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Electrostatic accumulation and determination of triclosan in ultrathin carbon nanoparticle composite film electrodes

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Abstract

A film composed of carbon nanoparticles and poly(diallyldimethylammonium chloride) or CNP-PDDAC is formed in a layer-by-layer deposition process at tin-doped indium oxide (ITO) substrates. Excess positive binding sites within this film in aqueous phosphate buffer at pH 9.5 are quantified by adsorption of iron(III)phthalocyanine tetrasulfonate and indigo carmine. Both anionic redox systems bind with Langmuirian characteristics ($K \approx 10^5 \text{ mol}^{-1} \text{ dm}^3$) and show electrochemical reactivity throughout the film at different thicknesses. Therefore, the electrical conductivity in CNP-PDDAC films is good and the positive binding sites are approximately 140 pmol cm^{-2} per layer. Structural instability of the CNP-PDDAC film in the presence of high concentrations of iron(III)phthalocyanine tetrasulfonate or indigo carmine is observed.

Triclosan, a widely used anti-bacterial and anti-fungal agent, exists in aqueous media at pH 9.5 as a negatively charged chlorinated poly-aromatic phenol. Due to the negative charge, triclosan is readily accumulated into CNP-PDDAC films with an efficiency consistent with that expected for simple electrostatic interaction with the cationic binding sites. Oxidation of bound triclosan occurs at 0.6 V versus SCE in a chemically irreversible process. The CNP-PDDAC film electrode is renewed by rinsing in organic solvent and the triclosan oxidation response is shown to correlate with the triclosan concentration in solution from 0.5 to 50 μM . Applications of the CNP-PDDAC film electrode (or improved versions of it) in analysis or in anodic extraction are proposed.

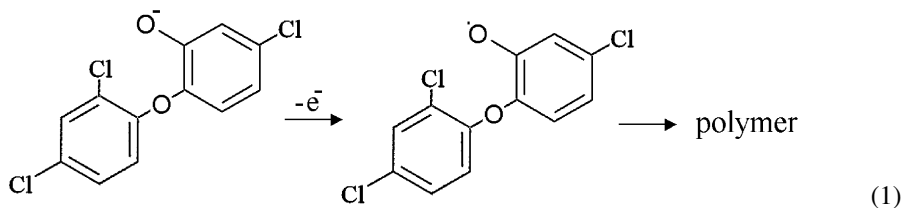
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Keywords: Carbon nanoparticle; Voltammetry; Triclosan; Irgasan; Phenol; Extraction; Anode; Sensor

1. Introduction

Triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether or Irgasan) is a widely used anti-fungal and anti-bacterial

formulation component with a phenolic chlorinated poly-aromatic hydrocarbon structure (see Eq. (1)). The phenolic compound is highly lipophilic and significantly soluble in water only as anion at sufficiently alkaline pH.



The oxidation of triclosan at electrode surfaces is facile but highly irreversible and usually associated with the formation of an insulating polymeric blocking film. The electroanalytical properties and the detection of triclosan have been investigated

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at mercury electrodes [1], at carbon microfibers [2,3], and at screen-printed carbon electrodes [4]. In a recent study the oxidation of triclosan has also been investigated at glassy carbon and at boron-doped diamond electrodes under high temperature conditions (induced by microwave radiation) [5]. The oxidation of triclosan is generally believed to follow a one electron pathway with adsorbed intermediates and strongly adsorbed oligomeric products (Eq. (1)). In order to overcome this problem new methods, for example the voltammetric determination in surfactant media [6], are required. Here, a novel structured mesoporous electrode based on a carbon nanoparticle composite is employed to accumulate triclosan and to minimize electrode blocking and polymerization of the oxidized phenol.

The adsorption of triclosan onto oxide surfaces has been exploited for the degradation, e.g. at TiO_2 particles in the presence of light [7] or chemically at MnO_2 colloid particle surfaces [8]. For analytical purposes solid phase microextraction (SPME) proved to be a powerful method for monitoring low levels of triclosan [9], the photochemical degradation products from triclosan [10], and triclosan traces in environmental samples [11]. The adsorption of hydrophobic triclosan onto surfaces is an important feature in its reactivity and adsorption onto positively charged CNP-PDDAC films should be facile in particular when the electrostatic interaction of the positively charged CNP-PDDAC film to triclosan can be exploited. The chemical processes associated with oxidation may be affected by the interaction with the CNP-PDDAC matrix.

In this study triclosan is adsorbed onto a carbon nanoparticle-poly(diallyldimethyl-ammonium chloride) or CNP-PDDAC nanocomposite film with positive excess charges. These kinds of films are prepared in a layer-by-layer electrostatic deposition procedure and have recently been demonstrated to bind anions from aqueous solution [12]. The number of binding sites is controlled by the number of deposition cycles or the film thickness. Starting with a single layer deposit an optically transparent carbon film is obtained [12], which upon further deposition gradually darkens. With each deposition layer the thickness is increased by approximately 6 nm [12]. It is demonstrated here that both the accumulation and detection of triclosan are possible within the same material, CNP-PDDAC, and over a wide concentration range. Triclosan oxidation within the nanocomposite does lead to water-insoluble products but these are readily removed by extraction into an organic solvent. In future this kind of CNP-PDDAC nanocomposite film could be employed to extract and determine triclosan and similar hydrophobic ions in a combined solid phase microextraction with electrochemical detection procedure (SPME-ED).

2. Experimental

2.1. Chemical reagents

Poly(diallyldimethylammonium chloride) (PDDAC, very low molecular weight, 35 wt.% in water, Aldrich), K_2HPO_4 (>99%, Sigma), sulfonated carbon nanoparticles (ca. 9–18 nm diameter, Emperor 2000, Cabot Corporation), indigo carmine (5,5'-indigodisulfonic acid, di-sodium salt), indigotrisulfonic

acid (tri-sodium salt), indigo tetrasulfonic acid (tetra-sodium salt) (all Aldrich), iron(III)phthalocyanine-4,4',4'',4'''-tetrasulfonic acid, monosodium salt (Sigma-Aldrich), triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether or Irgasan, Fluka) were obtained commercially and used without further purification. Demineralized and filtered water of resistivity not less than 18 M Ω cm was taken from an Elga water purification system. Argon (Pureshield, BOC) was employed for de-aeration of electrolyte solutions. If not stated otherwise, all experiments were carried out at $20 \pm 2^\circ\text{C}$.

2.2. Instrumentation

A three-electrode micro-Autolab III potentiostat system (Eco Chemie, NL) was employed to control the potential at the working electrode. The counter electrode was a platinum wire (0.5 mm diameter, 2 cm long) and a saturated (KCl) calomel electrode (SCE, Radiometer) was the reference electrode. The working electrodes were made from tin-doped indium oxide (ITO) coated glass (1 cm \times 6 cm, 30 Ω per square, Image Optics, Basildon, UK). The electrode area of working electrodes was kept constant at 1 cm². ITO electrodes were cleaned prior to use by rinsing in ethanol and distilled water followed by drying and 30 min heat treatment in an Elite tube furnace at 500 $^\circ\text{C}$ in air.

2.3. Procedures

Films of carbon nanoparticles were deposited onto ITO glass electrodes following a layer-by-layer assembly method [13]. In the first step the ITO electrode was dipped for 30 s in a solution containing 10 mg/10 cm³ carbon nanoparticles in demineralized water (sonicated for one hour prior to use). After rinsing with water, the electrode was then dipped for 30 s into 1 wt.% solution of poly-(diallyldimethylammonium chloride) (PDDAC) in water. With a final rinsing step with water the first deposition cycle was completed. The black colour of the deposit is immediately apparent [12]. Additional layers of the carbon nanoparticle-PDDAC nanocomposite (leading to a darker colouration of the electrode) were deposited by repeating this process.

3. Results and discussion

3.1. Formation and characterisation of carbon nanoparticle—PDDAC composite film electrodes

The layer-by-layer assembly and use of carbon nanoparticle-poly(diallyldimethyl-ammonium chloride) (CNP-PDDAC) films has been reported recently [12] and may be regarded as an example of a wider range of nanocomposite assemblies formed with PDDAC [14]. The CNP-PDDAC films assemble (at least in part) due to the electrostatic interaction between negatively charged carbon surfaces and the poly-cationic binder and remain structurally stable as long as no other strongly interacting cation or anion (vide infra) is present. Typical AFM images of the film are shown in Fig. 1.

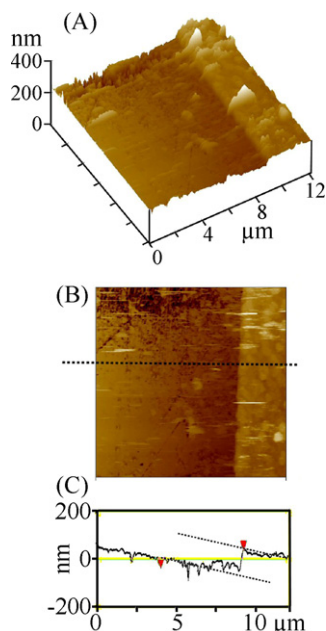


Fig. 1. AFM images of a 20-layer CNP-PDDAC film deposit on an ITO substrate. The film was scratched to expose the substrate and from the step height the overall film thickness of 120 nm can be estimated (or 6 nm per layer).

The deposit forms uniformly and the thickness increases by approximately 6 nm in each deposition cycle (see step height in Fig. 1C). The carbon nanoparticles in this film are tightly bound and electrical conductivity throughout the film is good. This is reflected for example in the increase in capacitive background currents which is increased by ca. $10 \mu\text{F cm}^{-2}$ per layer [12].

The properties of CNP-PDDAC films are to some extent dependent on pH and prior to triclosan accumulation experiments at pH 9.5 the films are characterized by adsorption of two anionic model redox systems, indigo carmine and iron(III)phthalocyanine tetrasulfonate. These redox systems are employed to “calibrate” the reactivity and the number anion binding sites within the film. The anion binding sites are then employed for the study of the triclosan binding and reactivity.

3.2. Calibration of anion binding sites in CNP-PDDAC by immobilisation of indigo carmine

Anionic redox systems such as indigo carmine are readily bound into CNP-PDDAC films [12] and this allows the film reactivity and binding capacity to be explored and correlated to the film thickness. Fig. 2 shows cyclic voltammograms recorded for the reduction and re-oxidation of indigo carmine (a 2-electron process [15]) for a 20 layer CNP-PDDAC film electrode. Indigo carmine was immobilized into the CNP-PDDAC film electrode during immersion (60 s) of the electrode into a solution of indigo carmine in 0.1 phosphate buffer solution pH 7 or pH 9.5 (the effect of pH during the adsorption step was negligible. However, CNP-PDDAC film stability during adsorption of high concentrations of indigo carmine is better at pH 7). Voltammetric measurements were carried out in a separate buffer solution without indigo carmine. The peak current is linearly correlated to the scan rate consistent with a surface immobilized redox

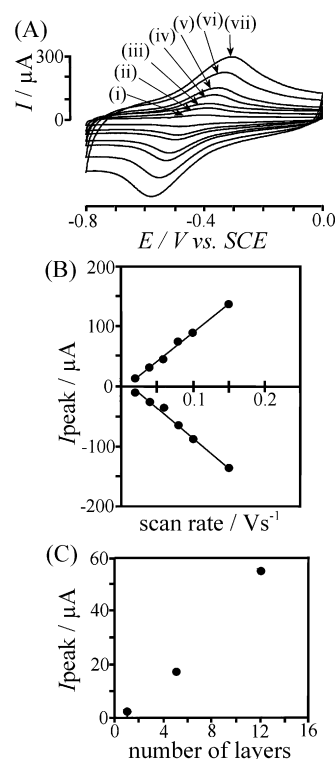


Fig. 2. (A) Cyclic voltammograms (scan rate (i) 20, (ii) 40, (iii) 60, (iv) 80, (v) 100, (vi) 150, and (vii) 200 mV s^{-1}) for the reduction and re-oxidation of indigo carmine adsorbed into a 20 layer CNP-PDDAC film electrode (adsorbed from 0.05 mM indigo carmine in 0.1 M phosphate buffer pH 7) and immersed in aqueous 0.1 M phosphate buffer pH 9.5. (B) Plot of the anodic and the cathodic peak current vs. the scan rate consistent with an adsorbed redox system. (C) Plot of the anodic peak current (from cyclic voltammograms with scan rate 100 mV s^{-1}) vs. the number of layers of CNP-PDDAC nanocomposite.

system (see Fig. 2B). The peak-to-peak separation can be seen to increase with scan rate and this effect is likely to be caused here by the resistance of the ITO film rather than slow interfacial electron transfer.

Voltammograms recorded as a function of the number of CNP-PDDAC layers deposited at the ITO electrode surface show the expected linear increase in peak current with film thickness (see Fig. 2C). Next, the effect of the indigo carmine concentration during immobilization is explored. Similar to observations made in experiments in pH 7 buffer solution, the binding of indigo carmine in pH 9.5 phosphate buffer follows a Langmuir trend (see Fig. 3). The binding constant can be estimated as $K = 10^5 \text{ mol}^{-1} \text{ dm}^3$ and the number of cationic binding site is approximately 140 pmol cm^{-2} per layer.

It is interesting to note that additional experiments with the more highly charged indigo tetrasulfonate and indigo trisulfonate failed due to instability of the CNP-PDDAC films in the presence of these more highly charged anions. CNP-PDDAC films were attacked and dissolved from the ITO electrode surface probably due to the stronger interaction of PDDAC with the poly-sulfonate anions rather than the poly-sulfonated carbon nanoparticles. This stronger interaction could have resulted in restructuring or even dissolution of film components. A similar effect occurs also at higher concentrations of indigo carmine.

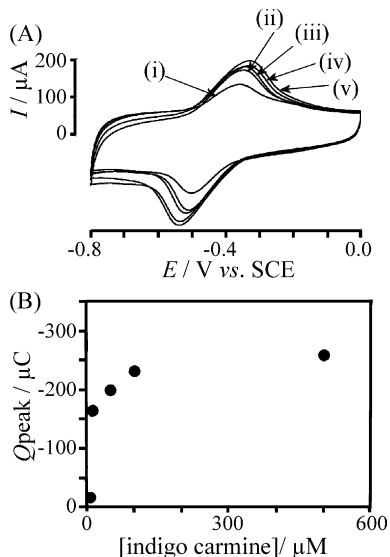


Fig. 3. (A) Cyclic voltammograms (scan rate 100 mV s^{-1}) for the reduction and re-oxidation of indigo carmine adsorbed from (i) 5, (ii) 10, (iii) 50, (iv) 100, and (v) $500 \mu\text{M}$ solution into a 20 layer CNP-PDDAC film electrode and immersed in aqueous 0.1 M phosphate buffer pH 9.5. (B) Plot of the anodic peak current vs. the adsorption concentration of indigo carmine in a 20-layer CNP-PDDAC film electrode and immersed in aqueous 0.1 M phosphate buffer pH 9.5.

3.3. Attempted calibration of anion binding sites in CNP-PDDAC by immobilisation of iron(III)phthalocyanine tetrasulfonate

A further anionic redox system suitable for the determination of binding sites in CNP-PDDAC film electrodes is

iron(III)phthalocyanine tetrasulfonate. Iron(III)phthalocyanine metal complexes have been employed in electrocatalysis [16,17] and in the analytical determination for example of ascorbic acid [18]. Phthalocyanine tetrasulfonate metal complexes are known to bind to PDDAC and to form assemblies at electrodes [19,20]. When adsorbed from aqueous phosphate buffer solution the iron(III)phthalocyanine tetrasulfonate metal complex is readily detected as a reversible redox system at 0.15 V versus SCE (see Fig. 4A). This reversible process is attributed to the $\text{Fe(III)}\text{--Fe(II)}$ one electron reduction of the metal complex [21]. The adsorption occurs with characteristics very similar to those for indigo carmine and with a Langmuirian binding constant of approximately $10^5 \text{ mol}^{-1} \text{ dm}^3$ (see Fig. 4B). The amount of deposit (or charge under the reduction peak) scales with the film thickness and the voltammetric waves for reduction and re-oxidation are consistent with an electrochemically reversible immobilized redox system. Integration of the charge under the voltammetric peak (for $500 \mu\text{M}$ iron(III)phthalocyanine tetrasulfonate) allows the number of binding sites to be estimated as 40 pmol cm^{-2} per layer of CNP-PDDAC. This value is considerably lower compared to that determined with indigo carmine. Data obtained by adsorption of the metal complex in 0.1 M phosphate buffer at pH 9.5 results in even lower values (not shown). Indeed, by further increasing the concentration of iron(III) phthalocyanine tetrasulfonate during the adsorption process a decrease of the peak current and dissolution of the CNP-PDDAC film are observed. Therefore the number of binding sites cannot be reliably determined with iron(III)phthalocyanine tetrasulfonate.

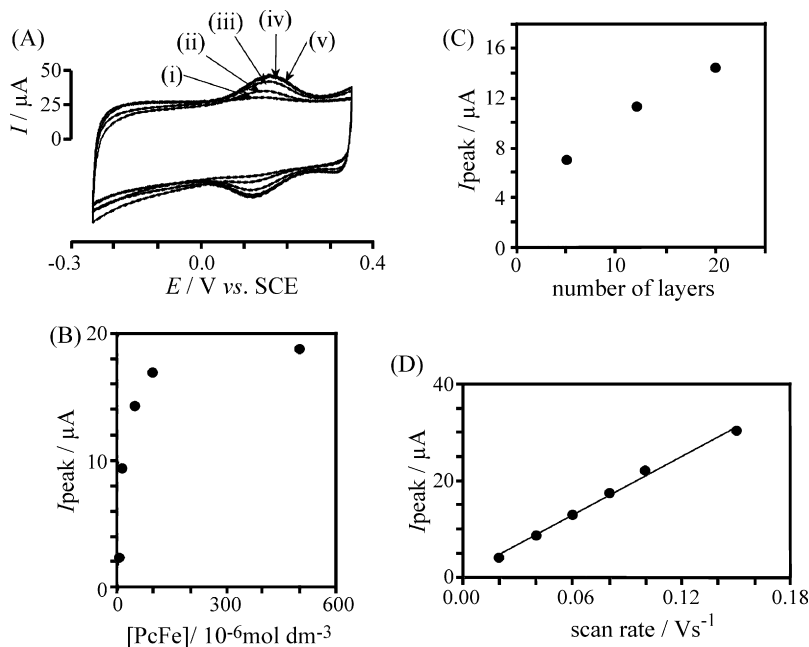


Fig. 4. (A) Cyclic voltammograms (scan rate 100 mV s^{-1}) for the reduction and re-oxidation of iron(III)phthalocyanine tetrasulfonate adsorbed from (i) 5, (ii) 10, (iii) 50, (iv) 100, and (v) $500 \mu\text{M}$ solution in phosphate buffer pH 7 into a 20 layer CNP-PDDAC film electrode and immersed in aqueous 0.1 M phosphate buffer pH 9.5. (B) Plot of the anodic peak current vs. various concentration of iron(III) phthalocyanine tetrasulfonate adsorbed into a 20 layer CNP-PDDAC film electrode and immersed in aqueous 0.1 M phosphate buffer pH 9.5. (C) Plot of the anodic peak current (at scan rate 100 mV s^{-1} , concentration $50 \mu\text{M}$) vs. the number of layers of CNP-PDDAC nanocomposite. (D) Plot of the anodic peak current (20 layer CNP-PDDAC, concentration $100 \mu\text{M}$) vs. the scan rate consistent with an adsorbed redox system.

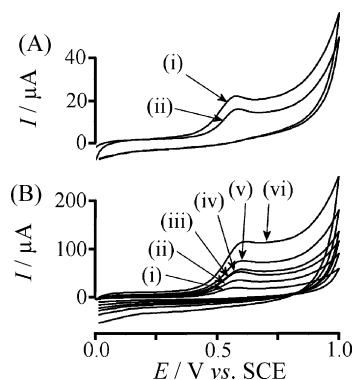


Fig. 5. (A) Cyclic voltammograms (1st and 2nd cycle shown, scan rate 0.02 V s^{-1}) for the oxidation of triclosan adsorbed from a 0.05 mM solution and immersed into aqueous 0.1 M phosphate buffer pH 9.5 at a 20 layer CNP-PDDAC film electrode. (B) Cyclic voltammograms (scan rate (i) 20, (ii) 40, (iii) 60, (iv) 80, (v) 100, and (vi) 150 mV s^{-1}) for the oxidation 0.05 mM Triclosan in 0.1 M phosphate buffer pH 9.5 at a 20 layer CNP-PDDAC film electrode.

3.4. Accumulation and determination of triclosan in aqueous buffer media

Triclosan is soluble in aqueous 0.1 M phosphate buffer at pH 9.5 solution but readily binds to CNP-PDDAC film electrodes. Fig. 5 shows voltammograms obtained for the oxidation of triclosan adsorbed from $50 \mu\text{M}$ solution into a 20 layer CNP-PDDAC film electrode. The oxidation is observed as a peak at 0.6 V versus SCE.

In Fig. 5A the first and the second potential cycle are shown. At triclosan concentrations higher than 0.1 mM the second potential cycle does not usually exhibit the oxidation peak presumably due to blocking. At lower concentration (see Fig. 5A) the peak disappears gradually. At a higher scan rate of 0.1 V s^{-1} the oxidation peak observed in the second potential cycle is reduced more rapidly. This may be attributed to effective binding and electrode blocking by oxidation products (see Eq. (1)) and a slow rate of re-adsorption of triclosan after the oxidation. The CNP-PDDAC electrode can be re-used after dipping into an organic solvent (such as dichloromethane) to remove hydrophobic oxidation products. This effect is believed to be caused by the lower probability of radical intermediates to form oligomeric products. When bound into the CNP-PDDAC matrix products of lower molecular weight may dominate. With increasing numbers of CNP-PDDAC layers, the anodic peak for triclosan oxidation increases (see Fig. 6). However, the increase is less than proportional and a second broad oxidation process is observed at more positive potentials. It is likely that products from the triclosan oxidation are responsible for this more complex behaviour.

Next, the effect of triclosan concentration during the adsorption process is investigated. Fig. 7 shows a typical set of triclosan oxidation responses as a function of triclosan concentration. The triclosan oxidation is observed at sub-micromolar level and the signal increases systematically with concentration.

The voltammetric peak current continues to increase with higher triclosan concentration but at a slower rate. It is possible to evaluate the charge under the oxidation response observed

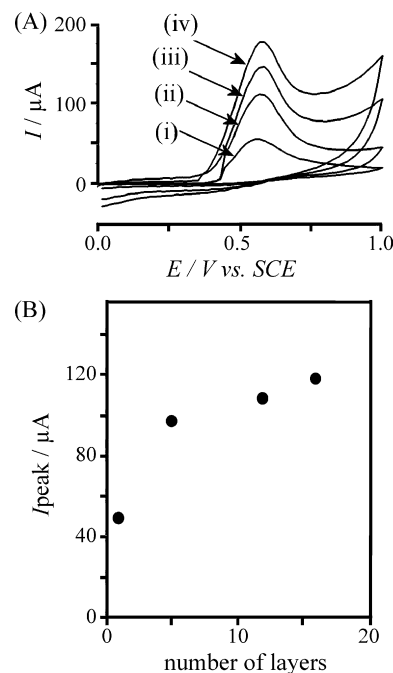


Fig. 6. (A) Cyclic voltammograms (scan rate 0.1 V s^{-1}) for the oxidation 0.05 mM triclosan in 0.1 M phosphate buffer pH 9.5 obtained at (i) 1 layer, (ii) 5 layer, (iii) 12 layer, and (iv) 16 layer CNP-PDDAC nanocomposite electrode. (B) Plot of the anodic peak current vs. the number of layers of CNP-PDDAC nanocomposite.

in the presence of $50 \mu\text{M}$ triclosan and this suggests binding of ca. 120 pmol cm^{-2} triclosan per layer of CNP-PDDAC. At higher concentration this value increases somewhat. However, this level of adsorption is clearly consistent to that observed for indigo carmine (or the number of cationic binding sites in the

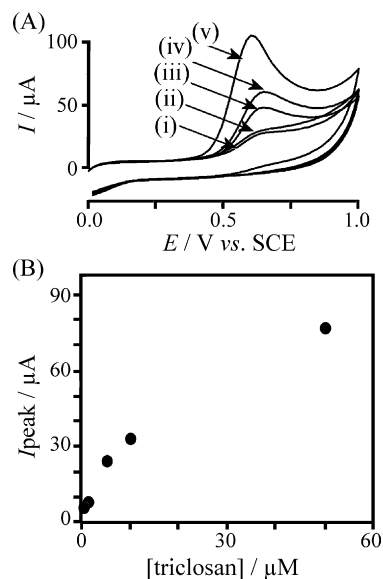


Fig. 7. (A) Cyclic voltammograms (scan rate 100 mV s^{-1}) for oxidation of triclosan adsorbed from (i) 0.5 , (ii) 1 , (iii) 5 , (iv) 10 , and (v) $50 \mu\text{M}$ solution and immersed in aqueous 0.1 M phosphate buffer pH 9.5 at a 20 layer CNP-PDDAC film electrode. (B) Plot of the anodic peak current vs. various concentration of triclosan in aqueous 0.1 M phosphate buffer pH 9.5 for a 20-layer CNP-PDDAC film electrode.

film) and therefore electrostatic binding of triclosan is likely to dominate the accumulation process. Therefore, by controlling the number and the density of cationic binding sites within the CNP-PDDAC film the accumulation of triclosan can be affected and the film properties further optimized.

4. Conclusions

It has been demonstrated that triclosan, a phenolic polychlorinated aromatic hydrocarbon, can be accumulated into a CNP-PDDAC film electrode and determined within the concentration range 0.5–50 μM by direct oxidation. The resulting poly-phenoxy coupling products appear to be of relatively low molecular weight and are readily desorbed into organic solvents and the electrode can be re-used. The structural stability of the CNP-PDDAC layer-by-layer deposit was found to be sensitive to multiply charged hydrophobic anions in particular in alkaline solution. Further study of the reactivity, stability, and application of these films in quantitative analysis will be required and the structural parameters e.g. the type of PDDAC polymer chain length need to be optimized. Overall, the electrostatic binding effect and the combined use of solid phase extraction and electrochemical detections are proposed as new methodological developments.

Acknowledgements

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