

CARBON DOTS/CHITOSAN MODIFIED SCREEN-PRINTED CARBON ELECTRODES FOR THE DETECTION OF BISPHENOL A

(Elektrod Karbon Bercetak Skrin Terubah Suai Karbon Titik/Kitosan untuk Pengesanan Bisfenol A)

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Abstract

Bisphenol A (BPA) is an organic compound in daily plastic products. The compound is primarily transferred from water bottles, food cans liners, and dental fillings into foods and beverages. The BPA is considered an endocrine-disrupting compound related to broad health concerns, such as reproduction problems and the development of various cancers. Consequently, developing a reliable analytical approach to determine BPA levels is urgent. The current study developed an electrochemical sensor from modified screen-printed carbon electrodes (SPCE) with carbon dots-chitosan (CDs-CS) to detect BPA. The CDs-modified SPCE provided a good electrocatalytic application with extraordinary electronic properties and significantly enhanced electrical conductivity. The modified SPCE/CDs-CS sensor was prepared through the drop casting technique. Subsequently, its BPA detection abilities were assessed via differential pulse voltammetry (DPV). In investigating the optimum parameters to elevate the performance of the developed sensors, 1% m/v CS concentration and 1:1 (v/v) CDs to CS ratio were recorded. The obtained CDs-CS/SPCE sensor demonstrated great electrocatalytic features for detecting BPA within the 0.4 and 10 μM concentration range with a sensitivity of 0.46 $\mu\text{A}/\mu\text{M}$ ($R^2 = 0.9911$) and 0.37 μM limit of detection (LOD).

Keywords: Bisphenol A, carbon dots, chitosan, electrochemical sensor, environmental

Abstrak

Bisfenol A (BPA) adalah sebatian organik yang terdapat dalam produk plastik yang kita gunakan setiap hari. Sebilangan besarnya dipindahkan ke dalam makanan dan minuman termasuk botol air, lapisan tin makanan, dan tampalan gigi. BPA dianggap sebagai sebatian yang mengganggu endokrin yang berkaitan dengan pelbagai jenis masalah kesihatan seperti perkembangan barah dan masalah pembiakan. Oleh itu, pembangunan pendekatan analisis yang boleh dipercayai untuk mengesan BPA adalah isu mendesak. Dalam kajian ini, sensor elektrokimia berasaskan modifikasi elektrod karbon bercetak skrin (SPCE) dengan karbon titik-kitosan (CD-CS) telah diterokai untuk mengesan bisfenol A (BPA). SPCE yang diubahsuai dengan CD memberikan aplikasi elektro-pemangkin yang baik mempunyai sifat elektronik yang luar biasa dan peningkatan besar dalam kekonduksian elektrik. SPCE yang diubahsuai dengan CDs-CS disediakan dengan menggunakan teknik penyalutan titis. Pengesanan BPA pada sensor SPCE / CDs-CS dikaji dengan menggunakan voltammetri denyutan pembezaan (DPV). Parameter optimum pembangunan sensor seperti kepekatan CS 1% (m/v) dan nisbah CD-CS 1/1 (v/v) dikaji untuk meningkatkan prestasi sensor yang dibangunkan. Hasil kajian menunjukkan bahawa SPCE yang dimodifikasi dengan komposit CD-CS mempunyai ciri elektrokatalitik yang hebat untuk

mengesan BPA dalam julat kepekatan dari 0.4 μM hingga 10 μM dengan kepekaan 0.46 $\mu\text{A}/\mu\text{M}$ ($R^2 = 0.9911$) dan had pengesanan (LOD) 0.37 μM .

Kata kunci: bisfenol A, karbon titik, kitosan, sensor elektrokimia, alam sekitar

Introduction

Bisphenol A (BPA) or 2,2-bis(4-hydroxyphenyl)propane is a compound predominantly employed as monomers in the synthesis of epoxy resins and polycarbonate (PC). A combination of BPA and other materials is utilised in plastic production. Products, such as packaging materials for food, beverages and wastewater samples and engineering plastics, contain BPA [1]. In 2015, the European Food Safety Authority (EFSA) proposed that the minimum amount of temporary tolerable daily intake (t-TDI) of BPA should not exceed 4 $\mu\text{g kg}^{-1}$ of body weight per day [2]. Minute amounts of BPA might endanger human health and, at worst, lead to prostate, testicular, or breast cancer, reproductive disorders, including low sperm quality, congenital disabilities, and impaired brain development [3]. Consequently, a rapid, simple, sensitive, and selective BPA detection technique is immediately demanded.

Commercialised techniques of BPA detection include high-performance liquid chromatography (HPLC), gas chromatography coupled with mass spectrometry (GC-MS) [4], and liquid chromatography-tandem mass spectrometry (LC-MS-MS) [5]. Although the methods are highly sensitive and offer low detection limits, the techniques involve several operational steps, making them time-consuming, and the procedure for processing the samples is tedious. Furthermore, the instrumentations required are intricate, expensive, and not convenient for on-site detection [6], hence the demand for a novel analytical technique to determine BPA levels.

The BPA is an electroactive species that contain phenolic hydroxyl groups that could be oxidised on electrode surfaces. Nonetheless, the direct determination of BPA with bare electrodes is infrequent due to its weak signal response, and its oxidation involves a relatively high overpotential [7]. Accordingly, to refine the selectivity and sensitivity of BPA detection, various materials have been recommended for the modification

of SPCE, such as ionic liquids [8], enzymes, molecularly imprinted polymers [9], carbon materials, including carbon nanotubes [10], single-walled (SWCNT) [11], multiple-walled (MWCNT) [12], and graphene, [13] and metal nanoparticle-based composites, such as gold nanoparticles (AuNPs) [14] and ferroferric oxide nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) [15].

Carbon dots (CDs) were accidentally discovered during the electrophoretic purification of single-wall carbon nanotubes (SWCNTs) and were derived from its arc-discharge soot [16]. A novel carbon nanomaterial, the CDs has drawn considerable attention in recent years due to its excellent properties, including low toxicity [17], remarkable conductivity [18], large surface area, and high stability [19]. Recently, methods of synthesising CDs, including hydrothermal ultrasonic, laser ablation, and microwave synthesis, have been studied extensively, where the hydrothermal method was reported to be the most simple, environmentally friendly, and inexpensive [20]. The potential applications of CDs were demonstrated in numerous areas, including biosensing [21], chemical sensing [25–27], bioimaging, electrocatalysis, and photocatalysis [25]. Additionally, CDs have been employed in the electrochemical detection of dopamine [26], L-cysteine [27], and curcumin [28], demonstrating the prospects of applying CDs in the electrochemical field.

Chitosan (CS) is a linear polysaccharide composed of randomly distributed β -(1 \rightarrow 4)-linked D-glucosamines (deacetylated units) and N-acetyl-D-glucosamines (acetylated units) [29]. The compound is a biocompatible, hydrophilic, cationic, and biodegradable biopolymer [30]. Consequently, CS could be utilised as a dispersant to form a stable film on the surface of electrodes with several kinds of modified materials due to its great film-forming ability, good adhesion, soaring permeability, nontoxicity, cheapness, and susceptibility to chemical modifications [29]. Furthermore, the compound is also applicable as energy storage materials [31], biosensors [29], and cell imaging [32], as it could

be electrodeposited on the broad surfaces of electrodes or conductive substrates to form coatings or patterns with precise spatial and temporal control [34-35]. Some biological materials (such as glucose oxidase and haemoglobin) and nanoparticles (for example, silver nanoparticles and carbon nanotubes) could also be deposited by employing CS [34], where the CS acts as a immobilisation matrix combined with CDs to modified electrodes and utilised as sensors [26].

In the present study, carbon dots-chitosan (CDs-CS) composite deposited on screen-printed carbon electrode (SPCE) for excellent catalytic performance and conductivity for BPA determination was explored. The nanocomposite offered several advantages, including remarkable conductivity, large surface area, good film-forming capabilities, and high stability. Furthermore, the CDs-CS based electrode provided an excellent electrocatalytic activity toward BPA oxidation, representing a new platform for electrochemical sensor development.

Materials and Methods

Reagents and materials

The BPA, potassium chloride (KCl), potassium ferricyanide ($K_3[Fe(CN)_6]$), citric acid, acetic acid, disodium hydrogen phosphate ($Na_2HPO_4 \cdot 7H_2O$), and potassium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$) were purchased from R&M Chemicals company (Petaling Jaya, Selangor, Malaysia). The CS was obtained from Sigma-Aldrich (Petaling Jaya, Selangor, Malaysia), while ethylenediamine was bought from Acros Organics (Geel W.Z.2., Geel, Belgium). In the current study, deionised water ($18.2 \text{ M}\Omega \cdot \text{cm}$ at 25°C , Milli-Q) was employed throughout the experiments.

The screen-printed carbon electrode (3 mm in diameter) consisted of a reference (AgCl), counter (carbon), and working (carbon) electrodes that were purchased from Rapid Labs Sdn. Bhd. (Bangi, Selangor, Malaysia). Each BPA standard solution was diluted with an 80:20 ethanol-to-water ratio in volume per volume (v/v) into a stock solution of $100 \mu\text{M}$ BPA. Electrochemical measurements were performed with Model Autolab Type III (Eco Chemie B. V., Netherlands). Cyclic voltammetry (CV) and differential pulse voltammetry

(DPV) data analyses were conducted via the Nova 1.11 software.

The synthesis of CDs and preparation of CS

The hydrothermal method was employed to synthesise the carbon dots in the present study [35]. First, the citric acid (3.0 g) and ethylenediamine (1.875 mL) were dissolved in deionised distilled water (ddH_2O , 30 mL). The solution was then transferred to a reactor and heated in an oven for five hours at 150°C . Subsequently, the clear brownish solution formed was stored at 4°C and wrapped with aluminium foil to maintain a dark condition. The CS solution (1%, w/v) was then prepared by dissolving 0.5 g CS powder in 1% (w/v) aqueous acetic acid solution (50 mL). The mixture was continuously stirred vigorously overnight.

The preparation of BPA stock solution and supporting electrolyte

A $100 \mu\text{M}$ BPA was prepared by adding 228 mg of BPA into 80% ethanol and 20% ddH_2O in a 100 mL volumetric flask. The $K_3[Fe(CN)_6]$ (5 mM) and 0.1 M KCl mixture was utilised as a supporting electrolyte, where 0.1646 g $K_3[Fe(CN)_6]$ and 0.7455 g KCl were dissolved in 100 mL of ddH_2O in a 100 mL volumetric flask. Subsequently, a phosphate buffer solution (PBS) was prepared by adding disodium hydrogen phosphate ($Na_2HPO_4 \cdot 7H_2O$) (2.0 g) and potassium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$) (0.339 g) into 80 mL of deionised water in a 100 mL conical flask. Hydrochloric acid and sodium hydroxide were employed to adjust the solution to the desired pH.

Modification of SPCE

A mixture (7 μL) of 1:1 (v/v) CDs solution to chitosan (1%, w/v) was spread on the surface of the SPCE before being dried for approximately five hours at room temperature. The modified electrode is then denoted as the CDs-CS/SPCE.

The electrochemical method

The CV analysis was implemented within the -0.4 and 0.65 V potential range at a 100 mV/s scan rate for five cycles to evaluate the performance of the modified SPCE by employing 5 mM $K_3[Fe(CN)_6]$ and 0.1 M KCl. A redox probe consisting of $K_3[Fe(CN)_6]$ was employed to evaluate the electrochemical behaviour of the SPCE

post-modification with CDs-CS [36]. Differential pulse voltammetry (DPV) measurements were recorded within the 0.1 to 0.8 V potential range with PBS (pH 7.4). The assessment parameters were 0.2 V deposition potential, 60 s deposition time, and 10 mV/s scan rate.

Results and Discussion

Electrochemical behaviour of the modified electrodes

The electrochemical behaviours evaluation of the modified electrodes was performed with CV analysis. Figure 1 illustrates cyclic voltammograms of the bare SPCE, CS/SPCE, CDs/SPCE, and CDs-CS/SPCE electrodes. The pair of redox peaks exhibited by the bare SPCE demonstrated its electrochemical characteristics, which provided a rapid location of redox potentials of the electroactive species.

The modified CDs/SPCE recorded enhanced redox peak current at a calculated enhancement factor of 1.85, which might result from the wider active surface area and good electron transfer, as CDs are good conducting material. The electrochemical response of the CS-modified electrode documented a lower redox peak signal than the bare SPCE, indicating that the CS/SPCE was non-electroactive in the selected scanning region [37]. The CDs-CS/SPCE nanocomposites demonstrated synergistic electron transfer, as evidenced by the significant redox peak current signal enhancement at a factor of 4.17 due to the presence of CDs-CSs on the SPCE surface. The CDs were excellent conductors and more stable when CS was employed as a fixative agent on the electrode that opposed the easy dissolution of the CDs from the surfaces of the SPCE into the PBS solution [16]. The oxidation (E_{pa}) and reduction (E_{pc}) peak potentials were recorded at 0.31 and -0.04 V.

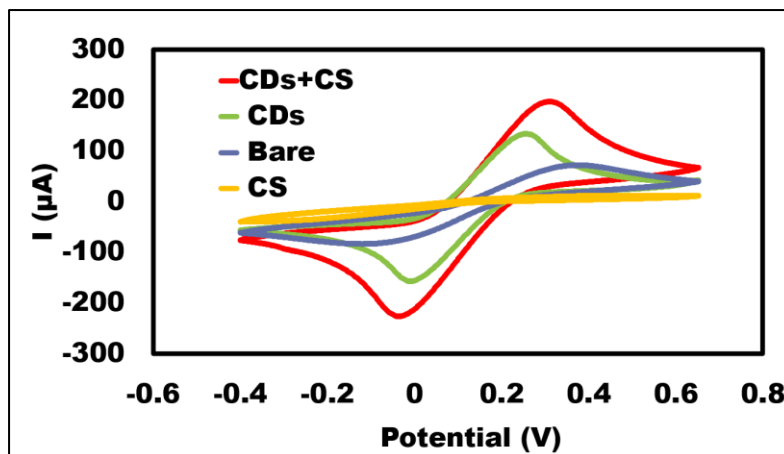


Figure 1. The cyclic voltammograms of the modified electrodes in 5 mM $K_3[Fe(CN)_6]$ /0.1M KCl within the -0.4 V to 0.65 V range potential at 100 mV/s scan rate

Optimisation: The influence of CS concentration (%) and volume and the CDs to CS ratio on the SPCE

The current study determined the optimised parameters for modifying the SPCE surfaces through CV. The optimum percentage of CS mixed with CDs, which could affect the performance of the CDs-CS/SPCE sensor, was investigated. Varying concentrations of CS, 0.1 to 2.0% (w/v), were employed. The current response increased from 0.1 to 1%, and the optimum current

response was observed at 1% (w/v) CS. At concentrations exceeding 1%, decreased current response was recorded [see Figure 2(a)]. The observations might be due to the increased resistance at the modified electrode surfaces with higher CS percentages [38]. Consequently, the present study employed 1% (w/v) CS concentration as the ideal percentage for the CDs-CS composite immobilisation onto the sensor.

The amount of CDs-CS composite immobilised on the surface of the SPCE affects the sensitivity of the developed sensor. Accordingly, different CDs-CS volumes (1 to 11 μL) were employed in the present study. The oxidation peak current was observed ascending with an increasing CD-CS volume up to 7 μL before slightly reducing [see Figure 2(b)]. The phenomenon might result from the thicker nanocomposite film formed with larger volumes of CDs-CS, which could obstruct the transfer of electrons and mass on the surface of the SPCE [38].

Consequently, the current study applied 7 μL CDs-CS in the fabrication of the sensor.

In the present study, the ratio of CDs to CS was varied (1:0.1, 1:0.5, 1:1, 1:1.5, and 1:2 v/v) to evaluate the optimum volume ratio of the CDs-CS composite. Figure 2(c) demonstrates that the oxidation current response increased from 1:0.1 to 1:1 before gradually dropping as the ratio rose to 1:2. The results could be due to the high volume of CS, which hindered electron transfer. Accordingly, a 1:1 (v/v) CDs to CS volume ratio was selected to fabricate the sensor developed.

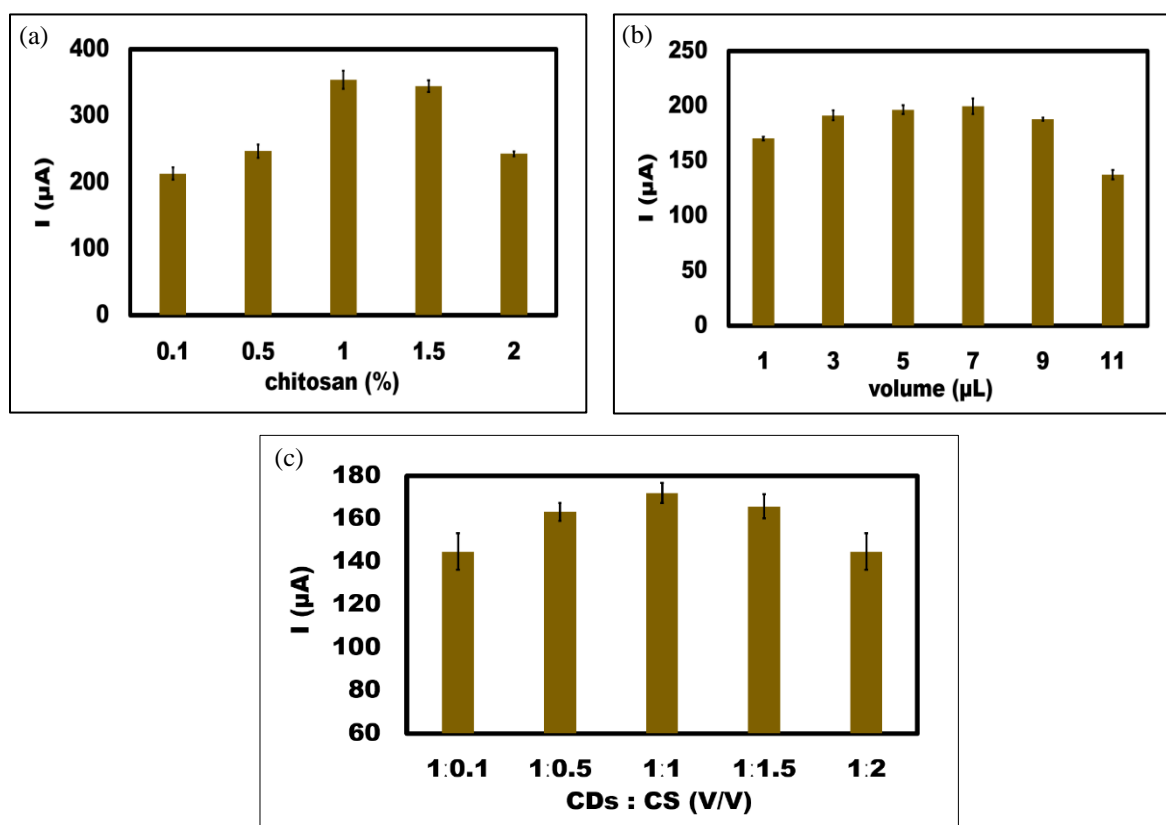


Figure 2. The influence of (a) CS concentration (% w/v), (b) volume of CDs-CS (μL), and (c) CDs to CS (v/v) ratio mixed drop casted onto the SPCE in 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/0.1$ M KCl at 100 mV/s scan rate

The effects of the supporting electrolyte

Supporting electrolytes play a significant factor in electrochemical studies for detecting analytes. Hydrochloric acid-potassium chloride buffer (HCl-KCl) (pH 3), PBS (pH 7.4), and carbonate-bicarbonate buffer (CBBS) (pH 9) solutions were employed as the

supporting electrolyte in the current study (see Figure 3). The buffers were selected due to their different pHs since BPA could be sustained at pHs 3-9 [39]. Nonetheless, numerous reports documented pH 7.4 as the ideal pH to determine BPA levels. The phenomenon might be due to the present form of BPA being affected

by the pH of the supporting electrolyte. In the present study, as 1 μ M of BPA was added to PBS (pH 7.4), a 4.0 μ A oxidation current was recorded, while HCl-KCl

buffer and CBBS documented 2.14 and 2.62 μ A, respectively. Consequently, PBS was selected for further analyses.

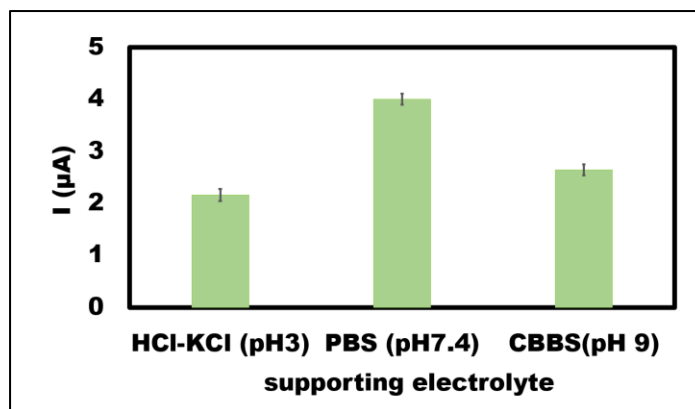


Figure 3. The effects of various supporting electrolytes on the sensor signals in the presence of 1 μ M BPA

The effects of pH

Another vital criterion for evaluating the performance of sensors in detecting BPA is pH, and in the current study, the effects were assessed within the 6–8 pH range. The PBS was utilised as the suitable pH to sustain the BPA was reported to be slightly acidic to slightly basic [39]. The anodic peak (E_{pa}) and anodic current (I_{pa}) potentials of 1 μ M BPA were examined. The I_{pa} increased from pH 6 to 7 and reached the highest value at pH 7.4. The I_{pa} value then gradually decreased as the pH rose to 8 [see Figure 4(a)]. The CDs could absorb the non-dissociated BPA more easily than the dissociated form in a neutral pH environment with the optimal pH value, which was lower than the pKa of BPA (pKa = 9.73) [35]. Moreover, the results agreed with previous reports that recorded pH 7.4 as the best pH for determining BPA levels [40–41]. Consequently, pH 7.4 was chosen as the optimum pH since it recorded the highest response from the sensor.

Figure 4(b) demonstrates the BPA E_{pa} shifting to a more negative value as the pH was increased due to deprotonation of BPA towards CDs-CS/SPCE [42]. At lower pHs, the H^+ ions of the analyte tend to compete with the excess H^+ ions originating from the supporting electrolyte. Consequently, a driving force (energy) is required for the BPA to be oxidised, resulting in the peak occurring at higher potentials. The equation $E_{pa} (V) = -0.0618 \text{ pH} + 0.9032$, $R^2 = 0.9724$ illustrates that the E_{pa} and pH possessed a better linearity with a high correlation coefficient. A shift of typically 61.8 mV per pH unit was very close to the Nernst theoretical value, which is 59.10 mV pH^{-1} . The value revealed that the deprotonation of BPA towards CDs-CS/SPCE occurred [42], revealing that equal numbers of proton and electron were present on the electrode that resulted from the electrochemical oxidation of BPA [43]. Accordingly, PBS at pH 7.4 was selected to determine BPA levels in the present study.

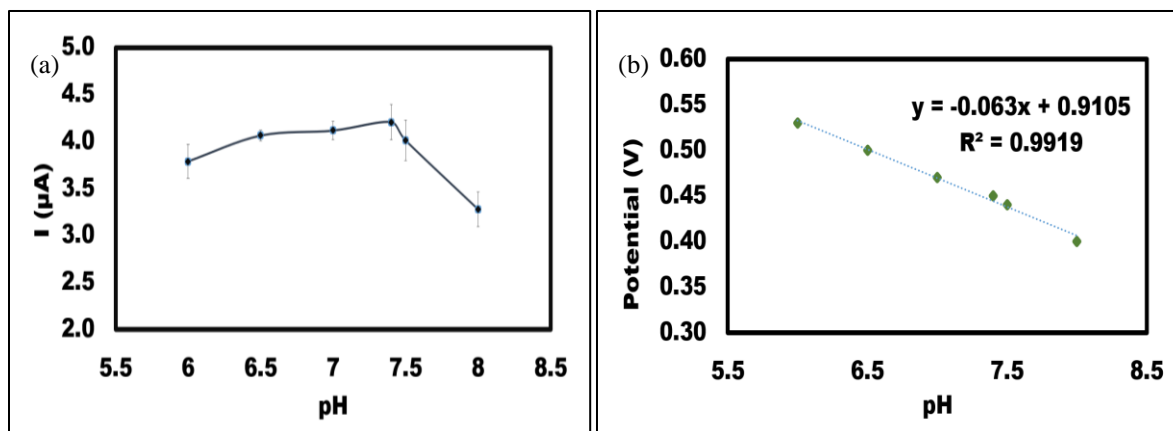


Figure 4. The effects of pH on the (a) oxidation peak current and (b) potential response of 1 μM BPA determined via DPV at 10 mV s⁻¹ scan rate

The effects of deposition time and potential

Deposition time is one of the essential factors in improving BPA detection. The data measures the optimum period for the BPA to be deposited onto the surface of the CDs-CS/SPCE sensor. The DPV was employed to evaluate the factor in the presence of 1 μM BPA in PBS (pH 7.4) within a 20-140 s time frame. Figure 5(a) demonstrates the increment of the oxidation peak current at 60 s. At more than 60 s, the oxidation peak current started to descend due to the saturation of the active surface site on the electrode surfaces with BPA, which lessened the electron transfer rate between them. Consequently, 60 s was selected as the best

deposition time to develop the sensor in the present study.

Figure 5(b) portrays the relationship between the BPA oxidation peak current signal and deposition potential. As the potential elevated from 0.1 to 0.2 V, the BPA oxidation peak current gradually increased. Conversely, the BPA deposited on the electrode surfaces decreased at deposition potentials exceeding 0.5 V. The phenomenon could be related to saturated adsorption of BPA on the SPCE surfaces. Accordingly, 0.2 V was selected as the optimal deposition potential for the present study.

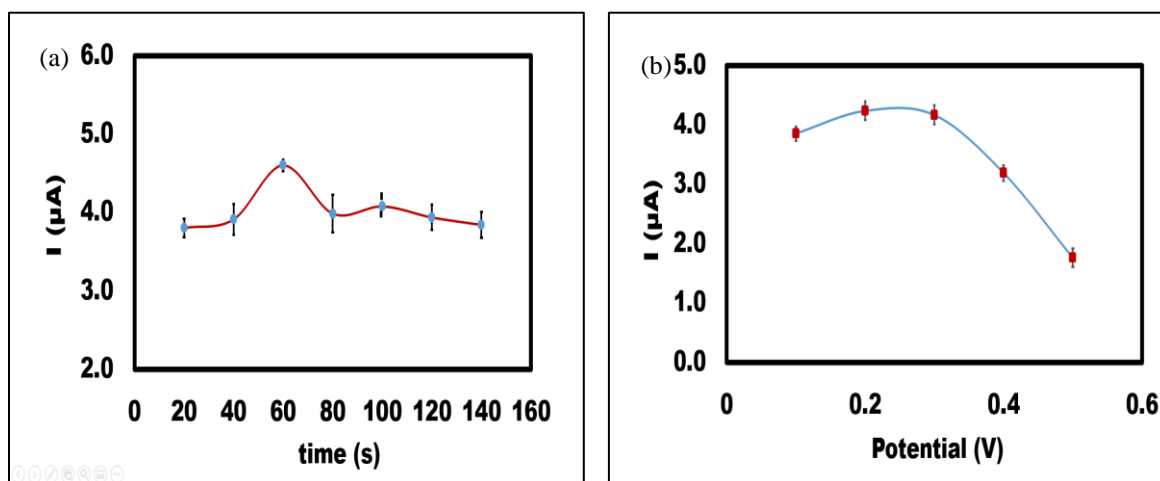


Figure 5. The effects of deposition (a) time and (b) potential on the 1 μM BPA oxidation peak current in PBS (pH 7.4)

Electrochemically active surface area

In the current study, the scan rate employed was within the 10 to 100 mV/s range in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as the probe via the CV technique. By exploring the relationship between the anodic current response and the square root of scan rate, the electroactive surface area of the bare SPCE and the modified CDs-CS/SPCE was determined with the Randles-Sevcik equation (Eq. 1).

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} V^{1/2} C_0 \quad (1)$$

where I_p is the maximum current, n is the number of electrons transferred ($n = 1$), A is the electroactive

surface area of the electrode (cm^2), D is $7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is the diffusion coefficient of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution, C_0 is the concentration of $[\text{Fe}(\text{CN})_6]^{3-/4-}$, and V is the scan rate (mV/s) [44].

Based on Figure 6(a), the current response constantly increased and shifted towards positive potential at higher scan rates (mV/s). The regression equations, E_{pa} , obtained for the bare SPCE and modified SPCE were slope = 5.778, $R^2 = 0.9627$ and slope = 21.956, $R^2 = 0.9987$, respectively. Consequently, the calculated electroactive surface area for the bare SPCE was 0.0016 cm^2 , while the CDs-CS/SPCE recorded 0.0049 cm^2 , which was approximately 3-fold higher.

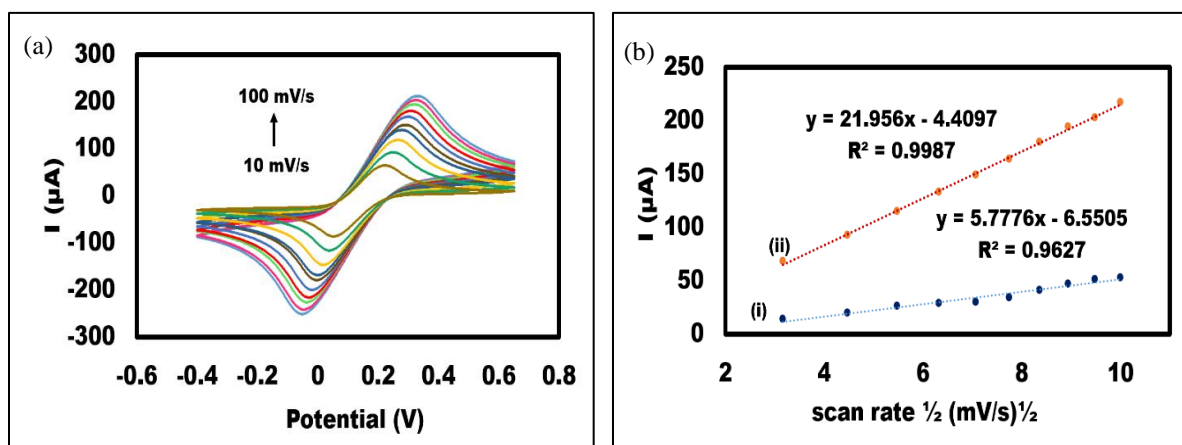


Figure 6. The (a) cyclic voltammograms of the modified electrode for scan rates between 10 and 100 mV/s and (b) oxidation current response towards the square root of scan rate for the (i) bare and (ii) CDs-CS/SPCE electrodes

The electrochemical behaviour of BPA

Figure 7(a) illustrates the cyclic voltammograms of the single oxidation peak current of BPA ($1 \mu\text{M}$) in PBS (0.1 M , $\text{pH } 7.4$). The absence of reduction peak current indicated the irreversible process of BPA determination [45]. Nonetheless, as the cycle increased, the anodic current of BPA significantly decreased. The behaviour could be due to the formation of polymeric products by BPA, which blocked the surfaces of the electrode.

The electrochemical responses of BPA at varying modification conditions of the SPCE were also

evaluated through DPV [see Figure 7(b)], consisting of $1 \mu\text{M}$ BPA in PBS ($\text{pH } 7.4$) and within the $+0.2$ to $+0.7 \text{ V}$ potential range. The oxidation peak was observed at the $+0.45 \text{ V}$ potential for the CDs-CS/SPCE, which was in agreement with previous studies that documented an anodic peak current of $4.23 \mu\text{A}$. The BPA electrochemical response for the bare SPCE, CS/SPCE, and CDs/SPCE were observed at 0.48 , 0.45 , and 0.43 V potentials with anodic peak currents of 0.37 , 2.37 , and $2.94 \mu\text{A}$, respectively.

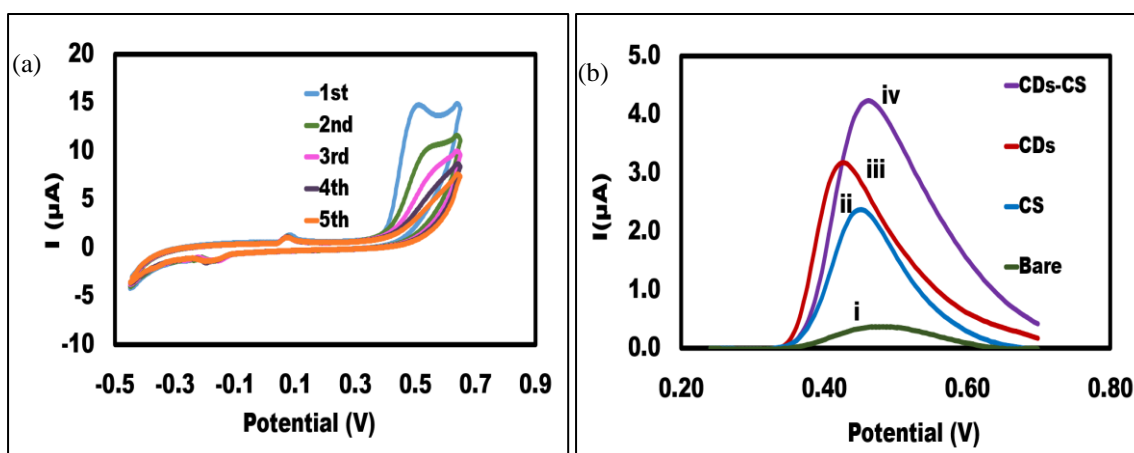


Figure 7. The (a) cyclic voltammograms of different cycles of CDs-CS/SPCE at 100 mV/s scan rate and (b) differential pulse voltammograms of the (i) bare (ii) CS (iii) CDs, and (iv) CDs-CS electrodes in 1 μ M BPA with 0.1 M pH 7.4 PBS

The CDs-CS/SPCE sensor recorded an absolute-defined oxidation peak at the +0.45 V potential in DPV. Under optimised conditions, the behaviour of the electrochemical response of the sensor towards BPA in PBS (0.1 M, pH 7.4) as a supporting electrolyte was

investigated. Figure 8 illustrates the oxidation peak current observed in varying concentrations of BPA, 0.4 μ M to 10 μ M, with a sensitivity of 0.4606 μ A/ μ M ($R^2 = 0.9911$) and a limit of detection (LOD) of 0.37 μ M.

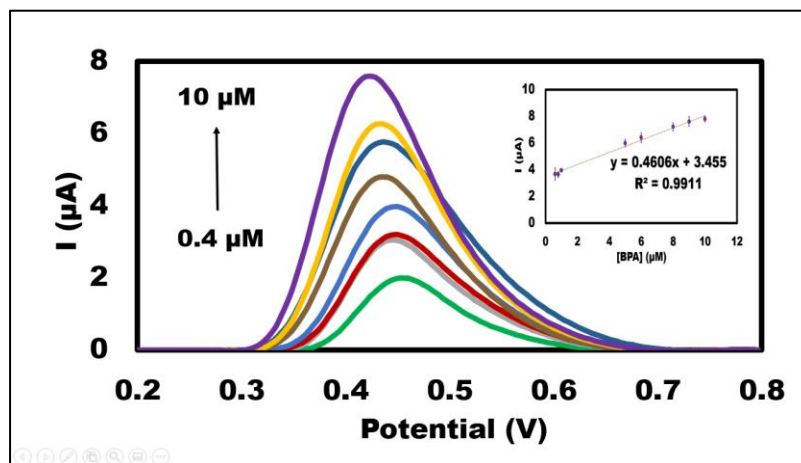


Figure 8. The differential pulse voltammograms of oxidation peak current in varying BPA concentrations (0.4– 10 μ M) in PBS (0.1 M, pH 7.4) at 10 mV/s scan rate within 0.2 and 0.8 V potential range versus AgCl. *Note:* The inset diagram denotes the correlation between the current response (μ A) and BPA concentration (μ M)

Reproducibility, stability, and selectivity of the CDs-CS/SPCE electrodes

The reproducibility of the CDs-CS/SPCE sensor was examined with fabricated sensors prepared

independently within similar parameters and evaluated with 1 μ M BPA in PBS (pH 7.4). The relative standard deviation (RSD) was 3.66 % ($n = 15$), indicating good reproducibility. The developed sensor was stored in a

dark box at room temperature for the stability study. The performance of the sensor was evaluated every week in the presence of 1 μM of BPA in PBS (0.1 M, pH 7.4). The sensor retained its performance. Nevertheless, after one, two, and three weeks, the performance decreased to 91.3, 89.5, and 79.5% of its initial response after a month of storage. The selectivity of the developed

sensor was also evaluated. Figure 9 demonstrates that the sensor recorded no significant current response towards phenol, 2,4-dinitrophenol, 4-chlorophenol, K^+ , Cu^{2+} , Cl^- , and SO_4^{2-} . The compounds were employed at a concentration 10-fold higher (10 μM) than the BPA, proving that the developed sensor was selective towards BPA.

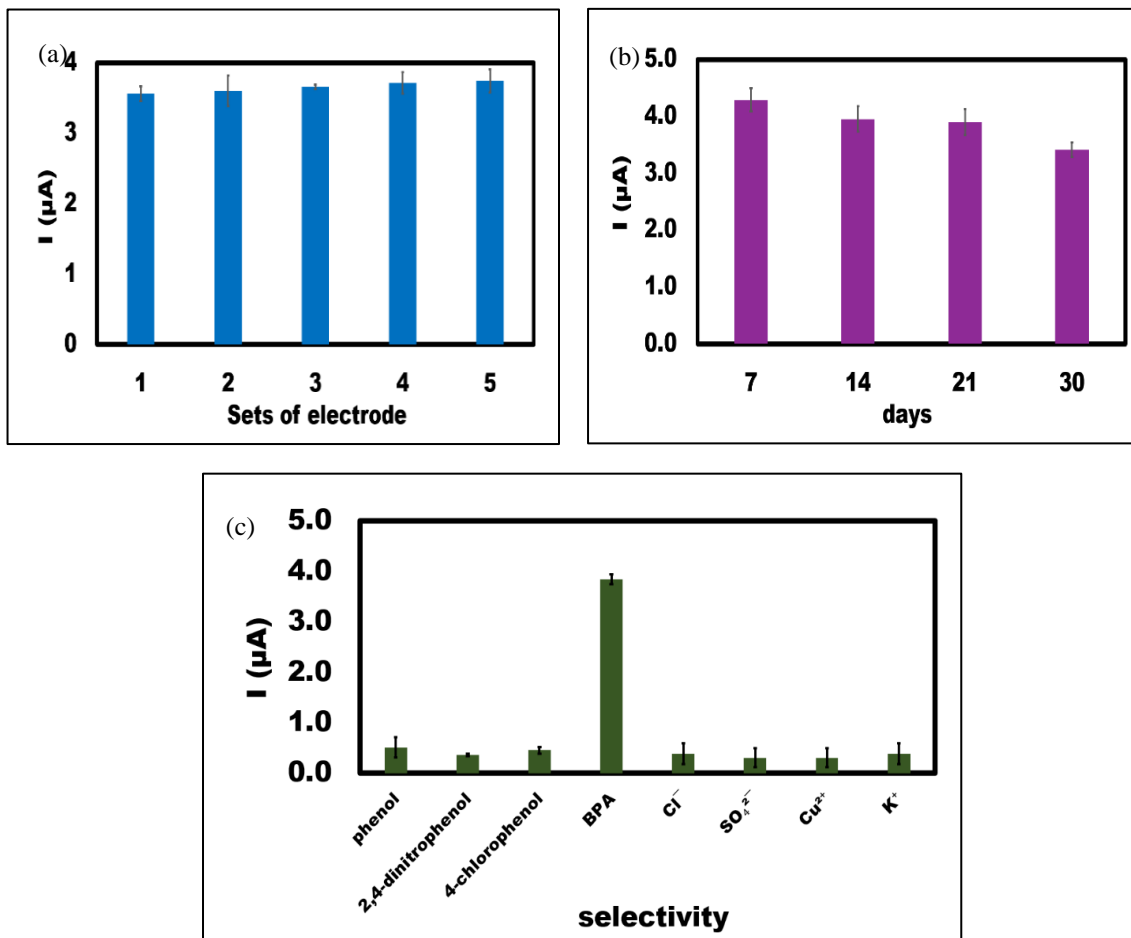


Figure 9. The current responses of (a) different sets of electrodes utilised in the reproducibility study, (b) electrodes analysed on different days in the stability study, and (c) various phenols and ions tested in PBS (pH 7.4) for the selectivity study

Conclusion

The present study successfully fabricated SPCE with CDs-CS to develop electrodes with good electrocatalytic performance to detect BPA. The CDs-CS/SPCE-based sensor exhibited good analytical performance in determining BPA within the 0.4 to 10

μM concentration range, with a sensitivity of 0.46 $\mu\text{A}/\mu\text{M}$ ($R^2 = 0.9911$) and LOD 0.37 μM . The developed sensor also provided a large surface area for BPA adsorption and good conductivity and selectivity. Furthermore, the sensor demonstrated potential

applications for the sensitive and rapid determinations of BPA levels in aqueous systems.

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