii) 8 mA, (iv) 10, and (v) 20 mA). (C) Cyclic voltammograms (scan rate 50 mV s^{-1}) for the oxidation of 12.0 mM phenol in aqueous 0.3 M NaOH obtained at a 500 μm diameter glassy carbon disk electrode in absence (i) and in the presence (ii) of microwave radiation (magnetron currents 20 mA). In all experiments the electrode was pretreated at 3 V vs. SCE for 10 s before each scan. (D) Plot showing the relation between phenol concentration and anodic limiting current (i) in absence and (ii) in presence of microwave radiation generated by 20 mA magnetron current.

versus SCE which corresponds to the oxidation of phenol at carbon electrode. At the lower phenol concentration, 1.0 mM (curve ii), the cyclic response shows a peak response (ca. 3 μA) and at higher phenol concentration, 12.0 mM (curve iii) the response is only slightly increased. The unusually sharp peak shape at higher phenol concentration is consistent with polyoxyphenylene formation and rapid blocking of the electrode surface.

Fig. 3B shows cyclic voltammograms (scan rate 50 mV s^{-1}) for the oxidation of 1.0 mM phenol in aqueous 0.3 M NaOH obtained at a 500 μm diameter glassy carbon disk electrode in the presence of different microwave radiation intensities. In the presence of moderate microwave intensity (see Fig. 3B, curves ii, iii and iv) the phenol oxidation current is enhanced by approximately one order of magnitude and the onset of the boiling process can be observed. While with stronger microwave activation (curve v), the phenol oxidation current is enhanced over 20-fold. The limiting current observed under these conditions can be used in conjunction with Eq. (1) to obtain an estimate for the number of electrons, n , transferred per phenol molecule diffusing to the electrode surface (ignoring any effects due to the diffusion coefficient). For data in Fig. 3B this number is consistently 4–5 and therefore suggesting a multi-electron oxidation process (see for example Eq. (4))

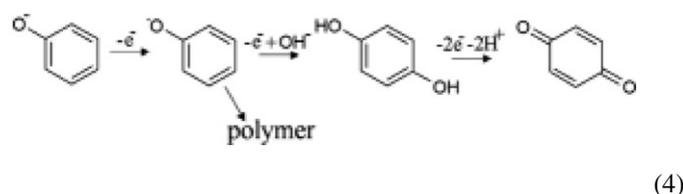


Fig. 3C shows the cyclic voltammograms for the oxidation of 12.0 mM phenol in 0.3 M NaOH at 500 μm carbon electrode in absence (i) and in presence (ii) of microwaves. From the peak shape of the response and the reduced limiting current partial blocking of the electrode surface seems likely. Therefore even under microwave conditions competition between multi-electron transfer and polyoxyphenylene formation and blocking occurs. At high phenol concentration an increase in current and a shift of the onset potential for phenol oxidation in the presence of microwave radiation are observed. This is consistent with the increase in mass transport and temperature at the electrode surface.

Fig. 3D shows a plot of the oxidation current versus phenol concentration at a glassy carbon electrode in 0.3 M NaOH in the presence (ii) and in the absence (i) of microwave radiation generated by 20 mA magnetron current. Under these conditions an approximately linear relationship has been obtained between oxidation current and phenol concentration in the 0.05–2.0 mM concentration range. The slope in presence of microwave radiation is ca. 20-fold increased.

When conducted at 500 $\mu\text{m} \times 500 \mu\text{m}$ boron-doped diamond electrodes, experiments gave very similar results. Both types of electrodes show very similar behaviour (see Fig. 2) and are suitable for the electro-oxidation of phenol under microwave conditions. Both types of electrodes are affected by partial blocking in the presence of elevated concentrations of phenol. For very

low concentrations of phenol, the background current at the electrodes was found to dominate the electrochemical response and for concentrations lower than 50 μM phenol in 0.3 M NaOH signals were not resolved anymore. Similar measurements in aqueous solutions containing lower concentrations of hydroxide or containing NaCl did not improve this situation. The concentration of hydroxide is particularly important in minimizing the blocking effect and allowing multi-electron transfer to phenol. However, increasing the concentration of NaOH does improve the voltammetric signal. Further work on the medium effects under microwave conditions will be required to reveal whether other types of additives allow electrode blocking to be suppressed more effectively.

3.3. Microwave activation effects for the triclosan oxidation at glassy carbon and boron-doped diamond electrodes in alkaline aqueous media

Triclosan is a regulated and widely used anti-bacterial and anti-fungal additive with a relatively short environmental half life. However, under sunlight or pyrolysis conditions it may form dioxin-type derivatives [41] and therefore monitoring of this compound is of interest. For the electrochemical oxidation of triclosan alkaline conditions are required to enhance solubility (pK_a 7.8) [42]. Experiments in 0.3 M NaOH were difficult to conduct and to reproduce at both glassy carbon and boron-doped diamond electrodes. Fig. 4A shows a typical set of data obtained at a 500 μm diameter glassy carbon disk electrode and in the presence of high microwave intensity and for different concentrations of triclosan. Although very noisy, the limiting currents can be observed and analysed. Based on Eq. (1) and calibration data in Fig. 2, the approximate number of electrons transferred per triclosan molecule reaching the electrode, $n = 0.8$, can be estimated.

Next, the experiments were conducted in 0.2 M NaCl at pH 12 to take advantage of the formation of anodic chlorine. Fig. 4B shows cyclic voltammograms (scan rate 50 mV s^{-1}) for the oxidation of 5.0 mM triclosan in aqueous 0.2 M NaCl (pH 12) obtained at a 500 $\mu\text{m} \times 500 \mu\text{m}$ boron-doped diamond electrode in the presence of microwave radiation generated by magnetron currents of (i) 0 mA, (ii) 15 mA, (iii) 20 mA, and (iv) 25 mA. The cyclic voltammograms recorded in the absence of microwave radiation (curve i) shows two anodic peaks at potentials of 0.55 V versus SCE and at 0.75 V versus SCE. The first peak is attributed to the direct oxidation of triclosan at the boron-doped diamond electrode and second peak arises from a secondary oxidation of triclosan probably through an initial blocking layer at the boron-doped diamond electrode (see for comparison [43]). In the presence of microwave activation (see Fig. 4B, curves ii, iii and iv) the triclosan oxidation current is enhanced by approximately one order of magnitude. However, electrode blocking which is enhanced by the hydrophobic nature of the triclosan molecule still occurs. Data in Fig. 4C shows the effect of scan rate on the oxidation of 5 mM triclosan at a boron-doped diamond electrode immersed in 0.2 M NaCl (pH 12) and in presence of microwave radiation generated by a 25 mA magnetron current. It can be seen that the anodic current

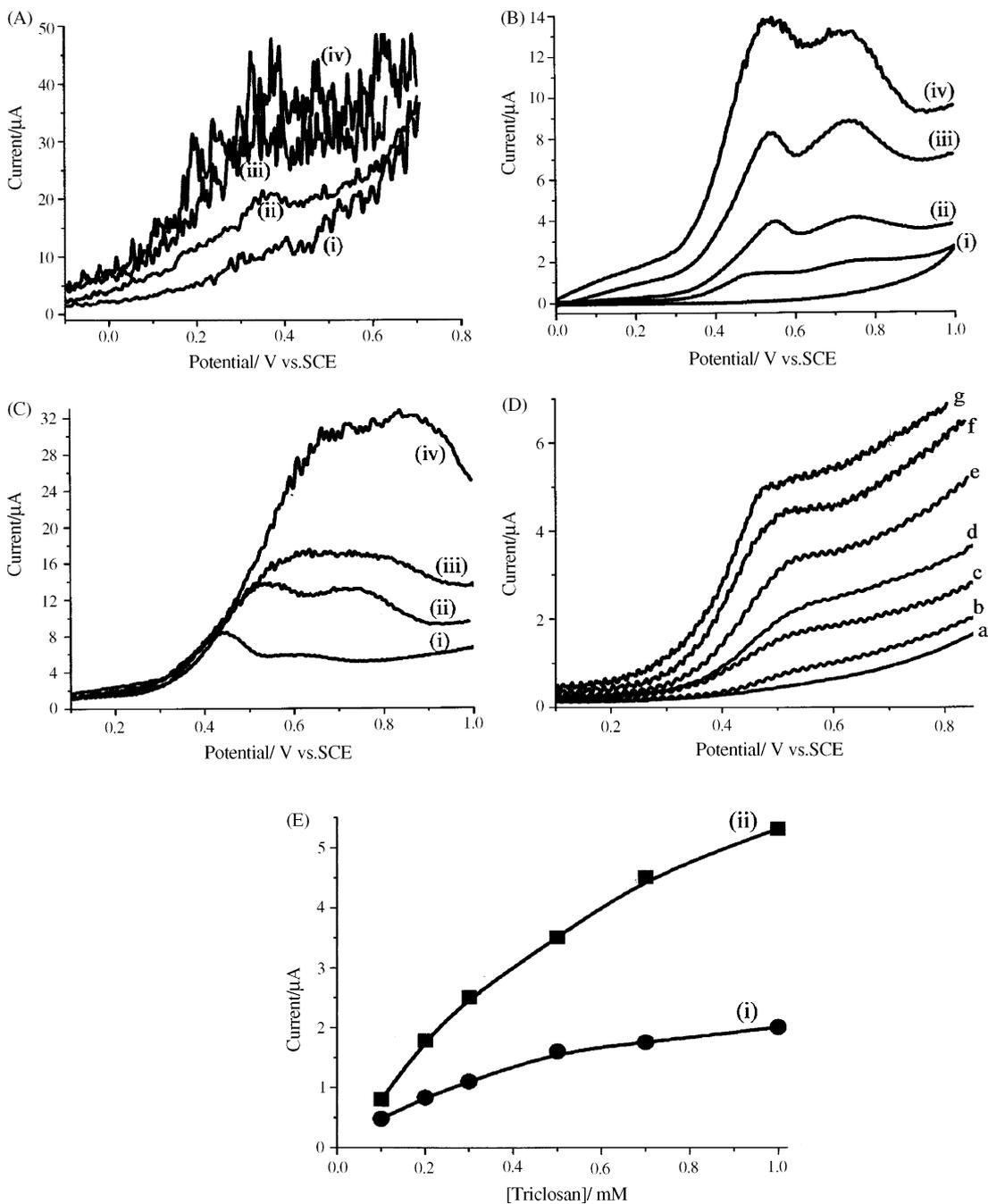
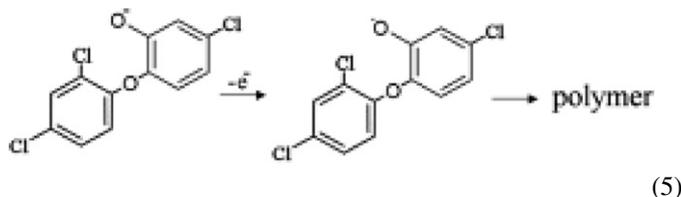


Fig. 4. (A) Cyclic voltammograms (scan rate 50 mV s^{-1}) for the oxidation of (i) 0.0 mM, (ii) 1.0 mM, (iii) 2.0 mM, (iv) 3.0 mM triclosan in aqueous 0.3 M NaOH obtained at a $500 \mu\text{m}$ diameter glassy carbon disk electrode in the presence of microwave radiation (magnetron current 20 mA). (B) Cyclic voltammograms (scan rate 50 mV s^{-1}) for the oxidation of 5.0 mM triclosan in aqueous 0.2 M NaCl (pH 12) obtained at a $500 \mu\text{m} \times 500 \mu\text{m}$ boron-doped diamond electrode in the presence of microwave radiation (magnetron currents (i) 0 mA, (ii) 15 mA, (iii) 20 mA, and (iv) 25 mA). (C) Cyclic voltammograms for the oxidation of 5.0 mM triclosan in aqueous 0.2 M NaCl (pH 12) obtained at a $500 \mu\text{m} \times 500 \mu\text{m}$ boron-doped diamond electrode in the presence of microwave radiation (magnetron currents 25 mA) at scan rates of (i) 10 mV s^{-1} , (ii) 50 mV s^{-1} , (iii) 100 mV s^{-1} , and (iv) 200 mV s^{-1} . The electrode was pretreated at 3 V vs. SCE for 10 s before each scan. (D) Cyclic voltammograms (scan rate 50 mV s^{-1}) in aqueous 0.2 M NaCl (pH 12) solution obtained at a $500 \mu\text{m} \times 500 \mu\text{m}$ boron-doped diamond electrode in the presence of microwave radiation (magnetron current 10 mA) and with added triclosan concentration of (a) 0.0 mM, (b) 0.1 mM, (c) 0.2 mM, (d) 0.3 mM, (e) 0.5 mM, (f) 0.7 mM, and (g) 1.0 mM. (E) Plot for the relationship between triclosan concentration and anodic oxidation current (i) in absence and (ii) in presence of microwave radiation generated by 10 mA magnetron current.

is considerably increased at higher scan rate and a current plateau is observed at ca. $32 \mu\text{A}$. It is possible to obtain an approximate number of electrons transferred based on the mass transport parameter (see Eq. (1) and Fig. 2) and this limiting

current. The result, $n=0.33$, is consistent with a transfer of less than or approximately one electron (the lower diffusion coefficient of triclosan is in part responsible for the low value) and therefore in agreement with the rapid formation of a polymeric

blocking layer at the electrode–solution interface (see Eq. (5))



Under optimized conditions and in the presence of microwave activation a triclosan concentration dependent anodic current response can be obtained. Fig. 4D shows voltammograms obtained at a boron-doped diamond electrode immersed in 0.2 M NaCl (pH 12) background electrolyte solution with different concentrations of triclosan subsequently added. At concentrations below 1 mM triclosan and in the presence of microwave radiation (10 mA magnetron current) a peak response is observed. At a scan rate of 50 mV s⁻¹ and higher triclosan concentrations, the cyclic voltammogram does not correlate with the concentration. The relation between the triclosan concentration and the limiting current of oxidation is shown in Fig. 4E. Plots for data obtained in the presence and in the absence of microwaves are non-linear and tend to reach a maximum at higher triclosan concentration even in the presence of microwave activation. Further experimental work will be required to overcome the blocking effect of hydrophobic molecules such as triclosan and to identify conditions for a cleaner anodic oxidation. The high temperature conditions and mass transport induced by microwave radiation clearly improve the redox processes and current densities but the interfacial polymer formation still remains a problem.

4. Conclusions

It has been shown that microwave activation is possible even at 500 μm sized carbon electrodes and that considerable mass transport and thermal effects are observed. For the case of phenol oxidation in alkaline aqueous media mass transport limited currents under microwave conditions are observed up to a concentration of ca. 2–3 mM and for triclosan up to ca. 1 mM. The hydrophobic nature of triclosan strongly enhances the ability to bind to the electrode surface and in future additives such as surfactants [19] may be beneficial to overcome this problem.

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