



A novel highly sensitive carbon-based HMPD/GC sensor electrode: copper ions analysis in flour and water samples

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ABSTRACT

In this research, (Z)-2-(2-(hydroxyimino)-2-(3-methyl-3-phenylcyclobutyl)ethyl)-3a,7a-dihydro-1H-isoindole-1,3(2H)-dione, HMPD molecule has been grafted to the glassy carbon (GC) electrode surface. The HMPD-modified GC electrode has been originally developed and it used for the quantitative determination of Cu(II) in flour and water samples. The modification steps have been performed using cyclic voltammetry (CV). CV, electrochemical impedance spectroscopy and scanning electron microscopy have been employed for the characterization processes. Cu(II) standard solutions changing from 1.0×10^{-9} to 1.0×10^{-3} M have been prepared and the corresponding peak currents have been measured. From the obtained data calibration equation has been calculated $I_p = -1.555C_{Cu} + 15.86$ which is having a 0.9974 correlation coefficient. 10.0 mL of flour and water samples have been mixed with 10.0 mL Britton–Robinson (BR) buffer solution (pH = 5.00) and HMPD/GC sensor electrode has been kept in these mixed solutions for 90 min. Differential pulse voltammetric (DPV) technique has been applied for the measurement of the peak currents. After the application of the developed sensor electrode for Cu(II) detection in flour and water samples, Cu(II) ion concentrations have been calculated from the obtained peak current values, 1.97 and 2.46 μ A. The Cu(II) ion concentrations have been calculated as 1.17×10^{-9} and 2.41×10^{-9} M, respectively.

Keywords: Chemical sensor electrode; Voltammetric techniques; HMPD/GC electrode; Surface modification; Surface characterization

1. Introduction

Recently, air, soil and water contamination have rapidly increased by the industrialization and urbanization [1]. In all environmental matrices, heavy metal contamination tends to concentrate, particularly in those involved in the food chain [2]. Heavy metal may exist in food either naturally or as a

consequence of anthropic sources. They have destructive effect to human health even at low concentration when ingested over a long period of time [3,4]. Thus, it is important to ensure that such heavy metal should be kept below the maximum limit that is allowed by WHO in milligrams per milliliter range [5,6]. Heavy metal pollution has become a serious threat to human health, living resources and ecological systems. They tend to accumulate in living organisms, causing various diseases and disorders in the living systems [7,8].

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Copper is one of the essential micronutrient for humans and other creatures. It has an important role in various physiological processes in living organisms such as blood formation, connective tissue development, functioning of a variety of metallo-enzymes and transcriptional events [9]. On the other hand, the excessive intake of copper ions through contaminated food and tap water is highly toxic to living organisms and it may damage the liver or kidney and cause many serious diseases [10,11].

Variety of analytical techniques have been employed for Cu(II) detection such as, flame atomic absorption spectrometry [12,13], inductively coupled plasma mass spectrometry [14], electrothermal atomization atomic absorption spectrometry (ET-AAS) [15], inductively coupled plasma optical emission spectrometry [16], graphite furnace atomic absorption spectrometry [17], inductively coupled plasma-atomic emission spectrometry [18] and anodic stripping voltammetry [19,20]. When it is compared with other methods, electrochemical method is advantageous for the detection of Cu(II) due to its high sensitivity, simplicity, miniaturization and low cost [21–23].

Modification of carbon surfaces is an important objective in electrochemistry and material science. In electrochemistry, carbon electrodes are widely used because of low background current, low cost, wide potential window, speed, low equipment, chemical inertness and minimum sample pretreatment required prior to analysis [24,25]. One of the reasons for the considerable current trend in modification of carbon materials is because it has good conductivity and resistance to environmental and chemical attack due to being inert. Electrochemical methods are based on the direct oxidation or reduction of substrate onto an electrode surface. Electrode reactions are very suitable for analytical applications due to their requirements of high potential. Moreover, these surfaces can be modified by a reductive substrate for analytical applications. Lately, the application of inorganic modified electrodes has increased [26,27]. Anodes, suitable for the active and high positive potentials are important for the electro-oxidation of organic pollutants. However, oxygen is released at higher potential which interferes obtaining good results [28,29]. In the electrooxidation, hydroxylation and hydrogen evolution take place which is a favored situation due to hydroxy adsorption [30–32]. The main purpose of this study was (1) to develop an electrochemically modified HMPD/GC – (Z)-2-(2-(hydroxyimino)-2-(3-methyl-3-phenylcyclobutyl)ethyl)-3a,7a-dihydro-1H-isoindole-1,3(2H)-dione (Fig. 1)/glassy carbon – electrode in non-aqueous media by CV; (2) to characterize the HMPD/GC electrode by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM); (3) to propose the structure of the complex formed between the HMPD/GC electrode with Cu(II); (4) to investigate the interference effects and apply the HMPD/GC sensor electrode for Cu(II) determination at trace level in water and flour samples for the first time.

2. Experimental setup

2.1. Chemicals and solutions

The used chemicals were obtained from Merck (Darmstadt, Germany), Fluka (Bucharest, Romania), Riedel

de Haen (Seelze-Hannover, Germany) and Sigma-Aldrich (St. Louis, Missouri, USA). They were of analytical reagent grade ultra pure quality water having a resistance of 18.2 MΩ cm (MP Minipure Dest Up Ultra Pure Water System, Ankara, Turkey) was used throughout the experiment. 1.0 mM HMPD solution was prepared in a mixture of 10.0 mL acetonitrile (CH₃CN) and 40.0 mL phosphate buffer solution (PBS) with a pH value of 7.00. Na₂HPO₄ and NaH₂PO₄ each of 0.05 mM were mixed to prepare the PBS solution. The pH was adjusted by a dropwise addition of NaOH or HCl solution.

Using a stock solution of 1,000 ppm Cu(II) in BR buffer solution at pH 5.00 was used to prepare a series of standard solutions of Cu(II) varies from 1.0×10^{-9} to 1.0×10^{-3} M. BR buffer solution was prepared by using H₃PO₄, CH₃COOH and H₃BO₃ according to the literature [31,34]. Fine pH adjustments were carried out using dropwise addition of 0.2 or 1.0 M NaOH.

2.2. Electrodes and apparatus

In our experiments, GAMRY Reference 600+ series potentiostat/galvanostat/ZRA having EIS 300 software from GAMRY Instruments (PA, USA) electrochemical analyzer with BAS (Bioanalytical Systems, West Lafayette, IN, USA) Model MF-2012 with traditional three-electrode cell, BAS model C3. The reference electrodes were Ag/Ag⁺ (10 mM AgNO₃) (BAS Model MF-2042) for non-aqueous medium and Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous medium. The counter electrode was Pt wire. VWR pH 1100L pH meter (PA, USA) was employed for pH measurements. SEM (Carl Zeiss LS10 Series SEM, Missouri, USA) was used for the morphology investigation of HMPD film on Tokai GC-20 disc electrode surface.

2.3. Preparation and modification processes

The GC electrodes were prepared for the experiments by polishing to gain a mirror-like appearance, first with fine wet emery papers (grain size 4000) and then with 1.0 and 0.3 mm alumina slurry on micro cloth pads (Buehler, USA). Following the initial polishing, the GC electrodes were resurfaced with 0.05 mm alumina slurry. The GC electrodes were sonicated both in water and in 1:1 (v/v) isopropyl alcohol (IPA) and CH₃CN (IPA + CH₃CN) mixture for 10 min in the following order [33,34].

1.0 mM HMPD (in 10.0 mL CH₃CN + 40.0 mL PBS, at pH 7.00) solution was used to modify the GC electrodes in +300 mV to +2,800 mV potential range using 100 mV s⁻¹ sweep rate and 30 cycles.

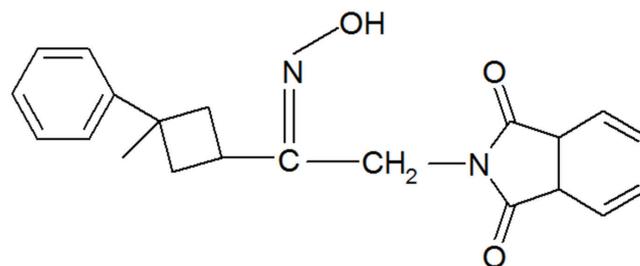


Fig. 1. Chemical structure of HMPD.

3. Results and discussion

3.1. Modification of HMPD onto GC surface and surface characterization

HMPD molecules were grafted to the electrode surface in the +300 and +2,800 mV potential ranges with a sweep rate of 100 mV s^{-1} and 30 cycles (Fig. 2). Fig. 2 clearly depicts that one cycle is enough for grafting of HMPD molecules to the GC electrode surface. This is a clear evidence for monolayer binding of HMPD molecule to the electrode surface. The surface was found to be stable after the first cycle. In the modification step, 30 cycles have been applied to fill any pin holes that may exist on the electrode surface. This application has not formed multi-layer on the electrode surface. The electro-oxidation mechanism has been discussed in recent papers [35,36]. After the modification process in non-aqueous

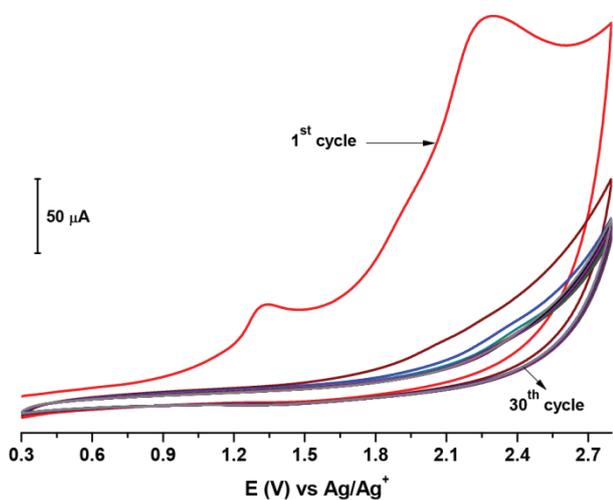


Fig. 2. Cyclic voltammogram of 1 mM HMPD in 100 mM NBu_4BF_4 (in CH_3CN) vs. Ag/Ag^+ (10 mM AgNO_3) on bare GC electrode surface. Potential range from +300 to +2,800 mV, sweep rate is 100 mV s^{-1} and 30 cycles.

medium was completed (Fig. 3), the sensor electrode was used for the determination of Cu(II) .

Surface characterization was carried out right after the modification process using CV and EIS techniques. In the characterization with CV, 1.0 mM ferrocene solution in 100 mM tetrabutylammonium tetrafluoroborate (NBu_4BF_4) was used in the potential range from -200 to $+400$ mV in Fig. 4(A) and 1.0 mM Fe(CN)_6^{3-} in BR buffer solution, pH 2.00, was used in the potential range from $+600$ to 0.0 mV in Fig. 4(B) at a sweep rate of 100 mV s^{-1} . Comparison has been made between the surface voltammograms of the modified electrode and the bare GC electrode. The electrode surface was negatively charged after the modification process. Thus, negatively charged ferrocyanide ions are repelled by the negatively charged electrode surface. Consequently, no electron transfer occurs.

Impedance measurements were carried out in 1.0 mM Fe(CN)_6^{3-} and Fe(CN)_6^{4-} mixture (in 100 mM KCl) in the range from 100.000 to 0.05 Hz frequency. The Nyquist plot of the modified electrode was compared with the EIS data of the bare GC electrode. The Nyquist plots of the EIS investigations are shown in Fig. 5.

The solution resistance (R_s), the charge transfer resistance (R_{ct}), constant value (Y_0), constant phase element (CPE) exponent (α) and the CPE are the elements of equivalent circuit. The experimental impedance values are coupled with the Randles equivalent circuit simulation using Gamry EIS300 EIS software.

It can be concluded from the data of characterization processes that HMPD molecule is grafted onto the GC electrode surface in non-aqueous medium. EIS is a valuable method to monitor the impedance changes of the electrode surface during the modification process. The semicircle diameter of Nyquist plot reflects the R_{ct} , which is from the electron transfer of the redox probe $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ solution. Fig. 5 shows the results of EIS for bare GC and HMPD/GC electrodes. The value of R_{ct} was obtained as $1.530 \times 10^3 \Omega$ for bare GC electrode surface. After completing the modification process, this value of R_{ct} increased to $2.450 \times 10^3 \Omega$, which is much higher than that of bare GC. This increase is

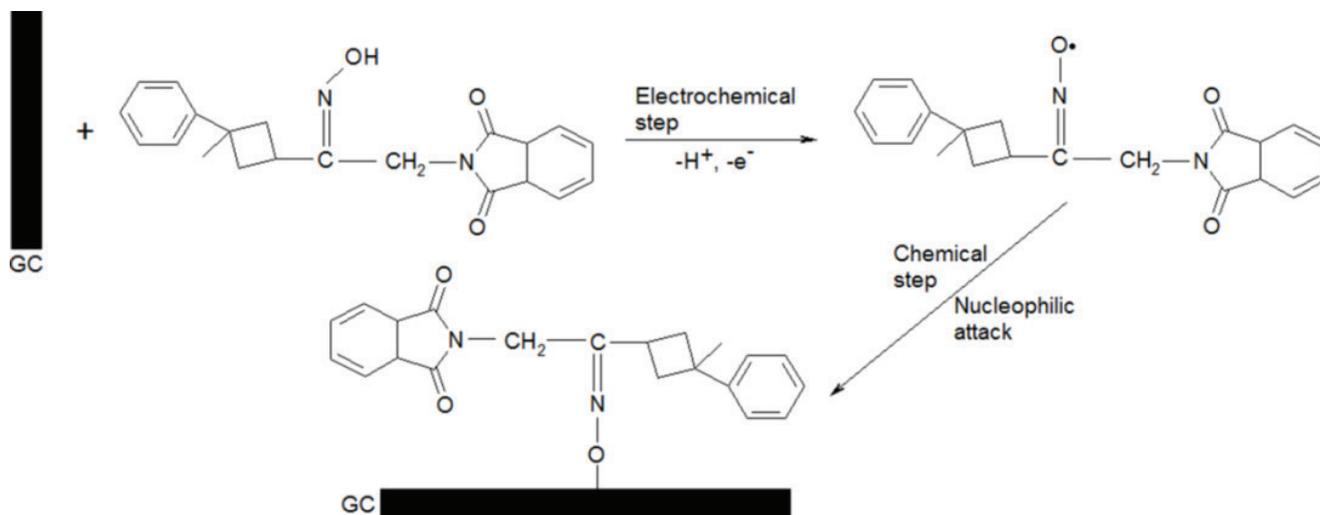


Fig. 3. Modification mechanism of HMPD at GC electrode surface (in CH_3CN containing 100 mM NBu_4BF_4).

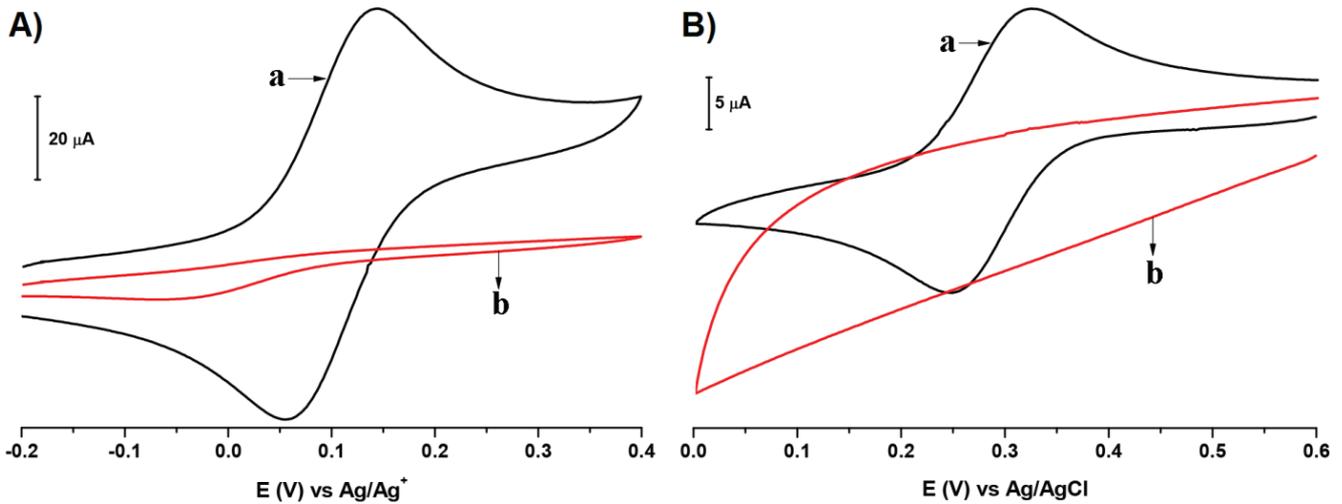


Fig. 4. Overlaying the bare GC and HMPD/GC voltammograms (A) 1 mM ferrocene redox probe solution vs. Ag/Ag⁺ (10 mM) in MeCN + 0.1 M NBu₄BF₄, (a) bare GC and (b) HMPD/GC; (B) 1 mM Fe(CN)₆³⁻ redox probe solution vs. Ag/AgCl/(3 M KCl) in BR buffer solution, pH 2.0, (a) bare GC and (b) HMPD/GC. Sweep rate was 100 mV s⁻¹.

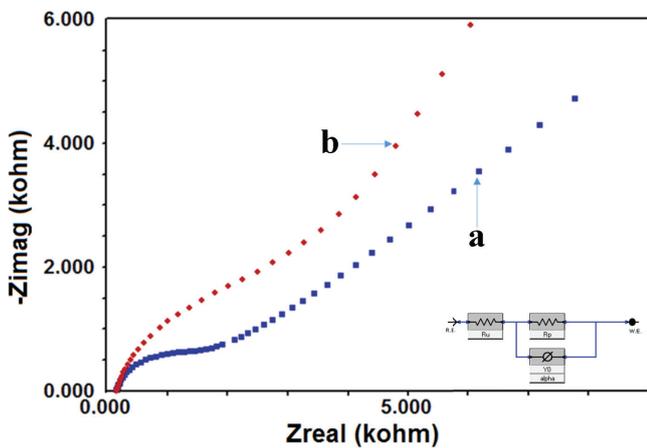


Fig. 5. Nyquist plots of 1 mM of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ in 0.1 M of KCl of bare GC (a), and HMPD/GC electrode (b). Frequency range is from 100.000 to 0.05 Hz, the modulation amplitude is 10 mV. Inset: equivalent circuit applied for calculations.

due to the presence of low conductive HMPD/GC electrode surface. A nearly straight line was gained with the R_{ct} value close to zero, indicating that HMPD/GC electrode acted as the electroactive layer for the electron and mass transfer, and hindered the diffusion of ferricyanide toward the electrode surface. Following the impedance measurement, the simulation was done for obtaining a plot to suggest an equivalent circuit model (CPE) using the calculated parameters $R_{ct} = 2.450 \times 10^3 \Omega s$, $R_s = 180.0 \Omega s$, $Y_0 = 13.0 \times 10^{-6} S$, $\alpha = 0.900$.

Eq. (1) was used to calculate the electron transfer rate constant, k^0 , for Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ for bare GC and HMPD/GC electrode surfaces.

$$R_{ct} = \frac{RT}{(nF)^2 Ak^0C} \quad (1)$$

Here A is the electrode area (cm²); n is number of electrons required for oxidation/reduction of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ mixed solution system; C (mol cm⁻³) is the molar concentration of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻; R (8.314 J mol⁻¹ K⁻¹) is the ideal gas constant, T (K) is temperature; F (96,485 C mol⁻¹) is Faraday constant [37]. The values for k^0 were calculated to be 2.45×10^{-6} and 3.75×10^{-4} cm s⁻¹ for bare GC and HMPD/GC electrodes, respectively.

Moreover, the covered electrode area was calculated according to Eq. (2),

$$\theta = 1 - \left(\frac{R_{ct}^0}{R_{ct}} \right) \quad (2)$$

Here R_{ct}^0 is the charge transfer resistance of the bare GC electrode and R_{ct} is the charge transfer resistance of the HMPD/GC electrodes and θ is the area that is modified with HMPD. The R_{ct} values of each electrode surface were obtained by fitting the Nyquist plots of the related electrode surfaces. According to the results represented in Nyquist plot, it was calculated that EIS signal is equivalent to 99.35% coverage of the GC surface.

Calculation of R_{ct} values of the Nyquist plots (Fig. 5) for 1.0 mM Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ solution (in 100 mM KCl) for the (a) bare GC and (b) HMPD/GC electrodes.

In addition to CV and EIS measurements, SEM was also used for the characterization of bare GC and HMPD/GC layers grafted on the GC electrode surface. The SEM images are presented in Fig. 6. The bare GC electrode surface is shown in Fig. 6(A). The granular structure of the HMPD/GC electrode (Fig. 6(B)) formed a larger surface area suitable for complex formation with Cu(II).

3.2. Detection of Cu(II) on modified HMPD/GC electrode by differential pulse voltammetric technique

Differential pulse voltammetric (DPV) technique was used to study the oxidation of HMPD complex of Cu ions in

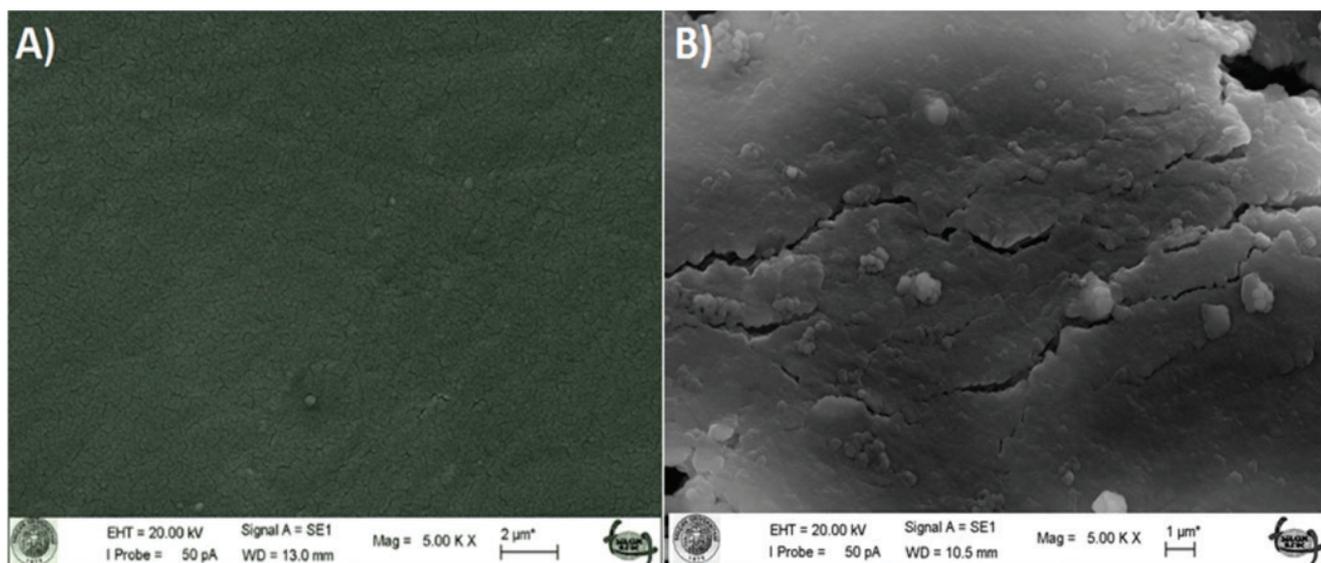


Fig. 6. SEM images of (A) bare GC and (B) HMPD/GC electrode surfaces.

BR solution at the pH 5.00. The result of this study is shown in Fig. 7.

In DPV experiments, the parameters were as follows: potential range: -400 to $+400$ mV, potential sweep rate: 50 mV s^{-1} , pulse amplitude: 25 mV, pulse period: 0.05 s and sample period: 1.0 s. The pH of Cu(II) solution and incubation time of the HMPD-modified GC electrode were investigated and optimized. For the optimization step, Cu(II) solutions (1.0×10^{-3} M) were prepared in various BR buffer solution changing pH value from 2 to 12. These Cu(II) solutions were used to incubate the modified electrodes. The incubated electrodes were used for the determination of Cu ions using DPV technique. The optimum pH value was determined to be 5.00 from this study and this result is supported by some studies [38–42]. At higher pH values, Cu ions cannot be detected due to the precipitation formation as hydroxide.

To optimize incubation time, prepared HMPD/GC electrodes were incubated in Cu(II) solutions (in BR buffer at pH 5.00). Different time periods (30, 60, 90, 120 min) were applied. Up to 120 min incubation time, DPV signal increased. Beyond this time, steady state was achieved. The overall obtained optimum conditions are as follows: BR buffer solution of pH 5.00, incubation time 90 min and is depicted in Fig. 7.

3.3. Calibration curve and calculations

First, HMPD molecule was modified to the GC electrode surface using CV and then the modified electrodes were incubated for 90 min in the prepared Cu(II) solutions changing concentration from 1.0×10^{-9} to 1.0×10^{-3} M. 1,000 ppm stock solution was used for the preparation of standard Cu(II) solutions. The measurements were taken using DPV technique. From the peak current values and concentrations of Cu(II) standard solution, a working curve is graphed (Fig. 8). The equation derived from the calibration curve is $I_p = -1.555C_{Cu} + 15.86$. Here, I_p is the peak current and C_{Cu} is the concentration of Cu ions. An acceptable correlation coefficient (R^2) was

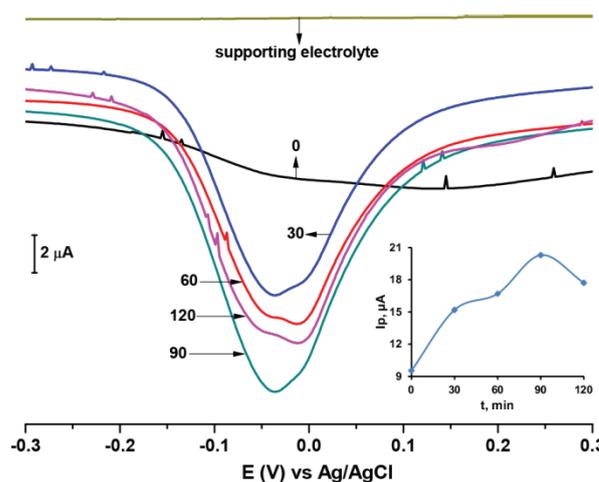


Fig. 7. Incubation time periods: (a) 0, (b) 30, (c) 60, (d) 90 and (e) 120 min in BR buffer solution, pH 5, and the time plot.

found to be 0.9974. Using the calibration curve, Cu ions were detected in water and flour samples.

3.4. Interference effects

For examining the interference effects, HMPD/GC electrode was incubated for 90 min in mixture of 1.0×10^{-6} M Cd^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and NO_3^- , SO_4^{2-} , CO_3^{2-} of each. Following 90 min incubation time, the voltammogram was taken. Generally, the tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the determination of Cu ions. We have found that relative error was below $\pm 5\%$ for all anions and cations. From this result, we accept that the interference effects of the cations and anions are within the tolerance limit under the specified optimum condition for this experiment. The developed electrode can successfully be used for the detection of Cu ions in the presence of studied anions and cations.

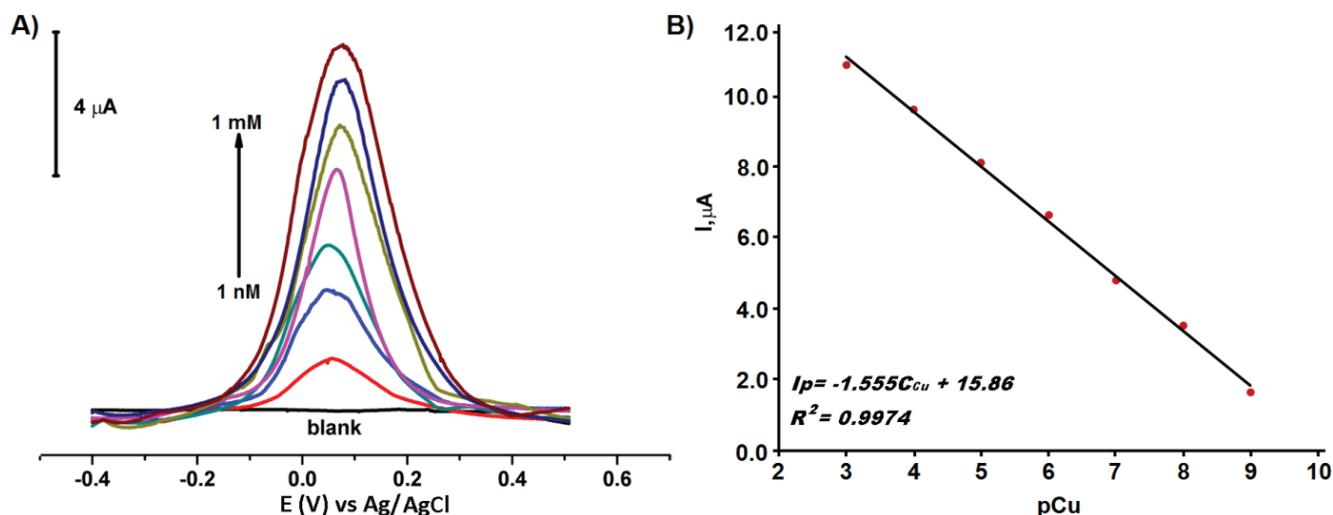


Fig. 8. (A) Differential pulse voltammograms of different concentrations of standard Cu(II) solution changing from 1.0×10^{-9} to 1.0×10^{-3} M (from 1,000 ppm stock solution) (BR buffer, pH 5.0) solution on HMPD/GC. The measurements were performed in BR buffer solution, pH 5.0, vs. Ag/AgCl/(3 M KCl). Sweep rate was 50 mV s^{-1} . (B) Linear relationship between peak currents and different concentrations of Cu(II) ions.

3.5. Determination of Cu(II) ions in flour and water samples

The proposed method was successfully applied for the detection of Cu(II) in water and flour sample in Konya, Turkey, without any pretreatment. For the detection of Cu(II), a homogeny mixture was prepared by sonicating the mixture of 10.0 mL BR buffer solution, pH 5.00, and 10.0 mL water sample for 10 min. HMPD-modified GC electrode was incubated for 2 h in the prepared mixture. On the other side, 5.0 g of flour sample was weighed and mixed with 50.0 mL of BR buffer solution (pH 5.00). The mixture was mixed with a magnetic stirrer for 12 h and then, it was filtered. A small portion of filtered solution was analyzed for its Cu(II) amount.

The voltammogram of incubated HMPD/GC electrodes was taken by differential pulse technique in BR buffer solution (pH 5.00). After grafting of Cu(II) in flour and water samples to the HMPD/GC electrode surface, peak current values were measured by DPV. Following this, the obtained peak current values (1.97 and $2.46 \mu\text{A}$) were used for the calculation of Cu(II) concentrations in flour and water samples from the calibration curve. The Cu(II) concentrations have been calculated to be 1.17×10^{-9} and 2.41×10^{-9} M, respectively. The obtained voltammogram is shown in Fig. 9. Each sample was determined by three times and the RSD was lower than 5%, revealing good precision.

4. Conclusions

Consequently, in this research, we developed a specific chemical sensor electrode for the detection of Cu ions in flour and water samples. Although there are few studies for the detection of Cu ions using chemical sensor, none has low detection limit. Some of the anions and cations have been tested for their interference effects. Their effects are found to be within the tolerance limit. The new developed method has quite low detection limit over the others. The dynamic linear range is from 1 to 1 mM, and the detection limit is 0.3 nM based on three signal-to-noise ratio. This method is

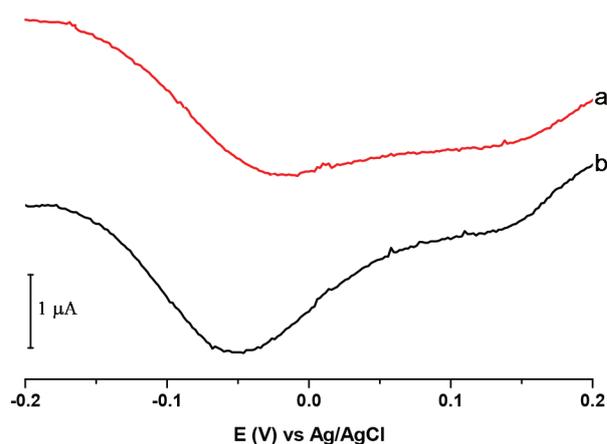


Fig. 9. Differential pulse voltammogram of Cu(II) ions in (a) flour sample and (b) water sample on the HMPD/GC electrode surfaces. The measurement was performed in BR buffer, pH 5.0, potential is referred vs. Ag/AgCl/(3 M KCl).

also very simple, sensitive, low cost and free of any pretreatment. HMPD structure has a significant role in the formation of Cu(II) complex which provides very low detection limit.

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