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Carvacrol electrochemical reaction characteristics on screen printed electrode modified with $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite

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Abstract

Electrochemical characteristics of carvacrol were investigated on a screen-printed electrode (SPE) modified with $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite by using voltammetric techniques, which displayed a well-defined peak for sensitive carvacrol determination in phosphate buffer solution (PBS) at pH 7.0. $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanoparticles demonstrated suitable catalytic activity for carvacrol determination by differential pulse voltammetry (DPV) technique. Besides, determination of carvacrol in a real samples was recognized in the light of electrochemical findings and a validated voltammetric technique for quantitative analysis of carvacrol in a real formulation was proposed. The DPV peak currents were found to be linear in the concentration range of 10.0 to 800.0 μM . The limit of detection (LOD) was found to be 1.0 μM .

Keywords

Carvacrol, electrochemical reaction, $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite, differential pulse voltammetry

Introduction

Carvacrol (5-isopropyl-2-methylphenol) is the main thyme oil constituent, crucial oil of *Origanum vulgare*, and plants including *Thymus vulgaris* [1]. This compound is an ordinary additive applied in numerous foods (as flavorings), pharmaceuticals and perfumes due to its antitussive, anticarcinogenic, antioxidant, antibacterial, anticancer and antifungal features [2-5]. As the standardization of pharmaceutical compounds is based on their carvacrol content, the development of a novel validated technique for its quantification is a challenging requirement [6,7].

Numerous analytical methods such as gas chromatography (GC), thin-layer chromatography (TLC) combined with densitometry, gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) with fluorimetric detection have been employed for carvacrol measurement in many matrixes [8-11]. In some cases, lower content of carvacrol in

complicated matrices makes an emergency task to the preliminary application of preconcentration and separation procedures [12]. As compared with above mentioned methods, which typically require time-consuming and complex sample pretreatment procedure involving separation, extraction, and adsorption, electrochemical sensors have been documented as more authoritative tools [13-16]. The advantages of electrochemical sensors are the possibility of miniaturization and portability, selectivity, sensitivity, a wide linear range, minimal space and power requirement and cost-effective instrumentation. Electrochemical sensors have a leading position among all currently accessible sensors that have already reached the commercial stage and found a vast range of important applications in the fields of clinical, industrial, environmental and agricultural analyses [17,18].

Compared with bare electrodes, modified electrodes have some advantages. Initially, the analyte overpotential can be decreased together with the possible interfering background current. Secondly, the current signal response can be improved and therefore, a lower detection limit can be attained. Thirdly, adsorption of analytes and products can be omitted [19-22]. Consequently, the sensitivity and selectivity of the analysis by using modified electrodes can be significantly increased [23,24]. In addition, nanomaterial-modified electrodes have many benefits over traditional material-modified electrodes [25]. Firstly, nanomaterials ensure the vast specific surface area for carvacrol determination on the electrodes. Secondly, some semiconductor nanomaterials, especially metal oxides, may act as promoters of electrochemical communication, accelerating the electron transfer rate between active sites and electrodes. Thirdly, nanomaterials can assist the electrode to preserve its characteristics for a long period of time [26]. So, a variety of nanomaterials have been synthesized and characterized for the electrochemical analysis [27-32].

Nanostructured materials are one of the most promising supporting materials for surface modification of electrodes, due to their unique properties, such as good biocompatibility, high surface-to-volume ratio, enhanced magnetic and electrical properties. Metal oxides of the nanometer size exploited in nanomaterial-modified electrodes for electroanalysis, have some distinct advantages such as low influence of the solution resistance, high mass transport rate, low detection limit and better signal-to-noise ratio compared to the conventional electrodes [33-38]. Thus, $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite has already been employed for carvacrol sensor transducer surface which facilitates the electron transfer, enhances the effective electroactive surface area and improves the carvacrol detection limit.

Nowadays, application of screen-printed electrodes (SPEs) for analyte analysis is in the main research focus in electrochemical sensors area, what is due to their reliability, mass production, reproducibility, and low cost [39]. As ductile devices, SPEs can be drawn in different shapes and made from various materials [40]. This study will focus on the design and fabrication of disposable SPE modified with $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite for electrochemical detection of carvacrol. Special emphasis will be put on the sensor fabrication procedure, operating details and performance characteristics for carvacrol monitoring. Electrochemical properties of fabricated sensor propose sensitive voltammetric determination of carvacrol with advantages of low detection limit, respectable stability and rapid response towards electro-oxidation of carvacrol compared to bare SPE. To the best of our knowledge, this investigation is the first report describing the application of SPE modified with nanoparticles for carvacrol determination in real-samples.

Experimental

Reagents

Carvacrol was purchased from Sigma-Aldrich (Tulsa, OK, USA). Sodium dihydrogen phosphate, sodium monohydrogen phosphate, orthophosphoric acid and sodium hydroxide were provided

from Merck (Darmstadt, Germany). Doubly distilled, deionized water was employed in all experiments. All other chemicals exploited in this study were of analytical reagent grade and purchased from Merck (Darmstadt, Germany). Stock solutions of carvacrol were prepared by dissolving the appropriate compound amount in acetonitrile. Working solutions were prepared by accurate dilution from stock solutions of these compounds using phosphate buffer solution (PBS). PBS was employed as the supporting electrolyte.

Apparatus

The SPE (DropSens, DRP-110, Spain) consists of three main parts which are silver pseudo-reference electrode, graphite counter electrode, and graphite working electrode, respectively. Voltammetric measurements (cyclic voltammetry and differential pulse voltammetry) were done using a potentiostat/galvanostat (PGSTAT 302N, Autolab, Eco-Chemie, The Netherlands) with the software GPES, version 4.9. Metrohm 710 pH meter, equipped with the glass electrode, was used for pH measurements.

The surface morphology of the composites was analyzed with KYKY, EM 3200 scanning electron microscopy (SEM). XRD studies were conducted on a Rigaku D/max 2500 V instrument with a graphite monochromator and a Cu target. The FT-IR spectrophotometer used for the studies was a Bruck Equinox 55 and KBr pellet technique was used for loading the samples into the instrument.

La₂O₃/Co₃O₄ nanocomposite synthesis

All chemicals used for the preparation of the nano-powders, namely cobalt acetate (Co(CH₃COO)₂·2H₂O), thiourea ((NH₂)₂CS) and ammonia (25 % NH₃), were of analytical grade. All the precursors were dissolved in deionized water. During the preparation of the nano-powders, ammonia was used as a complexing agent. Co₃O₄ nanostructures were prepared by dissolving 0.46 mol of cobalt acetate in 80 mL of deionized water, 0.18 mol of thiourea in 80 mL of deionised water and lastly by adding 19.76 mL of ammonia in 80 mL of deionised water. The amount of solutions of cobalt acetate, thiourea and ammonia was held constant at a ratio of 1:1:1. Then the cobalt acetate solution was added in a beaker in the reaction bath, followed by adding thiourea solution in the same reaction bath and the mixture was stirred for few seconds. Lastly, ammonia solution was added slowly into the mixture, while continuing stirring for 5 min. The temperature of the bath was then allowed to increase up to 80 °C. After the precipitates were formed, they were left overnight and filtered thereafter. The precipitates were then washed with ethanol. The obtained powders were dried at ambient conditions for several days.

La₂O₃/Co₃O₄ nanocomposites were prepared by La₂O₃ nanoparticles onto the surface of the Co₃O₄ hexagonal nanosheets. A solution of 0.2 mol of La(NO₃)₃·6H₂O (50 mL) was mixed with 0.1 g Co₃O₄ hexagonal nanosheets. Then appropriate amount of NaOH solution (1.5 M) was added dropwise into the solution until the pH value of the mixture reached to 10. The precipitate was brought to a reaction temperature of 80 °C and stirred for 1 h. After the reaction was completed and cooled to room temperature, the resulting products were centrifuged for 15 min at 3000 rpm. Finally, the precipitate was washed several times with water and vacuum dried at 60 °C overnight. The obtained black precipitate was La₂O₃/Co₃O₄ nanocomposite and was ready for use.

Real samples preparation

Urine samples were retained in a refrigerator immediately after collection. 10 mL of the samples were centrifuged for 15 min at 2000 rpm. The supernatant was filtered out by using a 0.45 µm filter. Next, different volumes of the solution were transferred to a 25 mL volumetric flask and diluted to the mark

with PBS (pH 7.0). The diluted urine samples were spiked with different amounts of carvacrol. The carvacrol contents were analysed by the proposed method and standard addition procedure.

SPE electrode fabrication

The bare screen-printed electrode was coated with $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite, as exposed in the following. The stock solution of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite in 1 mL of the aqueous solution was prepared by dispersing 1 mg of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite with ultrasonication for 1 h, while 2 μl of aliquots of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{H}_2\text{O}$ suspension solution was cast on the carbon working electrodes, followed by waiting until the solvent was evaporated at 25 °C.

Results and discussion

Nanostructures characterization

Figure 1 displays the FT-IR spectrum of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite sample in the frequency range of 400–4000 cm^{-1} . The FT-IR spectrum of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite shows strong vibrational bands in the lower frequency regions (at around 520 and 449 cm^{-1}), ascribable to the vibration of metal–O. The absorption seen at $\sim 3417 \text{ cm}^{-1}$ is thought to be due to the symmetric vibration of the -OH groups of absorbed H_2O molecules [41].

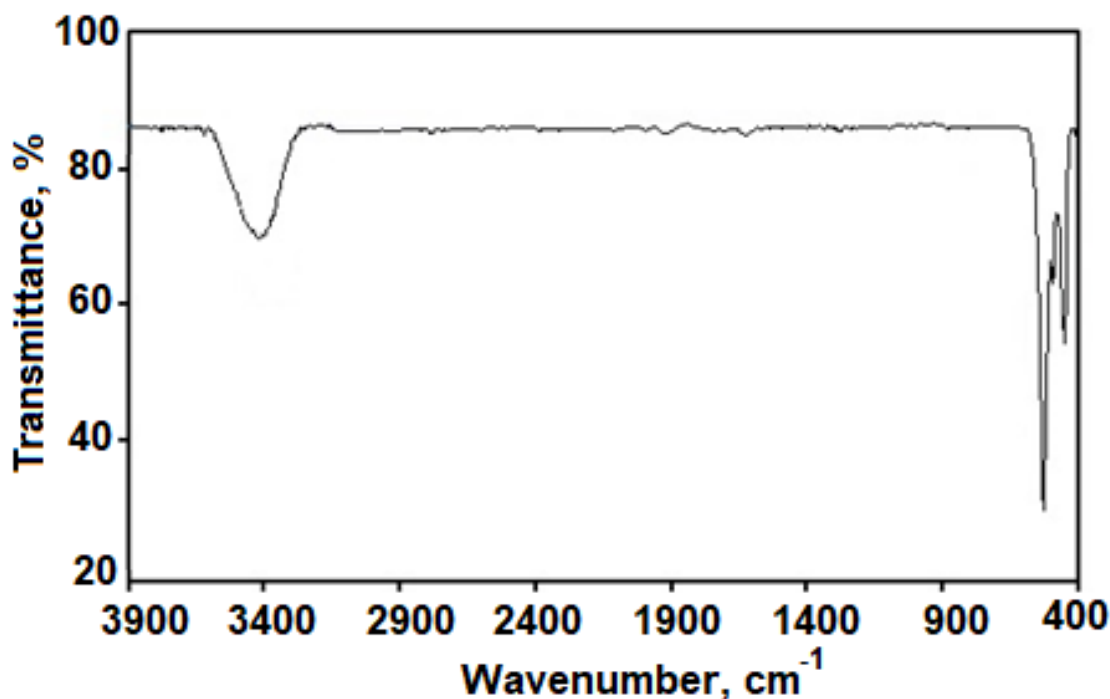


Fig. 1. FT-IR image of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite

From the X-ray diffraction (XRD) pattern of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite shown in Figure 2, it can be seen that all major diffraction peaks match well with the standard peak of this sample. For $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite, diffraction peaks at 31.7, 36.1, 44.5, 59.9 and 64.9° (JCPDS 74-2120) can be indexed to (220), (311), (400), (511) and (400) planes of Co_3O_4 , while diffraction peaks at 15.1, 28.5, 29.1, 39.8, 49.1 and 55.2° (JCPDS 41-4019) can be indexed to (100), (002), (101), (102), (211) and (201) plane of La_2O_3 , respectively [42,43].

The morphology of the product was examined by SEM. Figure 3 shows that Co_3O_4 nanosheets and La_2O_3 nanoparticles constitute $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite.

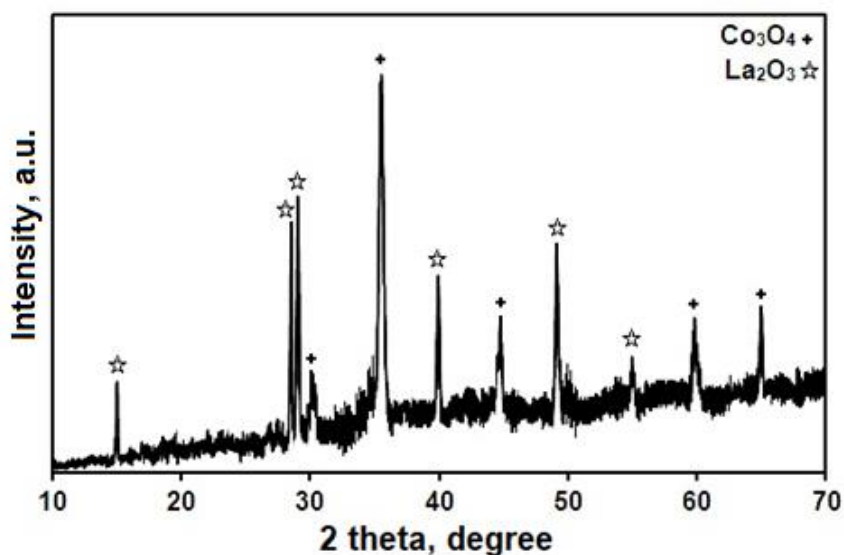


Fig. 2. XRD pattern of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite

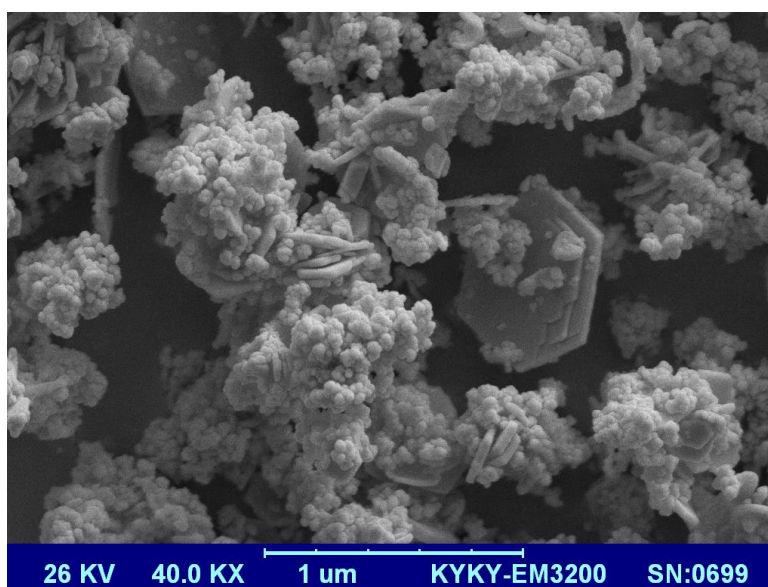


Fig. 3. SEM image of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite.

Electrochemical behaviour of fabricated sensor

The pH value of the aqueous solution is effective on the electrochemical behaviour of carvacrol. Therefore, pH of the solution was optimized to obtain highly accurate results for carvacrol electro-oxidation. Accordingly, the electrochemical behaviour of carvacrol at the surface of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ was studied by voltammetry in 0.1 M PBS at pH values between 2.0 and 9.0. It was revealed that neither acidic nor basic medium was appropriate for the electro-oxidation of carvacrol at the surface of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ and best results were obtained at neutral conditions. Accordingly, the pH 7.0 was chosen as the optimum pH for electro-oxidation of carvacrol at the surface of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$.

Figure 4 demonstrates the CV responses for electro-oxidation of 400.0 μM carvacrol at $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ (curve a) and unmodified SPE (curve b). The peak potential corresponding to the carvacrol oxidation occurs at 400 mV, which is about 180 mV more negative than for the unmodified SPE. Likewise, the anodic peak current for the oxidation of carvacrol at $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ is much higher in comparison with the unmodified SPE, indicating thus effectiveness of SPE modification with $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4$ nanocomposite in the carvacrol oxidation process. Based on the obtained results, the oxidation of carvacrol at the surface of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ can be considered as a simple

electrochemical reaction. Also, the effect of potential scan rates on the oxidation current of carvacrol was assessed and shown in Figure 5. According to the results, increase of the potential scan rate causes an increment in the peak current. The linear relationship between anodic peak current (I_p) and the square root of the potential scan rate ($v^{1/2}$) during the oxidation of carvacrol demonstrates that the oxidation process is under the control of diffusion (Fig. 5). From rising sections of the current–voltage curve recorded at 10 mV s^{-1} , the Tafel curve of analyte is constructed and plotted in Figure 6. The kinetics of electron transfer in the electrode reactions influences Tafel regions of the current-potential curve. The estimated Tafel slope is 0.1583 V implying that the rate of electrode process is determined by the electron transfer step (RDS) with charge transfer coefficient (α) of 0.63 [44].

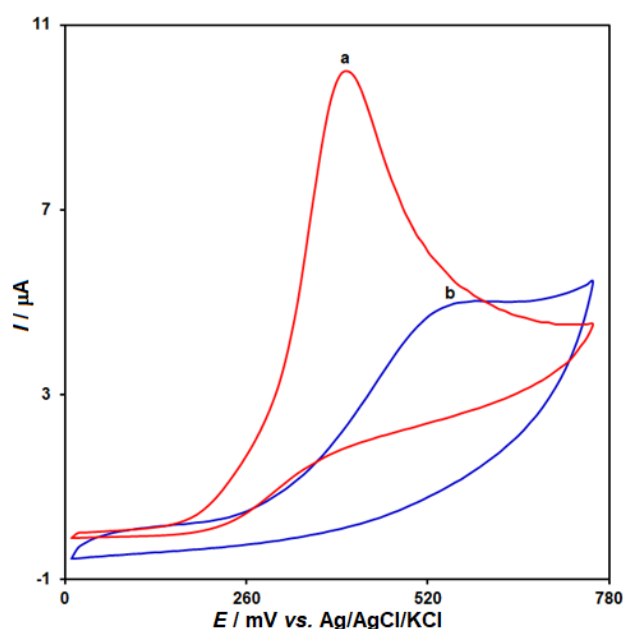


Fig. 4. CVs of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ (a) and unmodified SPE (b) in 0.1 M PBS (pH 7.0) containing $400.0 \mu\text{M CA}$. Scan rate = 50 mV s^{-1}

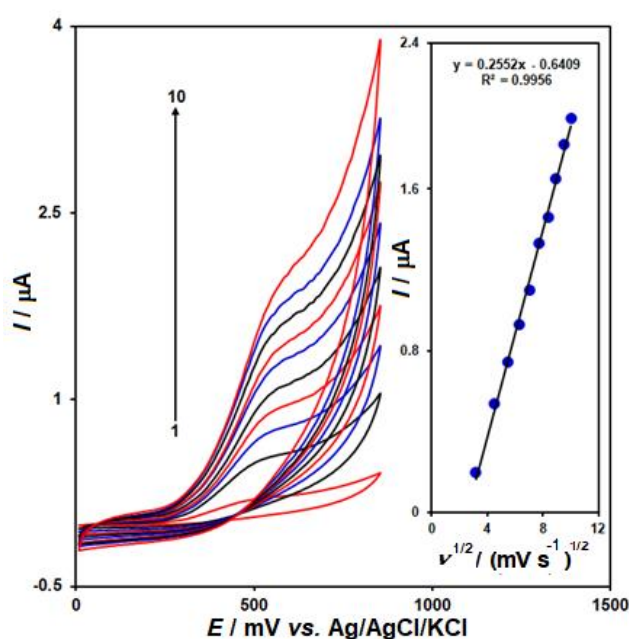


Fig. 5. CVs of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) containing $500.0 \mu\text{M CA}$ at various scan rates ($10, 20, 30, 40, 50, 60, 70, 80, 90$ and 100 mV s^{-1}). Inset: Variation of anodic peak current vs. $v^{1/2}$.

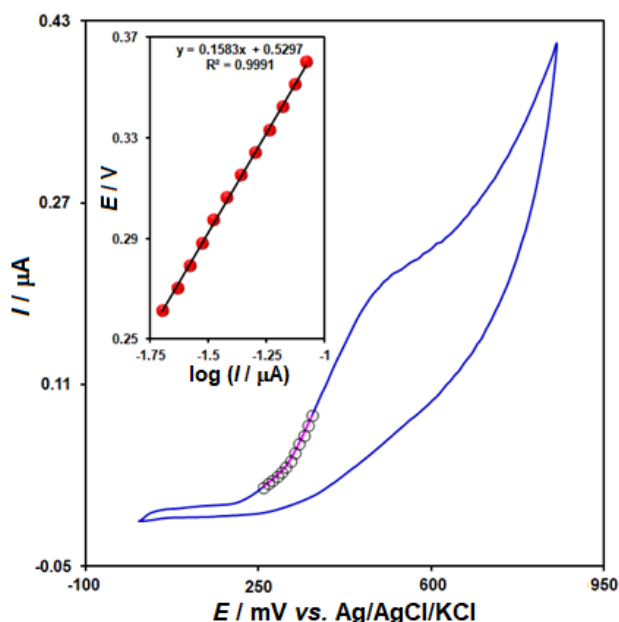


Fig. 6. CV for $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) with a scan rate of 10 mV s^{-1} in the presence of 500.0 μM CA. The inset shows the Tafel plot derived from the CV.

Chronoamperometric investigation

Chronoamperometric measurements of carvacrol at $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ were carried out by setting the working electrode potential at 0.5 V vs. Ag/AgCl/KCl (3.0 M) for various concentrations of carvacrol in PBS (pH 7.0) and the results are shown in Figure 7. The determination of diffusion coefficient for electroactive moieties (carvacrol in this case) with a diffusion coefficient of D , is performed using the Cottrell equation [44] which under the mass transport limited condition is defined as:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

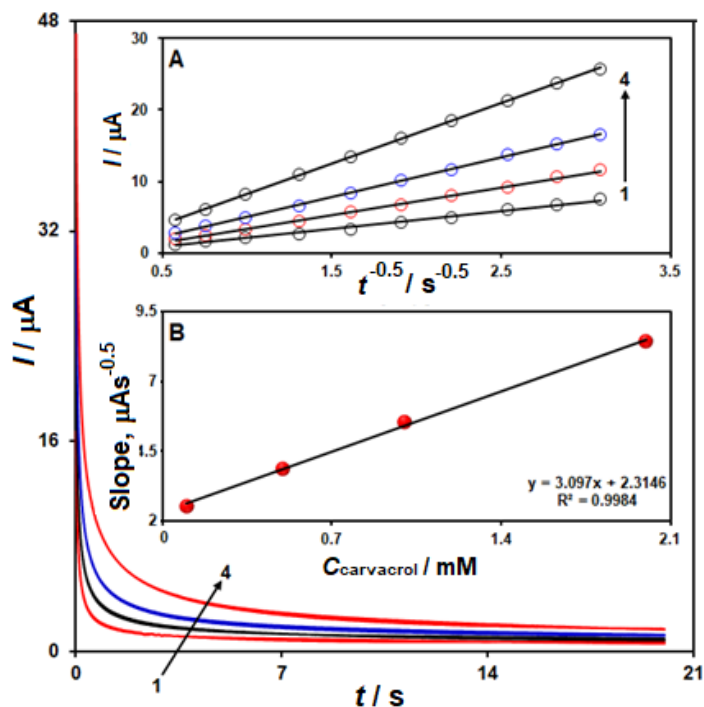


Fig. 7. Chronoamperograms of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) for different concentrations of CA. The numbers 1-4 correspond to 0.1, 0.5, 1.0 and 2.0 mM of CA. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms. (B) Plot of the slope of straight lines against CA concentration.

In eq. (2), n , A , D and C_b are number of transferred electrons, electrode area (cm^2), diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and bulk concentration of electroactive species (mol cm^{-3}), respectively. Experimental plots of I vs. $t^{-1/2}$ are for various concentrations of carvacrol presented in Figure 7A, while slopes of the resultant straight lines are plotted versus carvacrol concentrations in Figure 7B. From the resultant slope and the Cottrell equation, the mean value of D for carvacrol was determined as $3.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The working curve and detection limit

The higher sensitivity of pulse techniques with respect to CV is due to the reduction of charging currents. The electro-oxidation peak current of acetyl carvacrol at the surface of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ can be used to determine carvacrol in the solution. Due to the higher sensitivity and better performance of DPV in analytical applications, DPV experiments were carried out using $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH=7.0) containing various concentrations of carvacrol. The results shown in Figure 8 reveal that at the surface of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$, there is a linear dependency between electrocatalytic peak currents of carvacrol oxidation and its concentration within the range of 10.0–800.0 μM . The correlation coefficient is 0.9998, and the detection limit (3σ) was obtained as 1.0 μM .

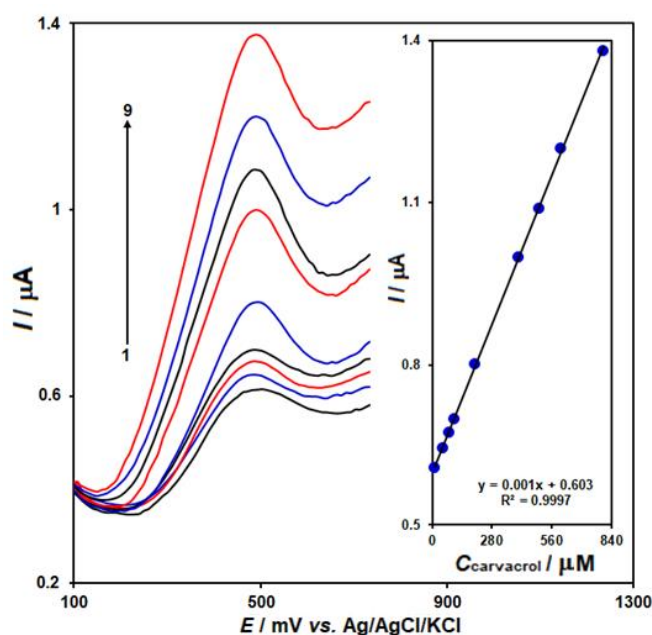


Fig. 8. DPVs of $\text{La}_2\text{O}_3/\text{Co}_3\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) containing different concentrations of CA (10.0, 50.0, 75.0, 100.0, 200.0, 400.0, 500.0, 600.0 and 800.0 μM). Inset: Plot of I vs. CA concentrations. Scan rate = 50 mV s^{-1} .

Interference studies

The influence of various substances as compounds potentially interfering with the determination of carvacrol was studied under optimum conditions. The potentially interfering substances were chosen from the group of substances commonly found with carvacrol in pharmaceuticals and/or biological fluids. The tolerance limit was defined as the maximum concentration of the interfering substance that caused the error less than $\pm 5\%$ in the determination of carvacrol. According to the results, l-lysine, glucose, NADH, acetaminophen, uric acid, l-asparagine, l-serine, l-threonine, l-proline, l-histidine, l-glycine, l-phenylalanine, lactose, saccharose, fructose, benzoic acid, methanol, ethanol, urea, caffeine, dopamine, epinephrine, norepinephrine, serotonin, ascorbic acid, isoproterenol, levodopa, carbidopa, Mg^{2+} , Al^{3+} , NH_4^+ , Fe^{+2} , Fe^{+3} , F^- , SO_4^{2-} and S^{2-} did not show interference in the determination of carvacrol.

The repeatability and stability of La₂O₃/Co₃O₄/SPE

The generation of reproducible surface of La₂O₃/Co₃O₄/SPE was examined by CVs data obtained in 0.1 M PBS (pH 7.0) containing CA. The calculated RSD for various parameters was accepted as the criteria for satisfactory surface reproducibility (2-4 %). This degree of reproducibility is virtually the same as that expected for the renewal of ordinary screen-printed electrode surface. In addition, the long-term stability of La₂O₃/Co₃O₄/SPE was tested over 3-week period. When CVs were recorded after the modified electrode was stored in atmosphere at room temperature, the peak potential for carvacrol oxidation was unchanged and the current signals showed less than 2.7 % decrease of the initial response. The antifouling properties of modified electrode towards carvacrol oxidation and its oxidation products were investigated by recording the CVs of modified electrode before and after using in the presence of carvacrol. CVs were recorded in the presence of carvacrol for 20 cycles at a scan rate 50 mV s⁻¹. The peak potentials were unchanged, and the currents decreased by less than 3.9 %. Therefore, at the surface of La₂O₃/Co₃O₄/SPE, not only the sensitivity increase, but the fouling effect of the carvacrol and its oxidation product also decreases. However, we regenerated the surface of La₂O₃/Co₃O₄/SPE before each experiment.

Analysis of real samples

The analytical practicality of the proposed method was evaluated through the quantification of carvacrol in urine samples by using the standard addition method. The outcomes for the carvacrol determination in real samples are presented in Table 1. The experimental results showed acceptable recoveries for carvacrol. The reproducibility of the method was investigated by the mean relative standard deviation (RSD).

Table 1. Determination of carvacrol in urine samples (n=5) using La₂O₃/Co₃O₄/SPE.

Spiked concentrations, μM	Found concentrations, μM	Recovery, %	RSD, %
0	-	-	-
7.5	7.6	101.3	1.8
12.5	12.4	99.2	2.1
17.5	17.3	98.8	3.1
22.5	22.7	100.9	2.7

Conclusions

For the first time, La₂O₃/Co₃O₄ nanocomposite modified-SPE demonstrates an outstanding behavior toward carvacrol oxidation in an aqueous PBS (pH 7.0) solution. Based on the electrochemical oxidation, the quantitative measurement of carvacrol in real samples was developed by a simple, rapid, selective and sensitive DPV technique. In the DPV determination, the detection limit of carvacrol was estimated as 1.0 μM. The developed method is reproducible and reliable. Good reproducibility of the modified electrode suggests application of the method in the routine analysis of carvacrol-containing samples.

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