Asian Review of Environmental and Earth Sciences
Vol. 6, No. 1, 38-46, 2019
ISSN(E) 2313-8173/ ISSN(P) 2518-0134
DOI: 10.20448/journal.506.2019.61.38.46

A Novel MPTHP Modified Glassy Carbon Sensor Electrode: Investigation of Electrochemical Behaviors and Determination of Cu (II) Ions in Drinking Water Sample

Ayşegül Adir[1]
Ecir Yilmaz[2] ✉
Ayşen Demir Mülazımoğlu[3]
Bedrettin Mercimek[4]
Alaaddin Çukurovalı[5]
İbrahim Yilmaz[6]
Ibrahim Ender Mülazımoğlu[7]

[1,2,3,4,7]*Necmettin Erbakan University, Ahmet Keleşoğlu Education Faculty, Chemistry Department, Konya, Turkey.*
[1]*Email: adiraysegul@gmail.com Tel: +905334059813*
[2]*Email: eciryilmaz@erbakan.edu.tr Tel: +905059022022*
[3]*Email: admulazimoglu@erbakan.edu.tr Tel: +905373305060*
[4]*Email: bmercimek@erbakan.edu.tr Tel: +905327722359*
[7]*Email: iemulazimoglu@erbakan.edu.tr Tel: +905061064651*
[5]*Fırat University, Science Faculty, Chemistry Department, Elazığ, Turkey.*
[5]*Email: acukurovali@firat.edu.tr Tel: +905324938773*
[6]*Karamanoğlu Mehmetbey University, Kamil Özdağ Science Faculty, Chemistry Department, Karaman, Turkey.*
[6]*Email: iyilmaz@kmu.edu.tr Tel: +905354744748*

(✉ Corresponding Author)

Abstract

In the present work report, 2-methyl-6-((2-(4-(3-methyl-3-phenylcyclobutyl)thiazol-2-yl)hydrazono)methyl) phenol (MPTHP) has been newly synthesized and characterized. The new molecule has been used to modify the glassy carbon (GC) electrode surface through the alcohol oxidation method due to –OH group on its structure. MPTHP modified GC (MPTHP/GC) electrode has been used as a chemical sensor electrode for the quantitative determination of Cu (II) ions. Following the modification process, the surface characterization process of the modified electrode has been carried out by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). In this work, Cu (II) ions have been quantitatively determined by using differential pulse voltammetry (DPV) technique. A quite low detection limit (based on $3s_{bl}/m$) for Cu (II) using developed sensor electrode was found to be as $1.0x10^{-9}$ M. For the calibration curve, solutions of Cu (II) ions changing from $1.0x10^{-9}$ M to $1.0x10^{-3}$ M have been prepared using Britton-Robinson (BR) buffer solution at pH 5. The developed sensor electrode has been applied to tap water sample for the quantitation of Cu (II) ions and the amount of Cu (II) was determined as 4.07 x 10^{-9} M in this sample.

Keywords: MPTHP, Cu (II) ions, Chemical sensor electrode, Differential pulse voltammetry, Drinking water sample, Glassy carbon.

Citation | Ayşegül Adir; Ecir Yilmaz; Ayşen Demir Mülazımoğlu; Bedrettin Mercimek; Alaaddin Çukurovalı; İbrahim Yilmaz; Ibrahim Ender Mülazımoğlu (2019). A Novel MPTHP Modified Glassy Carbon Sensor Electrode: Investigation of Electrochemical Behaviors and Determination of Cu (II) Ions in Drinking Water Sample. Asian Review of Environmental and Earth Sciences, 6(1): 38-46.

History:
Received: 6 August 2019
Revised: 10 September 2019
Accepted: 16 October 2019
Published: 4 December 2019

Publisher: Asian Online Journal Publishing Group

Acknowledgement: All authors contributed to the conception and design of the study.
Funding: Authors would like to thank to the Research Foundation of Necmettin Erbakan University, Konya, TURKEY (BAP-131210012) for financial support of this work.
Competing Interests: The authors declare that they have no conflict of interests.
Transparency: The authors confirm that the manuscript is an honest, accurate, and transparent account of the study was reported; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained.
Ethical: This study follows all ethical practices during writing.

Contents

1. Introduction **39**
2. Experimental **39**
3. Results and Discussion **40**
4. Conclusion **45**
References **45**

Contribution of this paper to the literature

In the present work report, 2-methyl-6-((2-(4-(3-methyl-3-phenylcyclobutyl)thiazol-2-yl)hydrazono)methyl) phenol (MPTHP) has been newly synthesized and characterized.

1. Introduction

Variety of metal is present in nature. Some of them are called heavy metals due to high atomic weight and high density at least 5 times than water [1]. Heavy metals may exist naturally almost in every created body. They have a great importance due to their existence in the center of enzymes and hormones. Copper is a member of heavy metals. So copper is indispensable for nutrition, it functions as a cofactor in at least 30 essential enzymes [2]. On the other hand, the maximum tolerable daily intake is 0.5 mg kg^{-1} body weight for copper [3]. If maximum daily intake amount is exceeded, enzymes structure is disrupted which may results in unwanted reactions that may cause toxic effects in living metabolism [4-7]. The concentration of copper varies in soil and water [8]. Therefore determination and monitoring of copper is vital for the good of all mankind.

To develop an easy, fast and more accurate method for the determination of copper at trace level is a great importance in all kinds of samples. In spite of the fact that, many methods such as inductively coupled plasma mass spectroscopy (ICP-MS), graphite furnace atomic absorption spectroscopy (GF-AAS) and neutron activation analysis (NAA) are present for trace determination of copper, they either require pre-concentration step or are too expensive for using in routine analysis [3, 9]. Thus, electroanalytical methods are quite promising among the analytical methods due to being more accurate, easy and fast in measurements.

At the beginning of the nineteenth century Hugo Schiff has claimed that condensation between an amine compound and an aldehyde compound resulting in a new compound that binds to or coordinates with metals [10]. After that Schiff bases have been worked on by many researchers. These works show that Schiff bases can be used for many purposes [11] such as biosensors [12] optic sensors [13], electro-catalytic [14], antimicrobial [15] inhibitors of corrosion [16]. Besides their sensitivity, metal can lead to electrochemical characterization of many biometalomolecules and metalomolecules [17-19]. These type of compounds having metal atoms in their structure can be easily characterized and determined by using electrochemical methods especially voltammetry techniques [20, 21]. In these techniques, applied reduction and oxidation potential must be determined depending on the metal atoms on the Schiff base structure especially when using GC electrode. From the obtained peak half-wave potential and redox potential of the metal can be deduced.

The aim of this work is; 1) to determine the electrochemical properties of newly synthesized MPTHP Figure 1 on GC electrode, 2) to develop a simple, highly sensitive, accurate and environmentally friendly method for copper determination in various matrices.

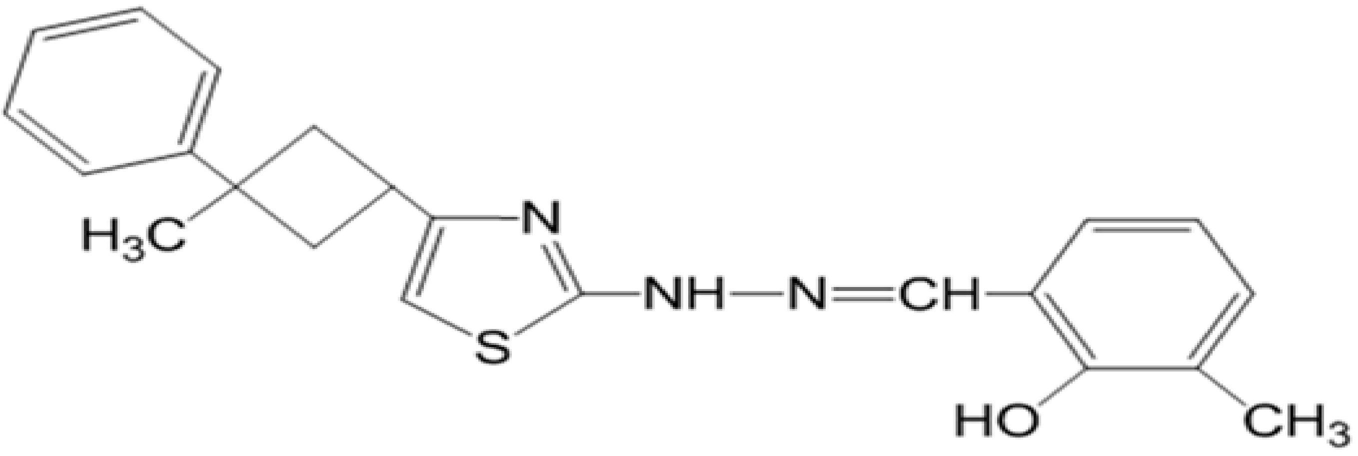


Figure-1. Molecular structure of 2-methyl-6-((2-(4-(3-methyl-3-phenylcyclobutyl) thiazol-2-yl)hydrazono)methyl)phenol (MPTHP).

2. Experimental

2.1. Chemicals

All chemicals which were used in experiments obtained from Merck, Fluka, Riedel and Sigma-Aldrich. All chemicals were analytical grade and were used without further purification processes. MPTHP is an original compound which was synthesized by our research group.

Ultrapure quality water with a resistivity of 18.2 MΩ cm (Millipore Milli-Q purification system, Millipore Corp. Bedford, MA, USA) was used throughout the experiments in all steps. The solutions for the characterization, analysis and the modification processes were prepared as follow: For non-aqueous medium studies; the solutions were 1mM in 100 mM tetrabuthylammonium tetrafluoroborate (NBu_4BF_4) in acetonitrile (CH_3CN) and ferri/ferrocyanide ($Fe(CN)_6{}^{3^-/4^-}$) redox probe mixture (1:1) in 100 mM KCl solution for aqueous medium. The used BR buffer solutions were prepared with specific proportions of H_3PO_4, CH_3COOH and H_3BO_3 compounds according to the literature [22, 23] and then pH was adjusted by dropwise addition of 0.2 M or 1 M NaOH with a digital Jenway 3010 pH meter (Staffordshire, UK).

2.2. Electrodes and Apparatus

All experiments were carried out with traditional three electrode systems for all electrochemical and spectroelectrochemical studies. Electrochemical measurements were made using GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA from GAMRY Instruments (PA, USA). The working GC electrode has 0.071 cm^2 geometric area and was purchased from BAS (Bioanalytical Systems, West Lafayette, IN, USA) model MF-2012. The reference electrodes were the Ag/Ag^+ (10 mM $AgNO_3$) (BAS Model MF-2042) for non-aqueous medium and the Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous medium. Pt wire (BAS Model MW-1032) was used as a counter electrode.

All electrochemical experiments were performed with using a BAS model C3 cell stand (IN, USA) at room temperature and also the electrodes were kept in CH_3CN when they were not in use.

The experiments with the CV technique were carried out PHE200 Physical Electrochemistry software (PA, USA). EIS was employed with EIS300 Electrochemical Impedance Spectroscopy software (PA, USA). SWV and DPV techniques were also used with PV220 Pulse Voltammetry Software (PA, USA). The morphology of the electrode surfaces was studied using scanning electron microscope (SEM) (Carl Zeiss LS10 Series SEM, Missouri, USA).

2.3. Cleaning and Polishing of Working Electrodes

The GC electrodes were polished to obtain a mirror-like appearance, first with fine wet emery paper (grain size 4000) and then with 1.0 µm and 0.3 µm alumina slurry on micro cloth pads (Buehler, USA) for all experiments. After that; the GC electrodes were re-polished with 0.05 µm alumina slurry. The GC electrodes were orderly kept in sonicator filled with water, in 1:1 (v/v) isopropyl alcohol (IPA) and CH_3CN (IPA + CH_3CN) mixture for 10 min before each step [22-26].

2.4. Synthesis and Characterization of MPTHP

The compound was synthesized as shown in Figure 2 by the following procedure. To a solution of 2-hydroxy-3-methylbenzaldehyde (1.3615 g, 10 mmol) in 50 mL of ethanol, thiosemicarbazide (0.9114 g, 10 mmol) was added portions by monitoring the reaction course with IR spectroscopy. Subsequently, a solution of 1-methyl-1-phenyl-3-(2-chloro-1-oxoethyl) cyclobutane (α-chloroketone) (2.2271 g, 10 mmol) in 20 mL of absolute ethanol was added. After the addition of the α-haloketone, the temperature was raised to 50-55 °C and kept at this temperature for 2 h. The solution was cooled to room temperature and then made alkaline with an aqueous solution of NH_3 (5%), and yellow precipitate separated by suction, washed with aqueous NH_3 solution several times, filtered and crystallized from ethanol. Yield: 81%, melting point: 440.5 K. Characteristic IR bands: –OH absorption of the compound could not been identified. 3118 cm^{-1} ν(N-H), 2961-2781 cm^{-1} (aliphatics), 1613 ν(C=N azomethine), 1691 cm^{-1} ν(C=N thiazole), 1563 ν(C=C), 1009 cm^{-1} ν(C-O), 704 cm^{-1} ν(C-S-C thiazole). Characteristic ^1H NMR shifts ($CDCl_3$, δ, ppm): 1.47 (s, 3H, $-CH_3$ on cyclobutane), 2.33 (s, 3H, $-CH_3$ on benzaldehyde ring), 2.49 (d, j = 8.8 Hz, 4H, $-CH_2-$ in cyclobutane), 3.58 (q, j = 9.1 Hz, 1H, >C-H on cyclobutane), 6.07 (d, j = 1.1 Hz, 1H, =CH-S in thiazole ring), 6.81 (t, j = 7.3 Hz, 1H, aromatic), 7.00 (dd, j_1= 1.1 Hz, j_2= 7.9 Hz, 1H, aromatic), 7.11-7.19 (m, 5H, aromatics plus –NH-), 7.26-7.32 (m, 2H, aromatics), 10.78 (s, 1H, –OH). Characteristic ^{13}C NMR shifts ($CDCl_3$, δ, ppm): 169.56, 156.24, 151.93, 151.52, 148.48, 132.48, 128.52, 128.35, 126.08, 125.75, 124.81, 119.34, 117.50, 99.79, 40.21, 39.19, 30.29, 29.95, 15.93.

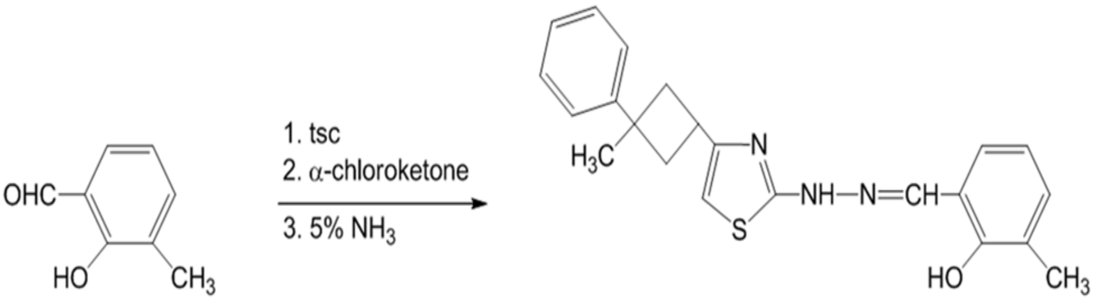


Figure-2. Synthetic pathway for the synthesis of the target compound.

3. Results and Discussion

Due to the toxicity and excessive amounts of Cu (II) ions in nature; quantitative detection of Cu (II) is essential and many techniques are available in the literature for this purpose. Especially; after the researchers have realized that carbon electrode can be modified with a variety of organic compounds, intensive study has been going on in this field. Most of these studies appear to be electrochemical investigation [27-29]. Whereas our aim is to detect environmentally toxic metals firstly by synthesizing a compound that is sensitive to one of these metals and then, graft this molecule onto the GC electrode surface [30]. Schiff bases play an important role about chelation of metal ions. For this reason we have synthesized a Schiff base for the quantitation of Cu (II) ions.

3.1. Electrochemical Grafting of MPTHP on to the GC Electrode Surface

Electrochemical modification technique which has an important of increasing every day, is the first step in the production of a sensor electrode for quantitative determination of different organic and inorganic species. Electrochemical modifications can be made basically in three ways. The first one is the reduction of diazonium salts which is the most stable and practical method [31-33]. The other two are alcohol [34, 35] and amine [22, 23] oxidation methods. The current work proposes to develop a sensor electrode for the determination of Cu (II) ions the natural sample. The GC electrode surface was modified with MPTHP via alcohol oxidation method using CV technique in non-aqueous medium. The modification process was carried out between +300 mV and +2600 mV potential range, under 100 mV s^{-1} scan rate with using 10 cycles. MPTHP solution used in modification process was 1 mM and was prepared in 100 mM NBu_4BF_4 (in CH_3CN) supporting electrolyte solution. The modification voltammogram and binding mechanism of MPTHP molecule on the GC electrode surface were given in Figure 3 and Figure 4, respectively.

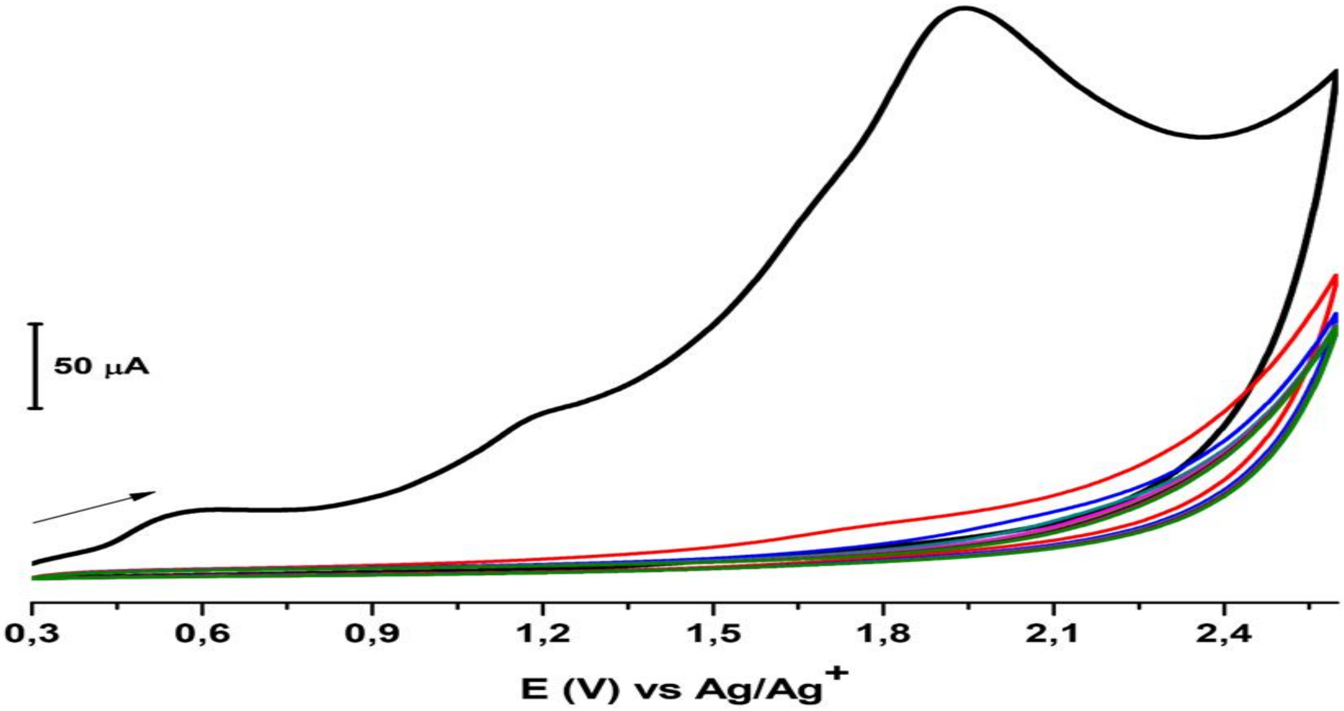


Figure-3. Cyclic voltammogram of 1 mM MPTHP in CH_3CN containing 100 mM NBu_4BF_4 vs. Ag/Ag$^+$/(10 mM $AgNO_3$) onto the GC electrode. Potential range from +300 mV to +2600 mV, scan rate is 100 mV s^{-1}.

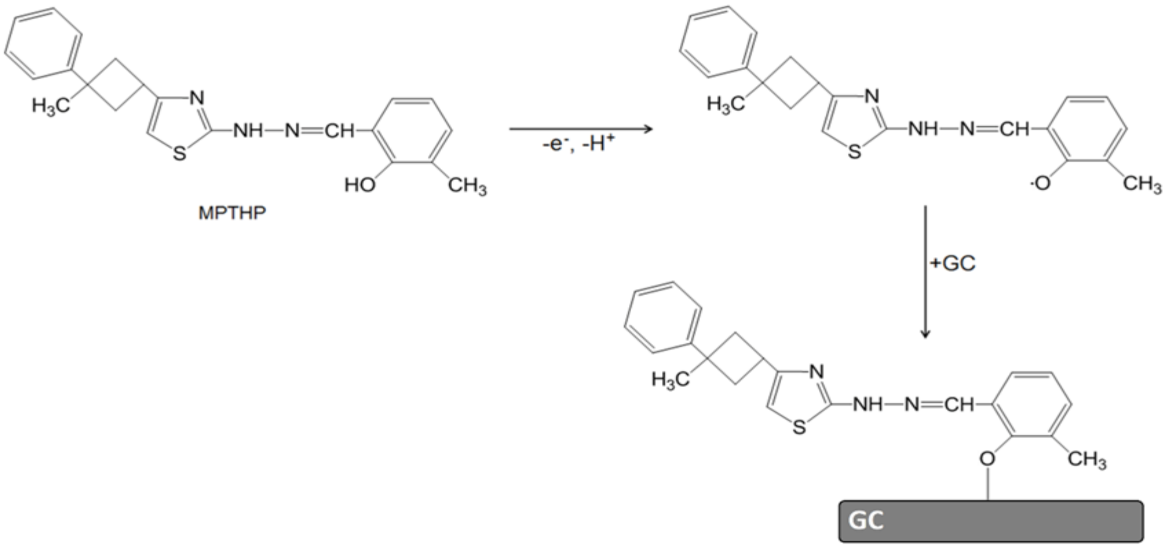


Figure-4. Modification mechanism of MPTHP at GC electrode surface (in CH_3CN containing 100 mM NBu_4BF_4).

The first peak in Figure 3 is the oxidation peak of the molecule owing to the removing of one proton from the molecule. The peak number 3 is the binding of the molecule on the GC electrode surface forming C-O-C bond on the oxygen tail. As it can be seen from the peak in Figure 3; the MPTHP molecule binds after the second cycle but modification processes was performed using 10 cycles. The reasons for that no pin holes remain on the GC surface and thus, more stable and smooth surface was obtained with MPTHP.

3.2. Surface Characterization of MPTHP/GC Electrode

Surface characterization process is the second important step in the electrochemical studies. For this purpose varying electrochemical, spectroscopic and microscopic techniques could be utilized. In the current study; the CV technique was used for surface characterizations as an electrochemical characterization technique, EIS was used as a spectroelectrochemical technique and SEM technique was employed for microscopic surface characterizations.

3.3. Characterization of MPTHP/GC Electrode Surface by CV and EIS

The surface characterization processes for both the bare GC and the modified GC electrodes were carried out using CV, EIS and SEM techniques in both aqueous and non-aqueous media. The CV electrode characterization technique was performed in the presence of hexacyanoferrate (III), $Fe(CN)_6^{3-}$, in pH 2.0 BR buffer solution and 1.0 mM of ferrocene solution in CH_3CN containing 100 mM NBu_4BF_4 as a supporting electrolyte. In non-aqueous medium studies, ferrocene solution was used in the potential range from −200 mV to +400 mV Figure 5A and $Fe(CN)_6^{3-}$ solution in pH 2 BR buffer solution was applied in the potential range from +600 mV to 0.00 mV in aqueous medium experiments Figure 5B at a sweep rate of 100 mV s^{-1} in the characterization process with CV technique. The cyclic voltammograms of modified and bare GC electrodes were compared with ferrocene and $Fe(CN)_6^{3-}$ redox probes. For the characterization with EIS, the measurements were recorded in a wide frequency range from 100.000 Hz to 0.05 Hz in 1 mM equiv. molar ratio of $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ in 100 mM KCl and the Nyquist plots were drawn. The Nyquist plots of modified electrodes were overlaid EIS data of the bare GC electrode Figure 5C. All potentials are referenced to Ag/AgCl/(3 M KCl) for aqueous medium and Ag/Ag$^+$/(10 mM $AgNO_3$) for non-aqueous medium.

It is shown in Figure 5A, the standard anodic and cathodic peaks of ferrocene redox probe were obtained on both the bare GC electrode surface Figure 5Aa and MPTHP modified GC electrode surface Figure 5Ab in oxidation and reduction directions, respectively. This is the expected case for MPTHP/GC electrode surface.

In the second step of CV characterization process is the one held with $Fe(CN)_6^{3-}$ redox probe in aqueous medium. According to the characterization process is practiced using $Fe(CN)_6^{3-}$ redox probe, the obtained surface is more electro-inactive than the bare GC electrode surface. This result could be easily deduced from the decrease of anodic and cathodic peak currents. The obtained active MPTHP/GC electrode surface is shown in Figure 5Bb in the order of the bare GC electrode surface given in Figure 5Ba.

It can be derived from the used characterization process using CV technique that MPTHP/GC electrode surface can be used as a sensor electrode.

In the electrochemical studies; EIS is very suitable technique for the examination of surface properties. It is capable of giving valuable data about defects/holes of the modified surface, the kinetics and the mechanism of the surface developing processes, surface coverage, and so forth. The EIS graphs of bare GC and MPTHP/GC electrode surfaces were displayed in Figure 5C.

The Figure 5Cb shows that MPTHP/GC electrode surface allows the electron transfer at nearly 80 kohm resistance. On the other hand, the electron transfer concession is at about 2 kohm resistance for bare GC electrode surface Figure 5Ca. The results of surface characterization studies done by EIS are consistent with the ones obtained from the CV characterization process.

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

According to the data obtained from the characterization processes, it can be concluded that MPTHP molecule is grafted on the GC electrode surface in non-aqueous medium. EIS is a valuable method to observe the impedance changes of the electrode surface during the modification process. The semicircle diameter of Nyquist plot reflects the R_{ct} is from the electron transfer of the redox probe $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ solution and Figure 5C put in the EIS of bare GC Figure 5Ca and MPTHP/GC Figure 5Cb electrodes. Firstly; the value of R_{ct} was recorded as $1.530\text{x}10^3$ Ω on the bare GC electrode surface. Secondly bare GC electrode surface was modified with MPTHP-DAS molecule, the value of R_{ct} that is much smaller than that of bare GC reduced to 810 Ω. This low R_{ct} value was obtained because of the existence of high conductive MPTHP/GC electrode surface. A nearly straight line was achieved with the R_{ct} value close to zero, proving that MPTHP/GC electrode taken part the electro-active layer for mass and electron transfer and also interfered the diffusion of ferricyanide toward the electrode surface. The simulation was made for the result plot to recommend an equivalent circuit model (based CPE) thanks to the calculated parameters R_{ct}=810.0 Ω s, R_s=130.2 Ω s, Yo=$3.6\text{x}10^{-6}$ S, α=0.820.

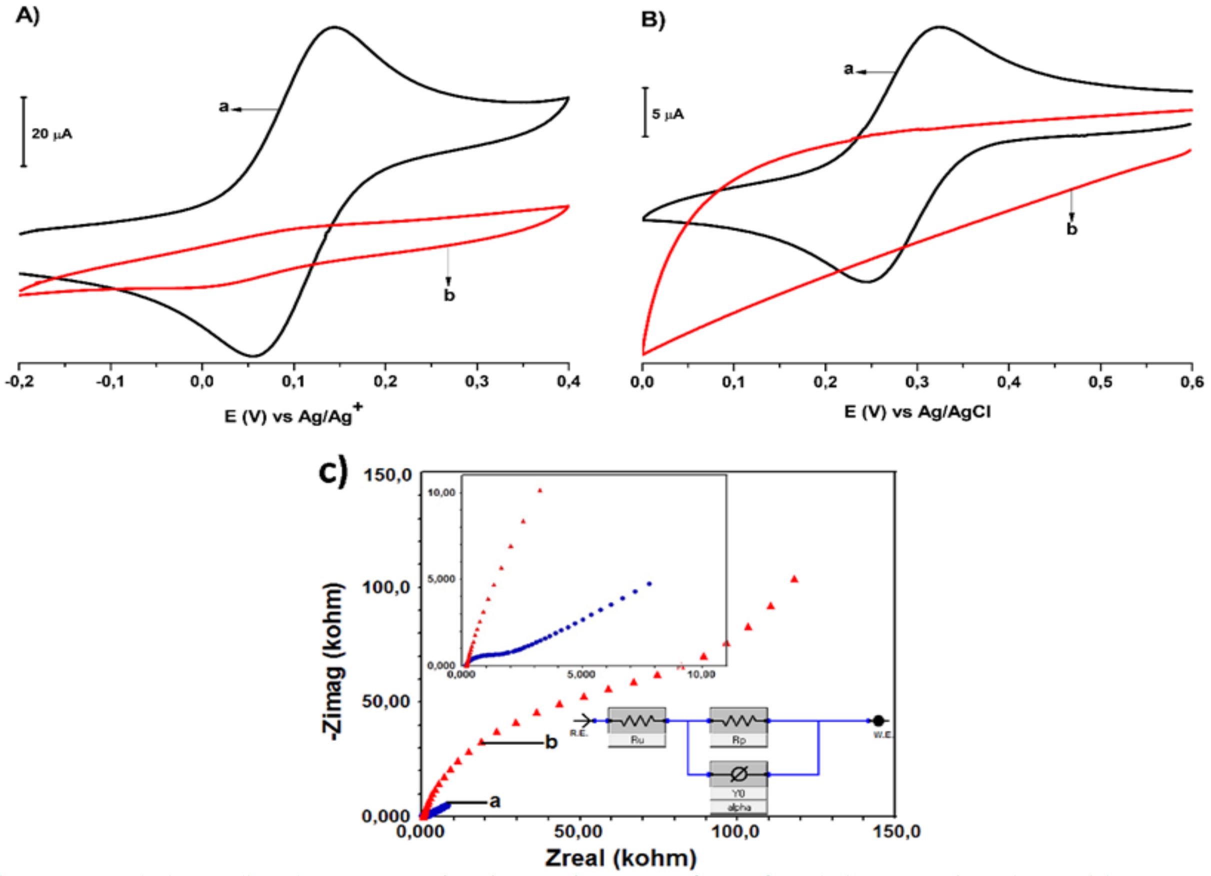


Figure-5. Overlaying cyclic voltammograms for **A)** 1mM ferrocene redox probe solution vs. Ag/Ag^+ (10 mM) in CH_3CN containing 100 mM NBu_4BF_4 using 100 mV s^{-1} scanning rate **B)** 1 mM $Fe(CN)_6^{3-}$ redox probe solution vs. Ag/AgCl/3 M KCl reference electrode in BR buffer solution, pH= 2 using 100 mV s^{-1} scanning rate and **C)** Nyquist plot for electrochemical impedance spectra of 1 mM $Fe(CN)_6^{3-/4-}$ redox couple solution in 100 mM KCl at the frequency range of 100.000–0.05 Hz at 10 mV wave amplitude.

Equation 1 was used to determine the electron transfer rate constant, k^0, for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ for bare GC and MPTHP/GC electrode surfaces.

$$R_{ct} = \frac{RT}{(nF)^2 A k^0 C} \qquad (1)$$

In this equation, *A* is the electrode area (cm^2); *n* is number of electrons needed for ox/red of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ mixed solution system; *C* (mole cm^{-3}) is the molar concentration of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$; *R* (8.314 J mol^{-1} K^{-1}) is the ideal gas constant, *T* (K) is the temperature; *F* (96485 C mol^{-1}) is the Faraday constant [42]. Respectively, the values for k^0 were computed as 2.45×10^{-6} cm s^{-1}, 4.63×10^{-6} cm s^{-1} for bare GC and MPTHP/GC electrodes.

In addition, to the covered electrode area was calculated according to Equation 2,

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

Here, R_{ct}^0 is the charge transfer resistance of the bare GC electrode while R_{ct} is the charge transfer resistance of the MPTHP/GC electrodes and θ is the modified area by MPTHP molecule. Surfaces are gained with superimposing of the Nyquist plots of related electrode surfaces. From the results given in the Nyquist plot, it was obtained that EIS signal is equivalent to 82.00% coverage of the GC surface.

Obtained of R_{ct} values of the Nyquist plots Figure 5C for 1.0 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ solution (in 100 mM KCl) at the (a) bare GC and (b) MPTHP/GC electrodes.

3.4. Microscopic Characterizations of MPTHP/GC Electrode Surface

The morphology studies of MPTHP film on GC electrode were carried out with SEM technique. This technique was employed to confirm the studies obtained using CV and EIS. The images of bare GC and MPTHP/GC electrode surfaces were recorded and shown in Figure 6.

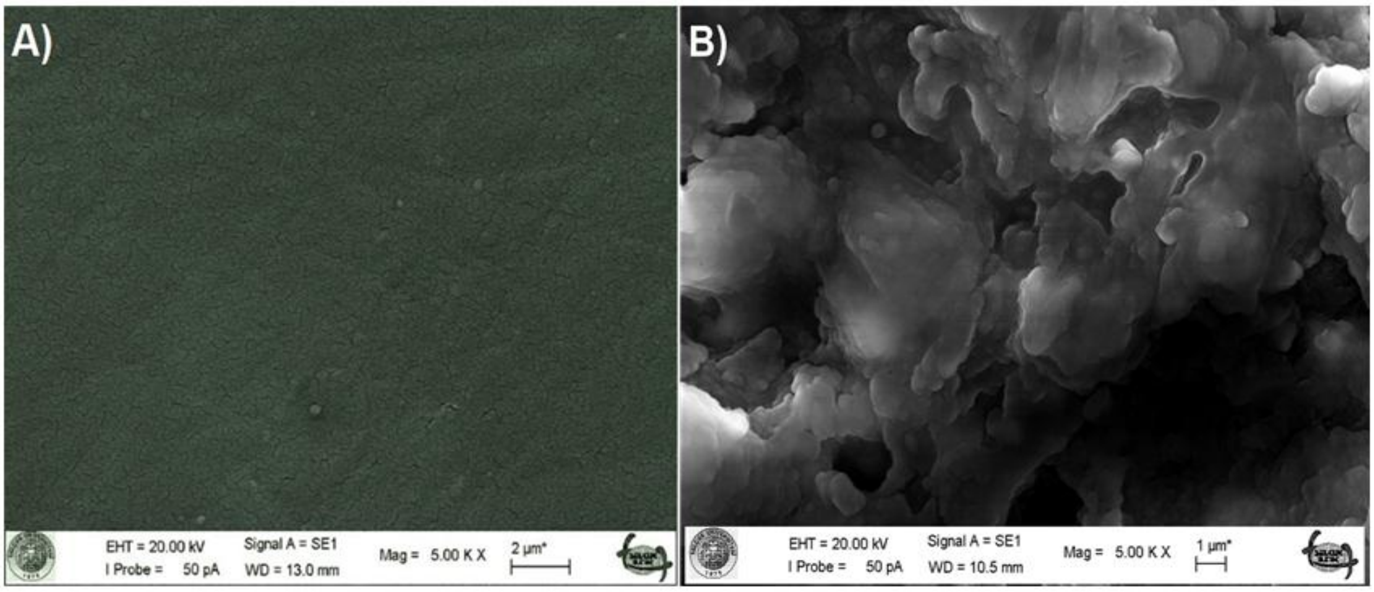


Figure-6. SEM images of A) bare GC and B) MPTHP/GC.

Here, Figure 6A and Figure 6B reveal smooth surfaces which owing to the bare GC Figure 6A and the modified surface which owing to MPTHP/GC Figure 6B_ electrode surfaces. These obtained data of the microscopic surface characterization are the proof of successive modification of the surfaces.

3.5. The use of MPTHP/GC Electrode as a Sensor Electrode

Making use of the chemical sensor electrode which is obtained using electrochemical methods is frequently operated in the recent years for the quantitative determination of organic and inorganic species. The main reasons of preference of these methods can be counted as getting rapid and reliable results, being relatively low cost, providing less sample consumption and reaching low detection limit. In this study, the developed MPTHP/GC electrode is used for the quantitative determination of Cu (II) ions in tap water. For this aim; firstly the response of MPTHP/GC electrode against Cu (II) ions was examined using SWV and DPV techniques. The obtained voltammograms are given in Figure 7.

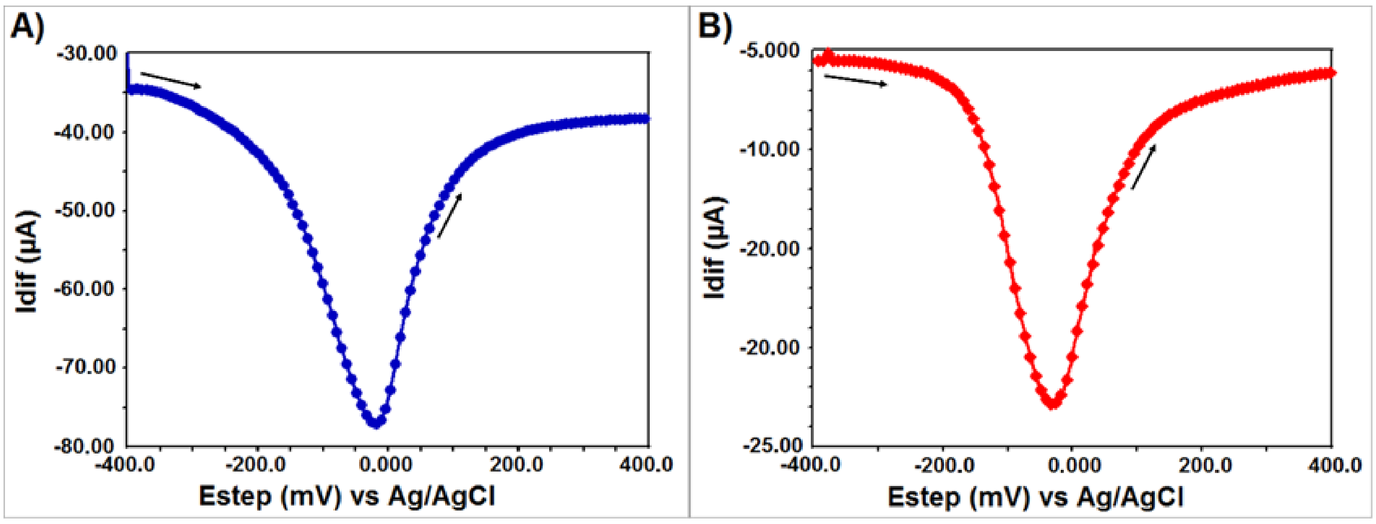


Figure-7. SWVs **(A)** and DPVs **(B)** of 1×10^{-3} M Cu (II) solution onto the MPTHP/GC electrode surface.

From the obtained voltammograms in Figure 7A (for SWV) and Figure 7B (for DPV), peak values are quite big and thus both methods could be used for the quantitative determination of Cu (II) ions in natural sample.

3.6. Setting of Optimum Incubation Time

According to the literature, the quantitative analysis of Cu (II) ions is performed spectroscopically and electrochemically around pH 5. Based on this information, 1 mM solution of Cu (II) ions was prepared in pH 5 BR buffer solution. The modified electrode was immensely kept in Cu (II) solution for different time period (30, 60, 90, 120 minutes) to determine the optimum complexation time. After that, the voltammograms were obtained from the scan between -400 mV to +400 mV potential range using DPV and SWV techniques Figure 8. The measured peak currents from the Fig 5 were plotted against the incubation time. As seen in both voltammograms in Fig 5, the most appropriate incubation time for quantitative determination of Cu (II) ions natural samples are defined as 90 minutes.

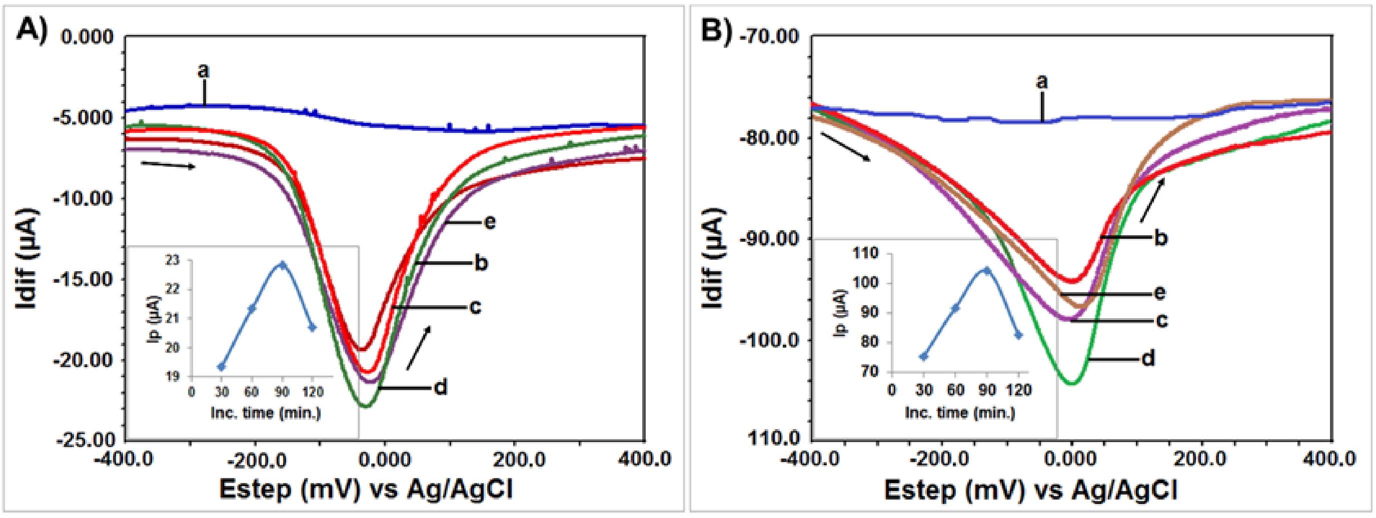


Figure-8. DPVs **(A)** and SWVs **(B)** of various incubation time periods of 1×10^{-3} M Cu (II) solution onto the MPTHP/GC electrode surface the measurements **a)** supporting electrolyte, **b)** 30, **c)** 60, **d)** 90 and **e)** 120 min were performed in BR buffer solution, pH 5.0, vs. Ag/AgCl/(3 M KCl).

3.7. The Using of MPTHP/GC Sensor Electrode in Cu (II) Ions Determination by DPV

Although we were able to use both SWV ($1\text{x}10^{-5}$ M) and DPV ($1\text{x}10^{-9}$ M) techniques, we have chosen DPV technique owing to the high sensitivity. After modification and characterization steps, the developed MPTHP/GC sensor electrode has become available for the detection of Cu (II) ions under the optimum pH and incubation time. A calibration curve was drawn using standard concentration and peak current values read from voltammograms. For this purpose; 1000 ppm Cu (II) ion stock solution was used to prepare a series of standards in the range of $1.0\text{x}10^{-3}$ M to $1.0\text{x}10^{-9}$ M in BR buffer solution (pH 5). Following this step, the designed MPTHP/GC sensor electrode was put in each standard solution of copper for 90 minutes. After completion of the complexation process, the measured voltammograms were recorded and shown in Figure 9A. The sketched calibration curve is shown in Figure 9B.

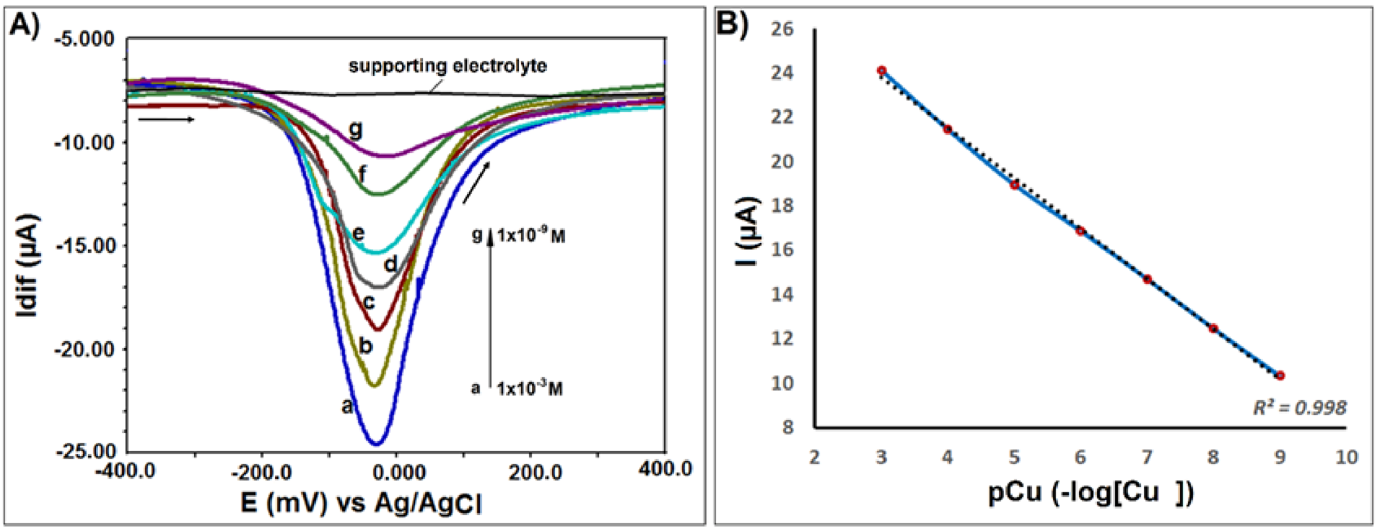


Figure-9. A. DPVs of different concentrations of standard Cu (II) solution onto the MPTHP/GC electrode surface **a)** 1×10^{-3}, **b)** 1×10^{-4}, **c)** 1×10^{-5}, **d)** 1×10^{-6}, **e)** 1×10^{-7}, **f)** 1×10^{-8} and **g)** 1×10^{-9}, the measurements were performed in BR buffer solution, pH 5.0, vs. Ag/AgCl/(3 M KCl). **B)** Standard calibration curve for the Cu (II) ions.

Low level of Cu (II) ions in tap water were quantitatively determined using the calibration curve. 10 mL of tap water sample was mixed with 10 mL pH 5 BR buffer solution. The mixture was then used for all measurements of Cu (II) amounts in drinking water. The DPV voltammograms are shown in Figure 10. By using calibration curve, the amount of Cu (II) was determined as $4.07\text{ x }10^{-9}$ M in drinking water sample.

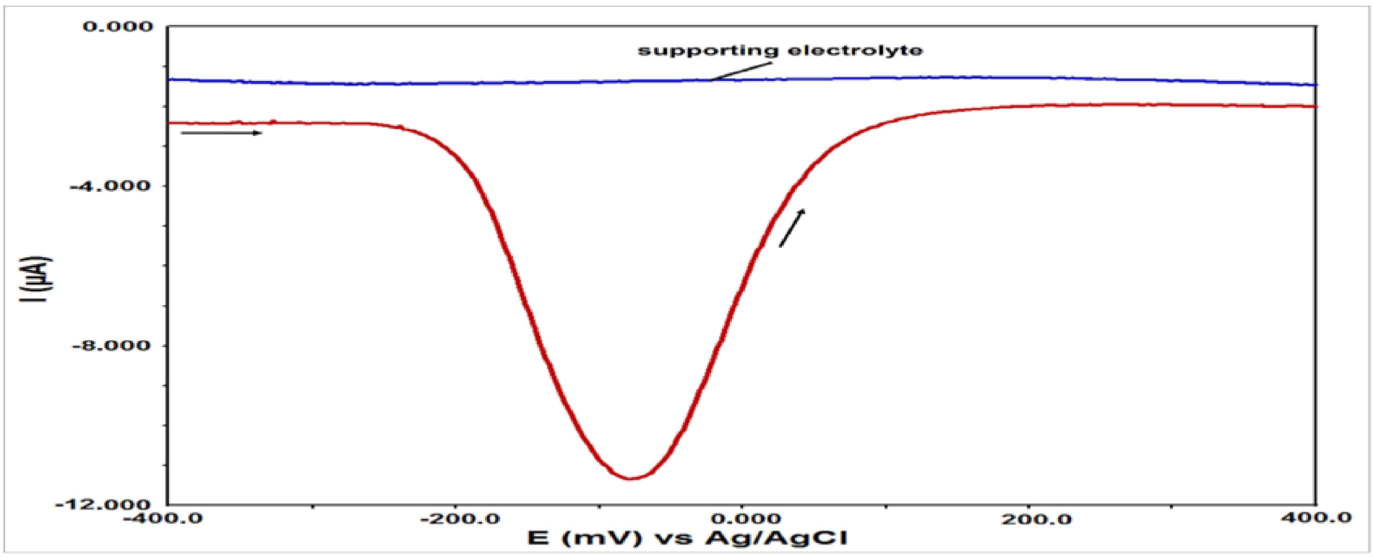
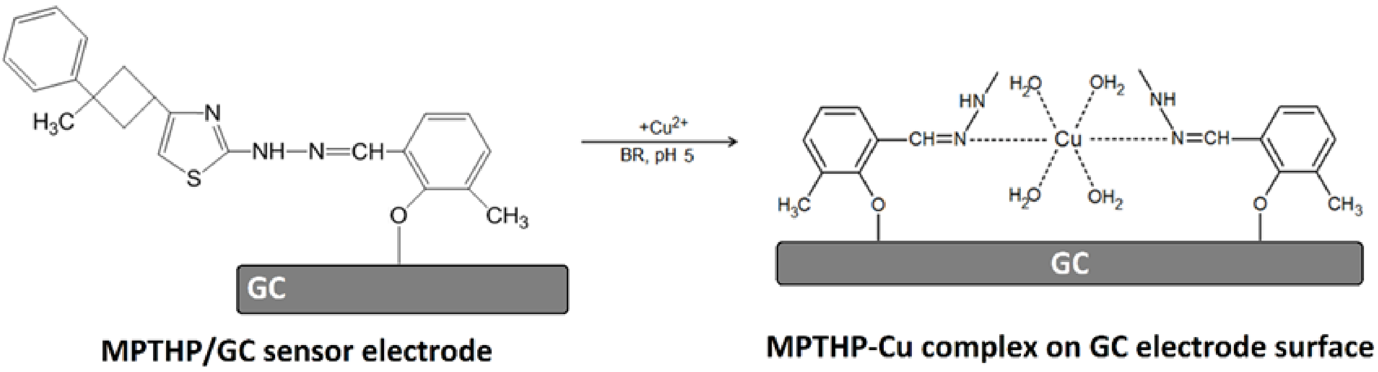


Figure-10. Differential pulse voltammogram of Cu (II) ions in drinking water sample onto the MPTHP/GC electrode surfaces. The measurement was performed in BR buffer, pH 5.0, potential is referred vs. Ag/AgCl/(3 M KCl).

After the analysis; the estimated reaction mechanism for MPTHP/GC-Cu (II) ion complex on the electrode surface was given Figure 11. Mainly, Cu (II) ions provide a six coordination complex. The copper ions are interacted with two points. The coordination is completed by four other water molecules.



MPTHP/GC sensor electrode

MPTHP-Cu complex on GC electrode surface

Figure-11. A) Oxidation of MPTHP on GC electrode surface and B) the proposed structure of the complex formed between the MPTHP/GC electrode with Cu (II) ion.

4. Conclusion

The results of this study were achieved with the developed MPTHP/GC sensor electrode in which MPTHP molecule is originally synthesized by our research team. With this designed sensor electrode Cu (II) ions were determined in tap water providing a low LOD. Under the optimum experimental conditions, LOD was found to be as 1.0×10^{-9} M ($D = 3s_{bl}/m$). With high stability and sensitivity, the new fabricated electrode was successfully employed to detect Cu (II) ions in real sample.

References

[1] J. Raj, A. Raina, and T. Dogra, "Direct determination of zinc, cadmium, lead, copper metal in tap water of Delhi (India) by anodic stripping voltammetry technique," in *E3S Web of Conferences*, 2013, p. 09009.

[2] M. B. Gholivand, A. Sohrabi, and S. Abbasi, "Determination of copper by adsorptive stripping voltammetry in the presence of calcein blue," *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, vol. 19, pp. 1609-1615, 2007. Available at: https://doi.org/10.1002/elan.200703891.

[3] E. Shams, A. Babaei, and M. Soltaninezhad, "Simultaneous determination of copper, zinc and lead by adsorptive stripping voltammetry in the presence of Morin," *Acta Chemical Analytics*, vol. 501, pp. 119-124, 2004. Available at: https://doi.org/10.1016/j.aca.2003.09.010.

[4] J. Camakaris, I. Voskoboinik, and J. Mercer, "Molecular mechanisms of copper homeostasis," *Biochemical and Biophysical Research Communications*, vol. 261, pp. 225-232, 1999.

[5] R. Uauy, M. Olivares, and M. Gonzalez, "Essentiality of copper in humans," *The American Journal of Clinical Nutrition*, vol. 67, pp. 952S-959S, 1998. Available at: https://doi.org/10.1093/ajcn/67.5.952s.

[6] S. G. Kaler, "Metabolic and molecular bases of menkes disease and occipital horn syndrome," *Pediatric and Developmental Pathology*, vol. 1, pp. 85-98, 1998. Available at: https://doi.org/10.1007/s100249900011.

[7] A. Baker, L. Harvey, G. Majask-Newman, S. Fairweather-Tait, A. Flynn, and K. Cashman, "Effect of dietary copper intakes on biochemical markers of bone metabolism in healthy adult males," *European Journal of Clinical Nutrition*, vol. 53, pp. 408-412, 1999. Available at: https://doi.org/10.1038/sj.ejcn.1600763.

[8] J. Opydo, "The determination of Zn, Cd, Pb and Cu in soil extracts by anodic stripping voltammetry," *Water, Air, and Soil Pollution*, vol. 45, pp. 43-48, 1989.

[9] A. Gonzales, M. Firmino, C. Nomura, F. Rocha, P. Oliveira, and I. Gaubeur, "Peat as a natural solid-phase for copper preconcentration and determination in a multicommuted flow system coupled to flame atomic absorption spectrometry," *Acta Chemical Analytics*, vol. 636, pp. 198-204, 2009. Available at: https://doi.org/10.1016/j.aca.2009.01.047.

[10] N. Aksuner, E. Henden, I. Yilmaz, and A. Cukurovali, "A highly sensitive and selective fluorescent sensor for the determination of copper (II) based on a schiff base," *Dyes and Pigments*, vol. 83, pp. 211-217, 2009. Available at: https://doi.org/10.1016/j.dyepig.2009.04.012.

[11] C. Fengying, L. Kezhi, and L. Hejun, "Synthesis, structural, and electrocatalytic properties of copper (II) complex of ONO donor acylhydrazone and 2-methylimidazole," *Synthesis and Reactivity in Inorganic and Metal-Organic, Inorganic and Nano-Metal Chemistry*, vol. 44, p. 1029, 2014.

[12] A. D. Kulkarni, S. A. Patil, and P. S. Badami, "SNO donor Schiff bases and their Co (II), Ni (II) and Cu (II) complexes: Synthesis, characterization, electrochemical and antimicrobial studies," *Journal of Sulfur Chemistry*, vol. 30, pp. 145-159, 2009. Available at: https://doi.org/10.1080/17415990802663133.

[13] M. Rizzi, M. Trueba, and S. P. Trasatti, "Polypyrrole films on Al alloys: The role of structural changes on protection performance," *Synthetic Metals*, vol. 161, pp. 23-31, 2011. Available at: https://doi.org/10.1016/j.synthmet.2010.10.029.

[14] M. Cañadas, E. López-Torres, A. Martínez-Arias, M. A. Mendiola, and M. T. Sevilla, "Spectroscopic and electrochemical properties of nickel (II), iron (III) and cobalt (II) complexes with benzilbisthiosemicarbazone—importance of working conditions and the metal salt used in the final complex," *Polyhedron*, vol. 19, pp. 2059-2068, 2000. Available at: https://doi.org/10.1016/s0277-5387(00)00505-2.

[15] G. B. Bagihalli, P. G. Avaji, S. A. Patil, and P. S. Badami, "Synthesis, spectral characterization, in vitro antibacterial, antifungal and cytotoxic activities of Co (II), Ni (II) and Cu (II) complexes with 1, 2, 4-triazole schiff bases," *European Journal of Medicinal Chemistry*, vol. 43, pp. 2639-2649, 2008. Available at: https://doi.org/10.1016/j.ejmech.2008.02.013.

[16] A. Erçağ, M. Şahin, A. Koca, and E. Bozkurt, "Synthesis, characterization, EPR, electrochemical, and in situ spectroelectrochemical studies of salen-type oxovanadium (IV) and copper (II) complexes derived from 3, 4-diaminobenzophenone," *Journal of Coordination Chemistry*, vol. 66, pp. 1635-1649, 2013. Available at: https://doi.org/10.1080/00958972.2013.787530.

[17] J. M. Fernández-G, F. A. López-Durán, S. Hernández-Ortega, V. Gómez-Vidales, N. Macías-Ruvalcaba, and M. Aguilar-Martínez, "The structures and cyclic voltammetry of three copper (II) complexes derived from bulky ortho-hydroxy Schiff bases," *Journal of Molecular Structure*, vol. 612, pp. 69-79, 2002. Available at: https://doi.org/10.1016/s0022-2860(02)00106-0.

[18] E. Franco, E. López-Torres, M. Mendiola, and M. Sevilla, "Synthesis, spectroscopic and cyclic voltammetry studies of copper (II) complexes with open chain, cyclic and a new macrocyclic thiosemicarbazones," *Polyhedron*, vol. 19, pp. 441-451, 2000. Available at: https://doi.org/10.1016/s0277-5387(99)00383-6.

[19] I. E. Mülazımoğlu, A. D. Mülazımoğlu, and E. Yılmaz, "Determination of quantitative phenol in tap water samples as electrochemical using 3, 3'-diaminobenzidine modified glassy carbon sensor electrode," *Desalination*, vol. 268, pp. 227-232, 2011. Available at: https://doi.org/10.1016/j.desal.2010.10.033.

[20] I. E. Mülazımoğlu and E. Yılmaz, "Quantitative determination of phenol in natural decayed leaves using procaine modified carbon paste electrode surface by cyclic voltammetry," *Desalination*, vol. 256, pp. 64-69, 2010. Available at: https://doi.org/10.1016/j.desal.2010.02.014.

[21] A. D. Mulazimoglu, I. E. Mulazimoglu, and B. Mercimek, "Synthesis, Characterizations and investigation of electrochemical behaviours of 4-[(2-Hydroxyphenylimino) methyl] benzene-1, 3-diol," *Journal of Chemistry*, vol. 6, pp. 965-974, 2009. Available at: https://doi.org/10.1155/2009/426170.

[22] I. E. Mulazimoglu, "Covalent modification of a glassy carbon surface by electrochemical oxidation of 3, 3'-Diaminobenzidine," *Asian Journal of Chemistry*, vol. 22, p. 8203, 2010.

[23] M. Zatloukalová, V. Křen, R. Gažák, M. Kubala, P. Trouillas, J. Ulrichová, and J. Vacek, "Electrochemical investigation of flavonolignans and study of their interactions with DNA in the presence of Cu (II)," *Bioelectrochemistry*, vol. 82, pp. 117-124, 2011. Available at: https://doi.org/10.1016/j.bioelechem.2011.06.005.

[24] M. Etienne, J. Bessiere, and A. Walcarius, "Voltammetric detection of copper (II) at a carbon paste electrode containing an organically modified silica," *Sensors and Actuators B: Chemical*, vol. 76, pp. 531-538, 2001. Available at: https://doi.org/10.1016/s0925-4005(01)00614-1.

[25] G. Herzog and D. W. Arrigan, "Application of disorganized monolayer films on gold electrodes to the prevention of surfactant inhibition of the voltammetric detection of trace metals via anodic stripping of underpotential deposits: detection of copper," *Analytical Chemistry*, vol. 75, pp. 319-323, 2003. Available at: https://doi.org/10.1021/ac026093f.

[26] Z. Ustündağ and A. O. Solak, "EDTA modified glassy carbon electrode: preparation and characterization," *Electrochimica Acta*, vol. 54, pp. 6426-6432, 2009. Available at: https://doi.org/10.1016/j.electacta.2009.06.015.

[27] A. R. Zanganeh and M. K. Amini, "Polypyrrole-modified electrodes with induced recognition sites for potentiometric and voltammetric detection of copper (II) ion," *Sensors and Actuators B: Chemical*, vol. 135, pp. 358-365, 2008. Available at: https://doi.org/10.1016/j.snb.2008.09.005

[28] A. O. Solak, L. R. Eichorst, W. J. Clark, and R. L. McCreery, "Modified carbon surfaces as "organic electrodes" that exhibit conductance switching," *Analytical Chemistry*, vol. 75, pp. 296-305, 2003. Available at: https://doi.org/10.1021/ac026107h.

[29] J. Pinson and F. Podvorica, "Attachment of organic layers to conductive or semiconductive surfaces by reduction of diazonium salts," *Chemical Society Reviews*, vol. 34, pp. 429-439, 2005. Available at: https://doi.org/10.1039/b406228k.

[30] İ. E. Mülazımoğlu and A. D. Mülazımoğlu, "Investigation of sensitivity against different flavonoid derivatives of aminophenyl-modified glassy carbon sensor electrode and antioxidant activities," *Food Analytical Methods*, vol. 5, pp. 1419-1426, 2012. Available at: https://doi.org/10.1007/s12161-012-9393-7.

[31] A. K. Timbola, C. D. d. Souza, C. Giacomelli, and A. Spinelli, "Electrochemical oxidation of quercetin in hydro-alcoholic solution," *Journal of the Brazilian Chemical Society*, vol. 17, pp. 139-148, 2006. Available at: https://doi.org/10.1590/s0103-50532006000100020.

[32] P. Janeiro and A. M. O. Brett, "Solid state electrochemical oxidation mechanisms of morin in aqueous media," *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, vol. 17, pp. 733-738, 2005. Available at: https://doi.org/10.1002/elan.200403155.

[33] D. D. Macdonald, "Reflections on the history of electrochemical impedance spectroscopy," *Electrochimica Acta*, vol. 51, pp. 1376-1388, 2006. Available at: https://doi.org/10.1016/j.electacta.2005.02.107.

[34] J.-B. He, Y. Wang, N. Deng, and X.-Q. Lin, "Study of the adsorption and oxidation of antioxidant rutin by cyclic voltammetry–voltabsorptometry," *Bioelectrochemistry*, vol. 71, pp. 157-163, 2007. Available at: https://doi.org/10.1016/j.bioelechem.2007.03.003.

[35] V. Ganesh, S. K. Pal, S. Kumar, and V. Lakshminarayanan, "Self-assembled monolayers (SAMs) of alkoxycyanobiphenyl thiols on gold—A study of electron transfer reaction using cyclic voltammetry and electrochemical impedance spectroscopy," *Journal of Colloid and Interface Science*, vol. 296, pp. 195-203, 2006. Available at: https://doi.org/10.1016/j.jcis.2005.08.051.