

TRICLOSAN DETECTION IN WATER USING nZnO IMMOBILIZED ONTO CARBON ELECTRODE WITH MULTIWALLED CARBON NANOTUBE

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Introduction

The extensive use of triclosan, (5-chloro-2-(2,4-dichlorophenoxy) phenol), as a common antibacterial agent in personal care products has increased in recent years. Triclosan is used in products such as toothpaste, soaps, cosmetics, socks and underwear [1,2]. Triclosan enters sewage systems during the use of the aforementioned products and, thereafter, can be transported to wastewater sewage treatment plants. The concentration of triclosan at ng L⁻¹ levels has been reported in different water systems [3]. Under UV irradiation and high pH, triclosan is known to degrade into products with chemical structures similar to that of dioxin compounds [4]. The effects of triclosan on humans include, but not limited to, mild itching and allergic redness on sensitive skins. Several analytical techniques have been used to detect triclosan. Of all the techniques, electrochemical methods offer the opportunity for portable, sensitive and rapid methodologies. One promising approach to further improve the oxidation of triclosan is the use of materials such as metal oxide nanoparticles such as nZnO and carbon nanotubes in composites. ZnO has a large excitonic energy, low-cost synthesis, biocompatibility, good electrochemical activities, non-toxicity, high-electron communication features and high mechanical strength [5]. It is also well known that CNTs are suitable materials for modification of electrodes and support in sensor applications because of good porosity, high electrical conductivity and high chemical stability [6]. Consequently, CNTs can be used to immobilize nZnO onto electrodes. For the aforementioned reasons, it is highly desirable to fabricate highly sensitive, rapid and reliable analytical methods for the detection of triclosan.

Materials and methods

All reagents were of analytical grade and were used without further purification. Stock solutions of triclosan were prepared by dissolving a measured amount in minimum amount of 0.1 M NaOH and diluting with water. N,N-dimethylformamide, nZnO < 50 nm, multi-walled carbon nanotube, K₃Fe(CN)₆, K₄Fe(CN)₆, were purchased from Sigma-Aldrich (South Africa). Phosphate buffers were prepared at different pH values by mixing standard stock solutions of 0.10 M Na₂HPO₄ and 0.10 M NaH₂PO₄ and adjusting the pH with either 0.1 M H₃PO₄ or NaOH from Merck, South Africa. All solutions were prepared using Milli-Q water (resistivity >18 M Ω cm⁻¹). Electrochemical measurements were performed using a BASi CV-50W voltammetric analyser (Bioanalytical Systems, West Lafayette, Indiana, USA) equipped with a conventional three-electrode cell consisting of a modified glassy carbon (GC) working electrode, a Ag/AgCl reference electrode and a Pt wire auxiliary electrode. The SWV was recorded with an amplitude potential and frequency of 25 mV and 15 Hz respectively. The phosphate buffer was purged with high-purity nitrogen for at least 15 min before use and during the experiments. The pH measurements were carried out with a Crison 2001 micro pH-meter (Spain).

Before modification, the GC electrode was thoroughly polished to a mirror finish using a BASi polishing kit containing 1.0, 0.3 and 0.05 μm diamond slurry, and thereafter, rinsed thoroughly using ultra-pure water before finally rinsed ultrasonically in ethanol and ultra-pure water for 10 min. Thereafter, the cleaned GC electrode was dried in air. The composite was prepared by dispersing nZnO-MWCNT (1: 3 w/w) with the aid of ultrasonic agitation for 1 h in 1 mL of DMF to give 1 mg mL⁻¹ dispersion. A 5 μL aliquot of this dispersion was then applied to the GC electrode surface. After drying the electrode in air, the resultant electrode, nZnO-MWCNT/GC, was stored at room. For comparison the nZnO/GC and MWCNT/GC electrodes were also prepared. The fabricated sensor was later applied to the detection of triclosan in spiked tap water.

Results and discussion

Figure 1 represents the CVs of (a) bare GC electrode, (b) nZnO/GC electrode (c) MWCNT/GC electrode and (d) nZnO/MWCNT/GC electrode, which were recorded in a 1 mM [Fe(CN)₆]^{3-/4-} solution containing 0.1 M KCl at 100 mV s⁻¹.

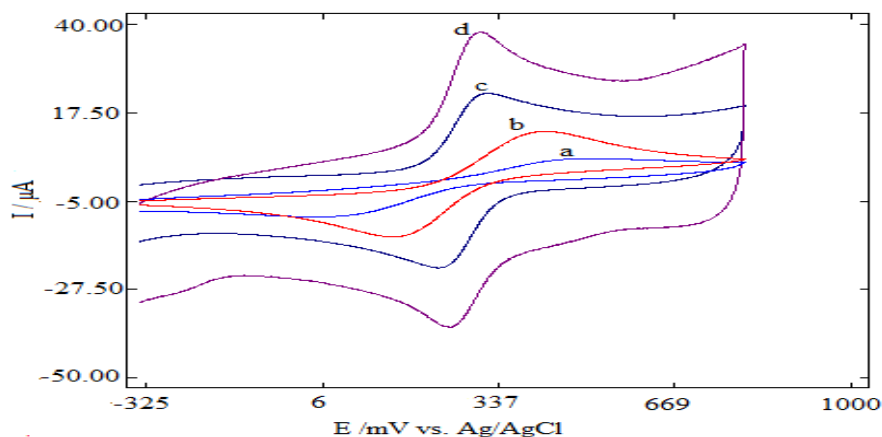


Figure 1 CVs of (a) bare GC electrode, (b) nZnO/GC electrode (c) MWCNT/GC electrode and (d) nZnO/MWCNT/GC electrode

A pair of peaks corresponding to the redox reaction of ferricyanide were observed (Figure 1). As can be seen in Figure 1, there is an increase in the peak current at nZnO/GC electrode compared to the bare GC electrode. There was a further increase in the peak current of MWCNT/GC electrode when compared to nZnO/GC electrode. However, the nZnO/MWCNTs/GC electrode exhibited the highest peak current, signifying the highest electrocatalytic activity as a result from its highest electroactive surface area. Furthermore, the peak-to-peak potential separation between the cathodic and anodic waves of the nZnO/MWCNTs/GC electrode is smaller as compared to the bare GC electrode, nZnO/GC electrode and MWCNT/GC electrode. To improve the analytical characteristics of the developed sensor, optimization of experimental conditions such as scan rate, pH, ratio of MWCNT: nZnO used, concentrations of MWCNT: nZnO and volume of MWCNT: nZnO injected were carried out. The optimized parameters were, thereafter, applied in the triclosan study. The oxidation of triclosan at modified GC electrodes was characterized by cyclic voltammetry. As can be seen in Figure 2A, a featureless cyclic voltammogram (*curve a*) of 0.1 M PBS (pH 7) alone at a nZnO-MWCNT/GC electrode was observed as only a background current at 100 mV s^{-1} . On addition of 4 mg L^{-1} triclosan into PBS, an irreversible oxidation peak at 600 mV was obtained at electrode, as shown in *curve b*. This is most likely caused by the oxidation of the phenolic function group of triclosan [7]. When this experiment was repeated using a bare GC electrode (*curve c*), an nZnO/GC electrode (*curve d*) and a MWCNT/GC electrode (*curve e*), the oxidation potential was observed to shift negatively from 680 mV, to 670 mV and 643 mV, respectively. The increase in peak currents and shift of the oxidation peak potential toward the lesser negative value obtained at nZnO-MWCNT/GC electrode in contrast to other electrodes, indicated that the coexistence of nZnO and MWCNT allowed fast electrode kinetics on the GC electrode.

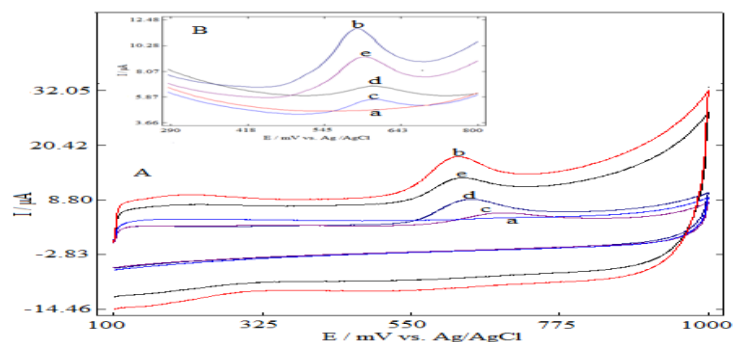


Figure 2 Cyclic voltammogram of (a) nZnO-MWCNT/GC (b) triclosan + nZnO/GC electrode, (c) GC electrode, (d) nZnO/GC electrode and (e) MWCNT/GC electrode

To further verify the oxidation of triclosan, the differential pulse voltammograms (DPVs) for triclosan at the modified and unmodified electrodes were also recorded (Figure 2B). As seen in Figure 2B, the DPV for blank (*curve a*) at nZnO-MWCNT/GC electrode did not show any anodic peak in the potential range studied. The DPVs for triclosan at the nZnO-MWCNT/GC electrode (*curve b*), GC electrode (*curve c*), nZnO/GC electrode (*curve d*)

and MWCNT/GC electrode (*curve e*) were also obtained. The DPV for GCE showed a small anodic peak while for nZnO/GC electrode, MWCNT/GC electrode, and nZnO-MWCNT/GC electrode showed sharp and well defined peak shapes. The peak for nZnO-MWCNT/GC electrode appeared at about 600 mV as observed in cyclic voltammetry.

The relationship between the anodic peak current and concentration of triclosan was studied using SWV under optimal experimental conditions for obtaining the voltammetric traces (Figure 3). The anodic peak current increased with the increase of triclosan concentration. The calibration plot Figure 3 (*inset*) was linear over the concentration range $1.5 \mu\text{g L}^{-1}$ to 2.0 mg L^{-1} . The linear regression equation at 95% confidence interval, degrees of freedom ($n-2$) can be expressed as $I_p (\mu\text{A}) = 0.0036 (\pm 0.00027) \mu\text{g L}^{-1} + 2.2 (\pm 0.27)$ with a coefficient of determination ($R^2 = 0.9931$, $n = 6$) [8]. The detection limit (LOD) was $1.3 \mu\text{g L}^{-1}$, calculated using the formula as $3 s/b$, where s is the standard deviation of the peak currents ($n = 3$) and b is the slope of the calibration plot. The performance of the developed nZnO-MWCNT/GC electrode sensor compared with other reported triclosan sensors are summarized in Table 1. From the results, it can be concluded that the nZnO-MWCNT/GC electrode sensor exhibited a wider range and lower detection limit. The study indicated that the synergistic effect of nZnO nanoparticles and MWCNT contributed to the excellent electrochemical performance of the hybrid film sensor. Consequently, the nZnO-MWCNT/GC electrode sensor could be an excellent platform for the detection of triclosan in different environmental matrices.

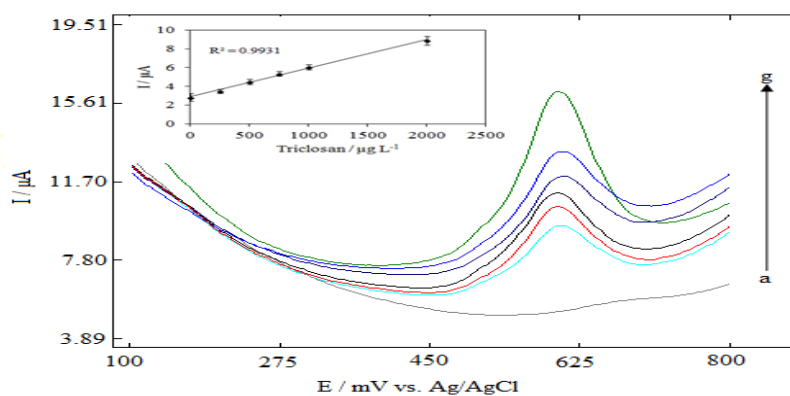


Figure 3 relationship between the anodic peak current and concentration of triclosan

Table 1: Comparison of the response of the fabricated sensor for detection of triclosan with other sensors based on different composites

Electrode	Linear range ($\mu\text{g L}^{-1}$)	Detection limit ($\mu\text{g L}^{-1}$)	Reference
Screen-printed carbon electrode	$1.2 \mu\text{M} - 1.0 \text{ mM}$	$1.2 \mu\text{M}$	[7]
Mercury electrode	$2.5 \mu\text{g L}^{-1} - 60 \mu\text{g L}^{-1}$	$1.9 \mu\text{g L}^{-1}$	[8]
MWCNT	$50 \mu\text{g L}^{-1} - 1.75 \text{ mg L}^{-1}$	$16.5 \mu\text{g L}^{-1}$	[9]
CNDS-CS/GCE	$2.9 \mu\text{g L}^{-1} - 0.29 \text{ g L}^{-1}$	$2.7 \mu\text{g L}^{-1}$	[5]
glassy carbon rod	$10-600 \mu\text{g L}^{-1}; 1-8 \text{ mg L}^{-1}$	$5 \mu\text{g L}^{-1}$	[5]
nZnO-MWCNT/GC electrode	$1.5 \mu\text{g L}^{-1} - 2.0 \text{ mg L}^{-1}$	$1.25 \mu\text{g L}^{-1}$	Present study

CNDS: Carbon nanodots; CS: chitosan; MWCNT: multiwalled carbon nanotubes; nZnO: zinc oxide nanoparticles; GCE: glassy carbon electrode

The stability of the nZnO-MWCNT/GC electrode sensor was also investigated by storing the same electrode at room temperature. For detection of 0.1 mg L^{-1} triclosan using SWV, there was a small decrease in anodic peak current of 5% in the first week. A 90% response current was still retained after one month. Consequently, the stability of the proposed electrode was good enough for continual operation. The intra-assay precision was evaluated by assaying triclosan level for five times on the same sensor. The relative standard deviation (RSD%) for the intra-assay was 3.1% at 0.1 mg L^{-1} triclosan. The same triclosan concentration was used for the inter-assay

precision on five sensors. The fabricated sensors showed a relative standard deviation (RSD%) of 3.5%. The obtained results demonstrated that the nZnO-MWCNT/GC electrode has good stability, repeatability and reproducibility, and could be used for triclosan detection.

To demonstrate the feasibility of the fabricated sensor for possible environmental applications, preliminary application of the sensor was examined by determination of triclosan in five tap water samples by standard addition method under the optimized conditions. The results are given in Table 2. The recoveries were in the range of 96.4–101.5%, which indicated the efficacy of the sensor for practical analysis.

Table 2 Recovery test for triclosan in tap water.

Sample (tap water)	Triclosan added ($\mu\text{g L}^{-1}$)	Triclosan found ($\mu\text{g L}^{-1}$) ^a	Recovery (%)
1	20	20.3 \pm 0.2	101.5
2	50	48.2 \pm 0.1	96.4
3	100	97.3 \pm 0.02	97.3
4	300	303.5 \pm 0.01	98.8
5	650	648.7 \pm 0.1	99.8

Quantitative determination of triclosan from tap water sources spiked with known quantity of triclosan; ^a Average of three determinations.

In the present paper, a simple, inexpensive and efficient method for the fabrication of nZnO-MWCNT-modified electrode which can be used as a sensor was studied. The irreversible oxidation of triclosan was investigated using PBS (pH 7.0) and was found to be pH dependent. The detection limit was 1.3 $\mu\text{g L}^{-1}$. Good recoveries were obtained and ranged from 96.4–101.5%. Stability test provides evidence that the sensor could be used as a management tool for determining the quality of water for the existence of triclosan and related products.

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