

RESEARCH PAPER

Sensitive Electrochemical Determination of Chlorocresol Using MWCNT Modified Glassy Carbon Electrode

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ABSTRACT

In this research project, an electrochemical sensor was developed to sensitively detect chlorocresol at a new level of glassy carbon using carbon nanotubes. The surface morphology of the modified electrode was determined by field emission scanning electron microscopy. Under optimal conditions, a significant improvement in the electrochemical behavior of chlorocresol was observed at the surface of the modified electrode compared to the unmodified electrode. Electrode modified by carbon nanotubes due to its high conductivity, good stability, ability to increase the electron transfer rate, and finally, the effective interaction of the analyte with the electrode surface increases the sensitivity in measuring chlorocresol and its electrocatalytic properties. As an electrochemical sensor improved analyte drug measurement. The transfer coefficient (α), the number of electrons involved in the rate-determining step, was calculated for the modified electrode using cyclic voltammetry data. Under the optimal condition, the linear range of the calibration graph was between 0.39 to 2.37 and 2.37 to 7.2 μM , and the detection limit was reported as 0.27 μM . The results showed that the mentioned sensor had remarkable repeatability and stability during the tests, and satisfactory results were obtained in the determination of chlorocresol with the modified electrode in blood serum samples.

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INTRODUCTION

Chlorocresol ($\text{C}_7\text{H}_7\text{ClO}$) (Fig. 1) is obtained by chlorination of methylcresol. This substance is soluble in water and is used as a disinfectant when dissolved in alcohol or some phenols. This substance has disinfectant and antiseptic properties and is used for various purposes. For example, it is used as an anti-inflammatory drug in the treatment of skin diseases and healing of skin wounds. Chlorocresol has potentially harmful effects, such as skin inflammation, which is the cause of disruption in treatment with this substance. The side effects caused by the

consumption of these substances can be tolerable or, if severe, intolerable, which can include very allergic reactions and eye inflammations.

Voltammetry is widely used by inorganic chemists, physicists, and biochemists for the fundamental study of redox processes in various media [1-3], surface adsorption processes, and electron transfer mechanisms at the surface of chemically modified electrodes. In general, voltammetry involves a series of analytical methods in which information about compounds is obtained by following the current as a function of the applied potential. In voltammetry

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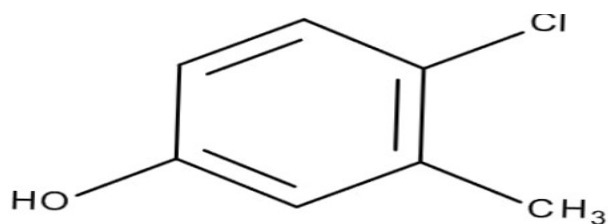


Fig. 1. Chemical structure of chlorocresol

methods, the species react at the electrode level, and by plotting the intensity of the resulting current relative and quantitative and qualitative information about the species is obtained [5-7]. Cyclic voltammetry is more practical than any other method for obtaining information about the characteristics of electrode reactions. The value of this method is due to the considerable data that is rapidly related to the nature of electrode reaction (whether cathodic or anodic) that is, by the kinetics of non-uniform electron exchange reaction or chemical reactions, the electrode reactions and finally, the adsorption processes and their effect on the electrode processes are provided [8,9]. The study of the mechanism of electrode processes is shown using cyclic voltammetry and hanging mercury droplet electrode. In the cyclic voltammetry method, the potentials applied to a working electrode in a stationary solution are changed according to a triangular program concerning the time [10]. However, in some cases, it is possible to repeat the change in the potential value of the electrode over several consecutive cycles. Then the current intensity changes are plotted according to the applied potential change.

The aim of this work was to conduct an electrochemical investigation of chlorocresol and to develop a sensitive electrochemical methodology for the quantification of chlorocresol in pharmaceutical formulations at modified electrodes using voltammetry techniques.

In recent years, chemically modified electrodes have attracted much attention. In chemically modified electrodes, a specific chemical compound called a modifier, is fixed on the surface of the electrode. This chemical participates as an intermediary in the electron exchange reaction. Electrochemists have found that placing different compounds as modifiers on a conductive or semiconductor substrate strongly affects the behavior of the electrode, so that the electrochemical properties of some electroactive

materials on the surface of such electrodes are quite different from unmodified electrodes. In studies, electrochemists have found that if the nature of the surface layer of an electrode can be changed in an appropriate way, a variety of electrochemical properties can be expected for a compound on the surface of that electrode. Modified electrodes also increase the selectivity of electrochemical reactions and eliminate the interference of the surface adsorption of different species on the electrode surface [11-14].

Carbon nanotubes were invented in 1991 by Sumio Iijima [15]. These compounds have received much attention due to their special electrical and mechanical properties. Recent studies show that carbon nanotubes have formed a new type of carbon material that has wider applications in various fields such as energy conversion and storage [16], electrochemical actuators [17], chemical sensors [18], lithium storage [19], and hydrogen [20]. Nanotubes were divided into two categories: single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). Carbon nanotubes, in addition to being very strong, also have good flexibility. One of its applications is composite. The most important property of nanotubes is their electrical conductivity, which varies depending on the order of the atoms. Carbon nanotubes themselves do not have any oxidative activity, but because of the properties mentioned above, they are significant for modifying the surface of the electrode.

MATERIALS AND METHODS

Reagents and materials

Chlorocresol, dimethyl formamide (DMF), and methanol were of analytical grade supplied by Merck. Multi-walled carbon nanotubes (OD=10⁻³⁰ nm, ID=5⁻¹⁰ nm, length=0.5⁻⁵⁰⁰ μm, 95%) were purchased from Aldrich. Deionized water was used for the preparation of all solutions. Phosphate buffer solutions were prepared with 0.1 mol L⁻¹

NaH_2PO_4 - Na_2HPO_4 and by adjusting the pH with $0.1 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$ and $0.1 \text{ mol L}^{-1} \text{ NaOH}$. The pH of the solutions was adjusted to 7 with phosphate buffer. All aqueous solutions were prepared in twice-distilled de-ionized water and used analytical-grade chemicals. To remove oxygen in experimental solutions, argon gas (99% purity) was used.

Apparatus

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat model PGSTAT 30 (Metrohm, Utrecht, Netherlands), and a system was run on a pc using GPES 4.9 software. A three-electrode cell, consisting of a GCE, modified with MWCNT as a working electrode. A platinum wire was employed as a counter electrode, and a saturated Ag/AgCl (saturated KCl) served as the reference electrode, and all potentials in the text refer to it. The pH measurements were made with a Metrohm 632 pH meter using a combined glass electrode. A personal computer was used for data storage and processing. The morphology of GCE modified with MWCNTs surface was observed using a scanning electron microscope (SEM) from SERON technology AIS-2100. All electrochemical

experiments were performed at room temperature (25 ± 0.5) °C.

Preparation of MWCNT (multi-walled carbon nanotubes)- modified GCE

Preparation of carbon nanotube suspension pour 1mg of multi-walled carbon nanotube powder into 1ml of DMF solvent (dimethyl form amide) and expose to sound waves in an ultrasonic device for 60 minutes to obtain a uniform solution. Prior to electrochemical modification, the surface bare GCE was polished with alumina powder (Al_2O_3) and first washed with acetone, and then rinsed. The electrode was then placed in 10 ml of 1mM hexacyanoferrate solution, and by applying one cycle in the potential range of -0.2 to 0.8 V, the surface of the electrode was ensured to be clean. In the next step, the electrode was placed in a fixed position, and 10 μl of carbon nanotube solution was injected into it by the sampler.

RESULTS AND DISCUSSION

The electrochemical response of chlorocresol at modified GCE

Fig. 2 shows CV curves of $2.0 \times 10^{-5} \text{ mol L}^{-1}$ chlorocresol at bare GCE (a) and modified GCE (b)

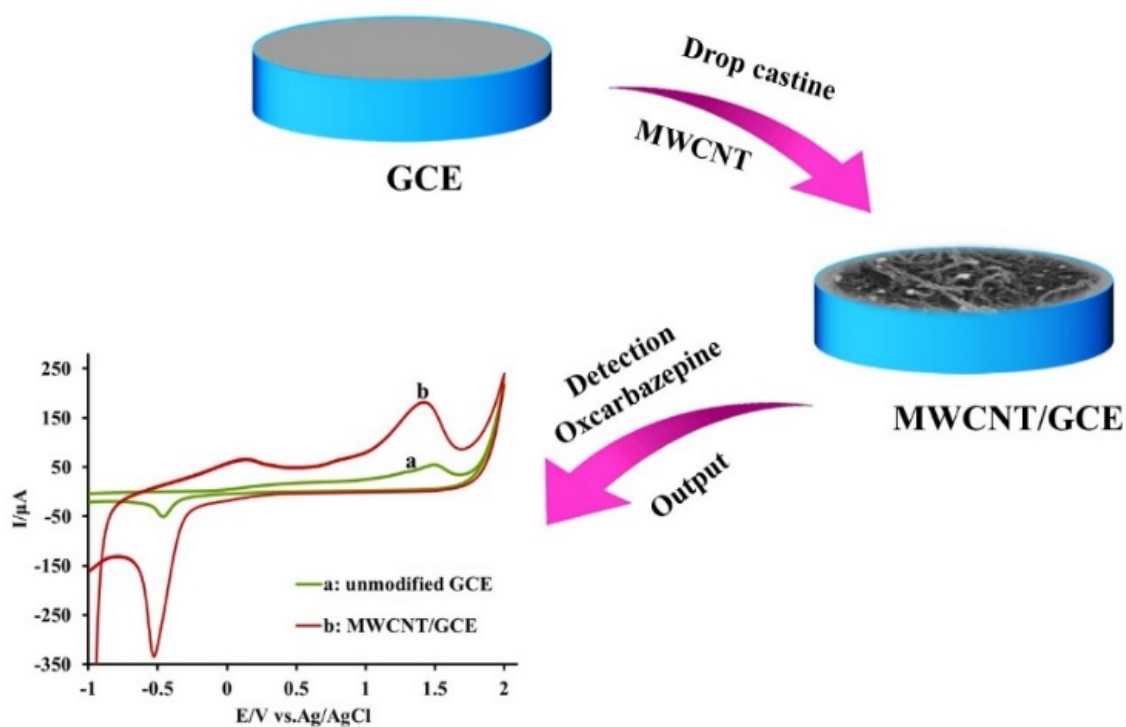


Fig. 2. Schematic of modified electrode preparation

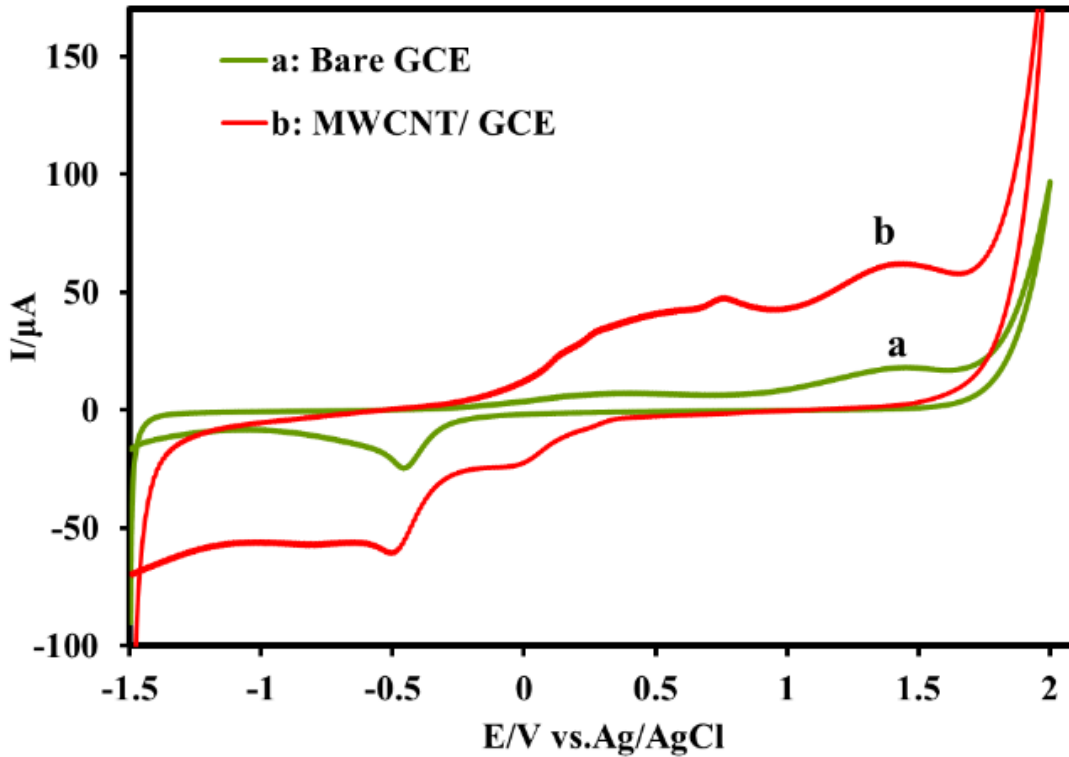


Fig. 3. Cyclic voltammograms of 2.0×10^{-4} mol L^{-1} chlorocresol (a) bare GCE and (b) MWCNT modified GCE in 0.1 M phosphate buffer solutions. Scan rate: 100 mVs^{-1} ; supporting electrolyte:

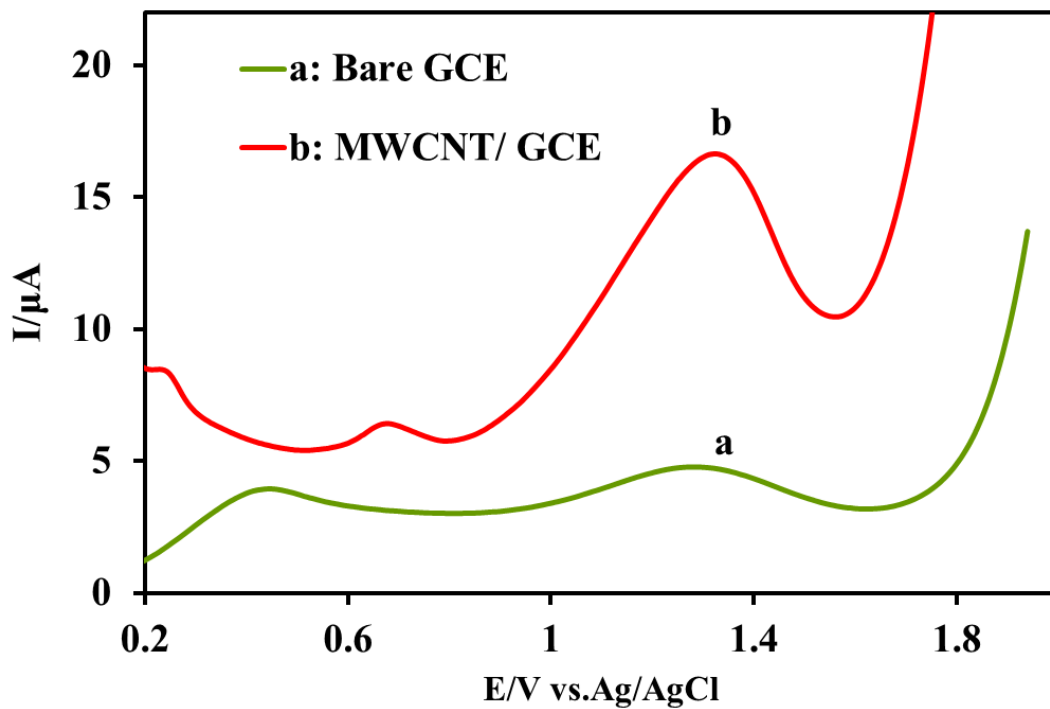


Fig. 4. differential pulse voltammograms of unmodified GCE (a), GCE modified with MWCNT (b) in the presence of chlorocresol $15 \mu\text{M}$ in phosphate buffer solution 0.1M, PH=7

in 0.1 mol L⁻¹ PBS (pH 7.0), respectively.

The electrochemical properties of the MWCNT modified carbon glassy electrode were studied using cyclic voltammetry. Fig. 3 cyclic voltammograms show the electrochemical behavior of chlorocresol on the surface of GCE modified with MWCNT and bare GCE. Signification increase in anodic current is due to the presence of carbon nanotubes. Also, the peak potential in the modified electrode is equal to 1.48 V, and the modified electrode is 1.36 V. This indicates a reduction in the oxidation potential of chlorocresol at the modified electrode surface.

Given that differential pulse voltammetry has a better sensitivity than cyclic voltammetry chlorocresol. DPV method is used to measure chlorocresol on the surface of carbon glass electrode modified with carbon nanotubes. Fig. 4

shows differential pulse voltagrams obtained on the unmodified surface in the buffer PH=7, 0.1M phosphate. As shown in Fig. 4, by modifying the electrode, in addition to increasing the current, the overvoltage also decreases. Therefore, the above electrode was introduced as a new sensor to measure chlorocresol.

Effect of potential scanning rate on oxidation of chlorocresol

In electrochemical studies using cyclic voltammetry methods, one of the variables affecting the behavior of electrochemical correction of electrodes is the scanning rate potential of the working electrode. To investigate the effect of potential scanning rate on the electrochemical behavior of chlorocresol, cyclic voltammograms of 2.0x10⁻⁵ mol L⁻¹ of chlorocresol

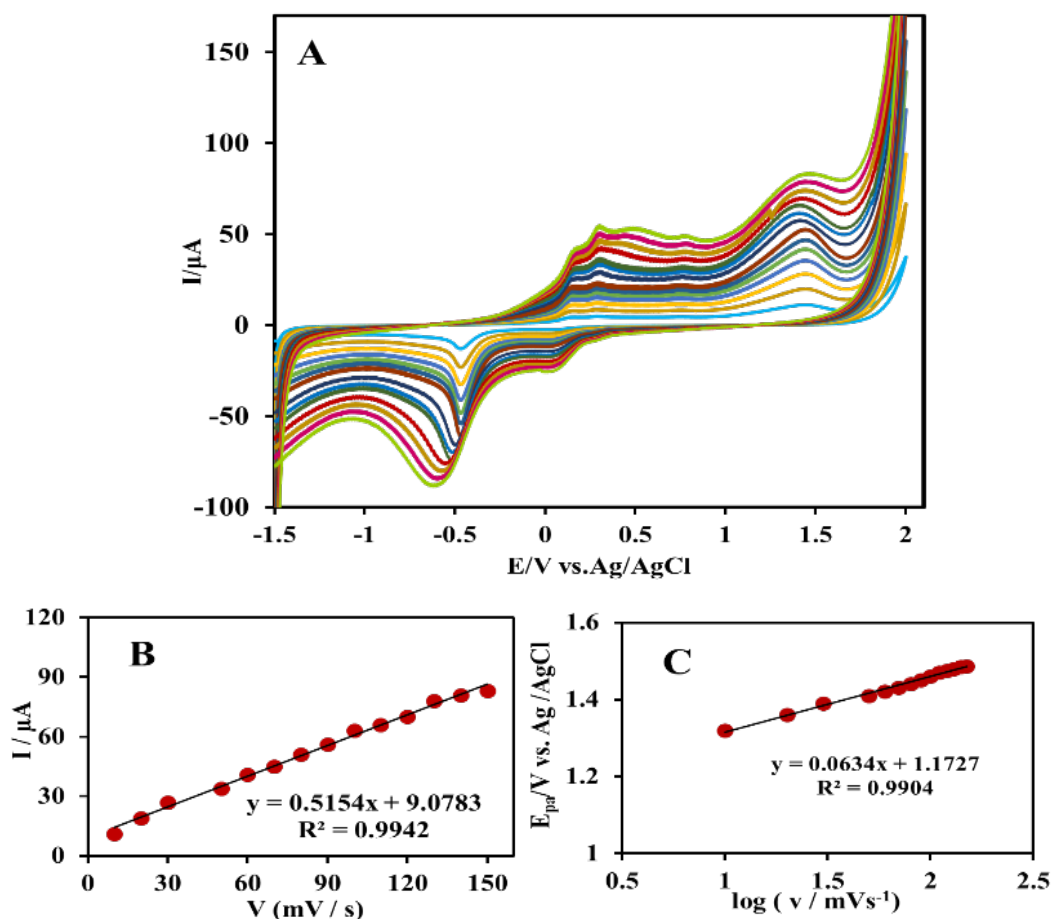


Fig. 5. A). CV voltammograms of 2.0x10⁻⁵ mol L⁻¹ chlorocresol at modified GCE with MWCNT; scan rate 10-150 mV s⁻¹ B) plot of change current anodic peak relative scan rate; c) diagram of potential changes according to the logarithm of the potential scan rate.

were obtained at different scanning rates from 10-150mV s⁻¹. As shown in Fig. 5, gradually increasing the peak oxidation potential of chlorocresol shifts to a more positive potential; this indicates a kinetic constraint in the oxidation process that is chlorocresol, which means that the above potential is required to perform the electrode process increases. In the case of a modified electrode with a fixed surface coating of a modifier, the peak height of the cyclic voltammogram increases as the potential scan rate increases. A good linear relationship between the square root of the scan rate and peak current was obtained between the range of 10-150 mV s⁻¹ (Fig. 5).

As shown in Figs. 5 (B, C), it can be concluded that the linearity of the peak current change diagrams is higher in terms of scanning rate. Therefore, we conclude that the electrode process is controlled by surface adsorption. Because the process is controlled by adsorption, the electrode reaction is based on absorption. According to Lauren's theory, for a completely irreversible absorption reaction and in the absence of any ohmic drop, the relationship between the logarithm of the scan rate and the potential of the peak is described by

the following equation;

$$E_p = b \log v + \text{constant} \quad (1)$$

Where E_p is peak potential, b is TOEFL slope, and v is the potential scan rate. The slope obtained for this line (TOEFL slope) equals 63.4 mV, and the anode transfer coefficient αa is calculated to be 0.47 mV.

Effect of chlorocresol concentration

One of the suitable and ideal properties of the electrode for use in the oxidation of the desired material is its linear response in exchange for increasing certain amounts of analyte. As this linear range increases, the efficiency of the electrode increases. To investigate the effect of chlorocresol concentration on anodic current from its oxidation under optimized conditions and to draw a measurement curve using the cyclic voltammetry method was used. (Fig. 6) Cyclic voltammogram the GCE shows the modified flow of the nostrils relative to the concentration of chlorocresol during increasing different concentrations of chlorocresol and (Fig.

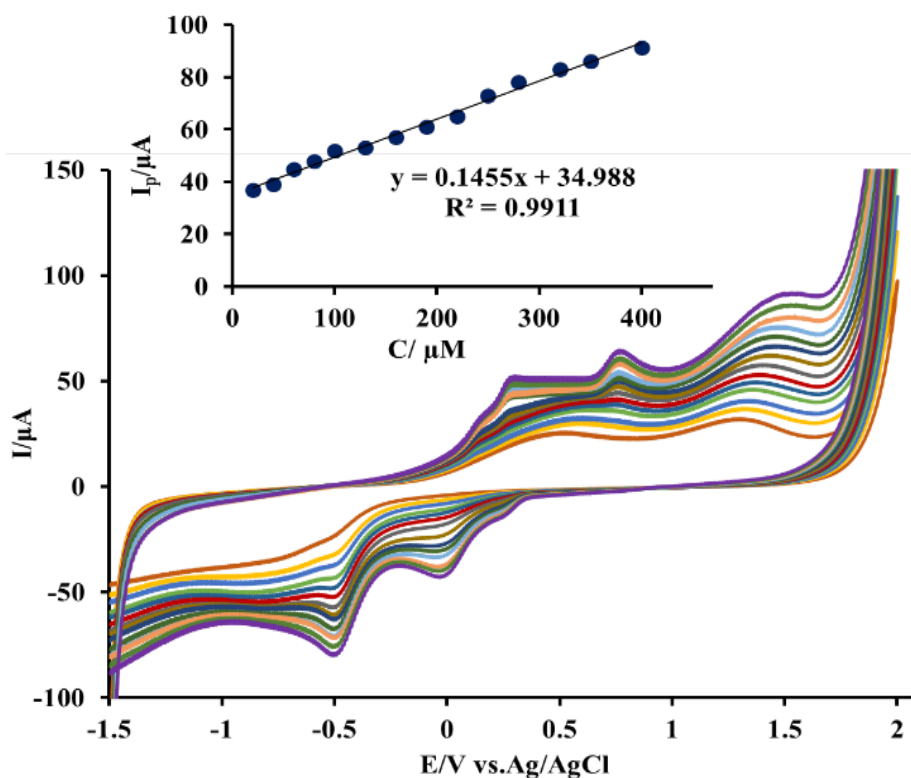


Fig. 6. Plot of concentration versus current for chlorocresol

6) shows the changes in peak current relative to the concentration of chlorocresol. Increasing the concentration of chlorocresol from this limit has little effect on the resulting current. The reason for this can be attributed to the saturation of active electrocatalyst sites. The current diagram in terms of concentration shows a good linear relationship between current and concentration. From the slope of the linear region (20-400 μM) and using the $k.s_p.m^{-1}$ relation, the detection limit of 16.89 μM was obtained.

Investigation of the effect of chlorocresol concentration on peak current using differential pulse voltammetry (DPV)

Determination of chlorocresol concentration at modified GCE with MWCNT was performed with differential pulse voltammetry (DPV). In optimal analytical conditions, chlorocresol was determined in different concentrations. A linear calibration curve (Fig. 7) was obtained for chlorocresol in the range of 1-65 μM for 0.1 mol L^{-1} PBS supporting

electrolyte. (Fig. 7)

As can be seen, with increasing analyte concentration, the peak current increases, and the peak potential shifts to more positive values. The oxidative current is linearly dependent on the concentration of chlorocresol. The peak current diagram for the concentration of chlorocresol in Fig. 6 has a linear region with the following equation:

$$I_p = 0.1537C + 6.8744 (R^2 = 0.9903) \quad (2)$$

The detection limit of 0.63 μM was obtained from the slope of the linear region using the $k.S_p.m^{-1}$ relation.

Investigating the characteristics of the electrode surface modified with carbon nanotubes by electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is an effective tool for investing charge transfer kinetics on modified electrode surfaces. The

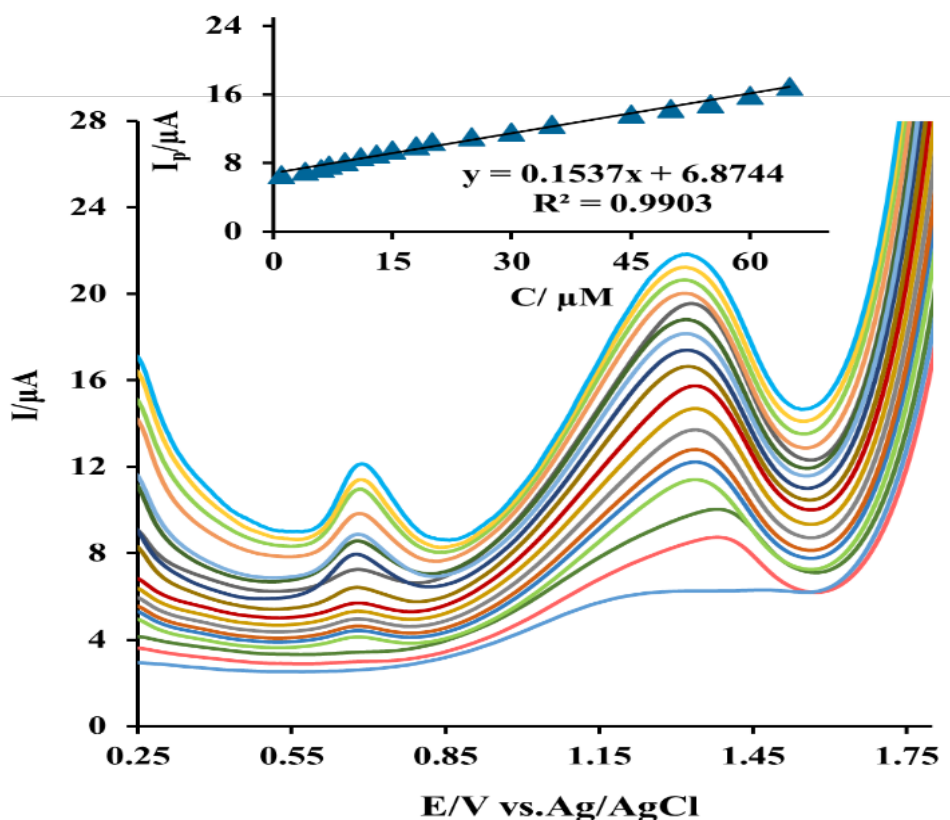


Fig. 7. DPV voltamograms of chlorocresol at modified GCE with MWCNT in the range 1-65 μM for 0.1 mol L^{-1} PBS supporting electrolyte.

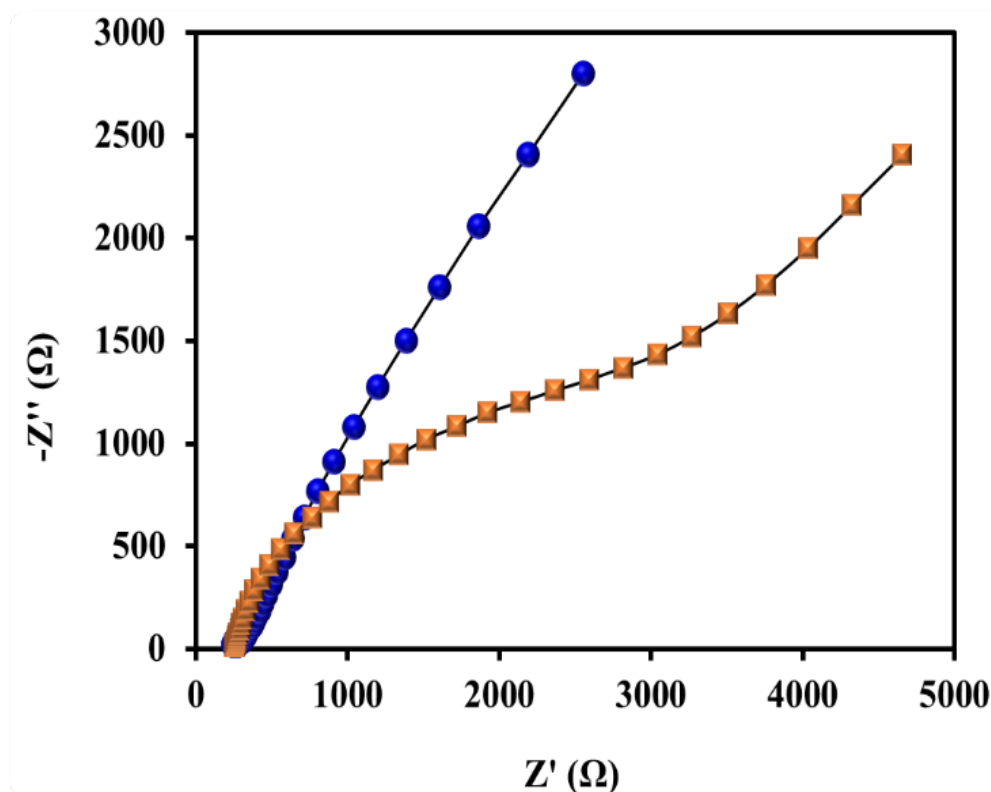


Fig. 8. impedance curve related to bare electrode surface and modified electrodes in $1 \mu\text{M}$ potassium hexacyanoferrate in 0.1M potassium chloride carrier electrolyte.

impedance spectrum consists of a half circle that is related to limiting the electron transfer process.

(Fig. 8) showed the impedance of bare and modified electrodes in potassium hexacyanoferrate solution. At the surface of the unmodified electrode, the resistance of the electrode is about 900Ω . By placing carbon nanotubes on the surface of the electrode, the resistance of the electrode is significantly reduced; this indicates the increase in the kinetic speed of electron transfer. The results show the improvement of the electrode surface for electrode reaction.

CONCLUSION

This study presented a new sensor to investigate the electrochemical behavior of chlorocresol with carbon glass electrodes coated with carbon nanotubes. Examination of cyclic voltammograms of chlorocresol on a modified electrode with carbon nanotube powder shows that the current is due to absorption oxidation. Some kinetic and thermodynamic parameters related to chlorocresol oxidation, such as load transfer coefficient, and

the number of electrons involved in the velocity determination step, can be evaluated by cyclic voltammetry methods. The advantages of the mentioned electrode can be a detection limit of $1.9 \mu\text{M}$, surface stability, and high sensitivity; he pointed out that the correction steps were not time-consuming. A sensor prepared to measure chlorocresol in a serum sample was successfully used.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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