Desalination and Water Treatment
www.deswater.com

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doi: 10/5004/dwt.2012.2994

44 (2012) 161–167
June

Electrochemical determination of copper(II) ions at naringenin-modified glassy carbon electrode: application in lake water sample

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Received 26 May 2011; Accepted 14 December 2011

ABSTRACT

Electrochemical modification of glassy carbon (GC) electrode by naringenin (NG), a flavonoid derivative, and applicability of electrode modified in this way for determination of copper(II) (Cu(II)) ions is reported in this study. Surface modification experiments were performed in phosphate buffer solution (PBS), pH 7, in the 0.0 mV and +1400 mV potential ranges with a sweep rate of 100 mV s^{-1} and 30 cycles. The surface modification of GC electrode was performed with NG using cyclic voltammetry (CV), whereas the characterization of this sensor electrode was performed using CV and electrochemical impedance spectroscopy (EIS). The sensitivity of GC electrode modified in described way towards Cu(II) ions was investigated in Britton–Robinson (BR) buffer solution, pH 5, by differential pulse voltammetry (DPV). For the calibration curve, a series of standard Cu(II) solution from 1.0×10^{-12} M to 1.0×10^{-6} M was prepared. The NG modified GC (NG/GC) sensor electrode, has a good repeatability, was applied for Cu(II) ions determination in Beyşehir lake (in Konya, Turkey) water sample. Detection limit was obtained as lower as 1.0×10^{-12} M. The proposed method was simple, rapid, low cost and sensitive for the determination of Cu(II) ions.

Keywords: Flavonoid; Cu(II) ions; Surface modification; Surface characterization; Differential pulse voltammetry; Cyclic voltammetry

1. Introduction

Copper is one of the essential trace elements in the body. Very low and high intakes of this element can cause adverse health effects [1]. Copper has a very complex role in many body functions such as normal function of the central nervous system, connective tissue development, hemoglobin synthesis, and oxidative phosphorylation [2]. However, excessive copper intake could result in deposition of the metal in liver cells and thus can cause hemolytic crisis, jaundice, and neurological disturbances [3].

Trace metals commonly exist as environmental pollutants. These pollutants can easily be taken up by mankind, animals, plants and waters in the environment. These metals enter human bodies through water and food, thus copper determination in these samples is very important. Besides, these types of data may also give us some information about copper contamination of the environment [4].

Various analytical techniques have been proposed for Cu(II) determination such as, flame atomic absorption spectrometry (FAAS) [5,6], electrothermal atomization atomic absorption spectrometry (ET-AAS) [7], inductively coupled plasma optical emission spectrometry (ICP-OES) [8–10], graphite furnace atomic absorption spectrometry (GF-AAS) [11], chromatography [12], anodic stripping voltammetry [13,14], and gravimetry [15].

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 [16,17]. One of the reasons for the considerable current interest in modification of carbon materials is because the carbon material is inert and has good conductivity and resistance to environmental and chemical attack. 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. Recently, the application of inorganic modified electrodes has increased [18–21]. 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 [22–24]. In the electro-oxidation, hydroxylation and hydrogen evolution take place which is a favored situation due to hydroxy adsorption [25,26].

Flavonoids are the best example of polyphenols. Flavonoid term refers to a class of aromatic, oxygen-containing heterocyclic pigments widely distributed among higher plants as secondary metabolites. Flavonoids constitute one of the most characteristic classes of compounds containing hydroxyl groups attached to ring structures [27]. These molecules belong to a large family of compounds with a common diphenylpropane structure ($C_6C_3C_6$) with different degrees of hydroxylation, oxidation and substitution. As antioxidants, flavonoids have been reported to be able to interfere with the activities of enzymes involved in reactive oxygen species generation, quenching free radicals, chelating transition metals and rendering them redox inactive [28,29].

The main structure of the polyphenols is composed of by binding of one or two hydroxyl group to benzene ring. Polyphenols are classified according to binding of hydroxyl groups to different positions. Flavonoids are the best example of polyphenols. Flavonoid term refers to a class of aromatic, oxygen-containing heterocyclic pigments widely distributed among higher plants as secondary metabolites. Flavonoids constitute one of the most characteristic classes of compounds containing hydroxyl groups attached to ring structures [16]. Many flavonoids are easily recognized as flower pigments in most angiosperm families. However, their occurrence is not restricted to flowers but include all parts of the plants. They constitute most of the yellow, red and blue colors in flowers and fruits [17]. Flavonoids are broken down into categories of isoflavones, anthocyanidins, flavans, flavonols, flavones, and flavanones [30]. The molecule structure of NG, a derivative of flavonoids, is given in Fig. 1.

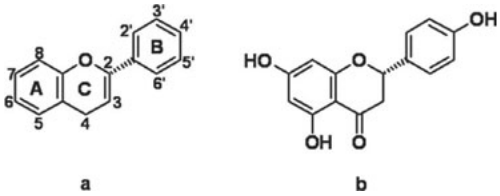

Fig. 1. Chemical structures of flavonoids (a) general structure, (b) naringenin.

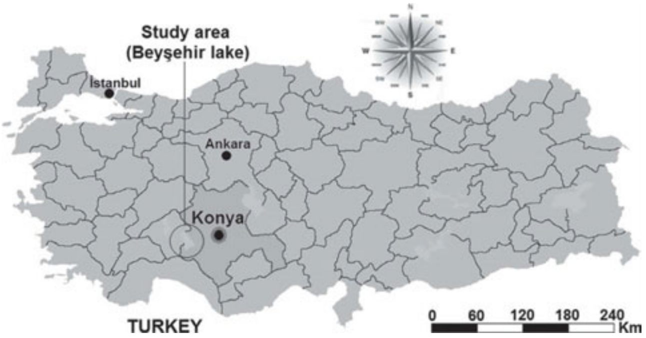

Fig. 2. The location of the Beyşehir lake in Konya, Turkey.

The aim of this study was to perform the electrochemical modification of NG on the GC electrode and to apply this modified electrode in lake water sample for determination of Cu(II) ions. The objectives of this work were (i) to create electrochemically modified NG/GC electrode in aqueous medium by CV, (ii) to characterize modified NG/GC electrode by CV and EIS, (iii) to determine the interaction of this modified electrode with Cu(II) by DPV, (iv) to investigate of the interference effect and (v) to apply this modified electrode in Beyşehir lake (Fig. 2) water sample for determination of Cu(II) ions.

2. Experimental

2.1. Chemicals and solutions

All chemicals were of analytical-reagent grade supplied from Merck, Fluka, Riedel and Sigma-Aldrich. Ultra pure quality of water with a resistance of 18.3 MΩ cm (Millipore Milli-Q purification system, Millipore Corp. Bedford, MA, USA) was used in preparations of aqueous solutions, cleaning of the glassware and polishing the electrodes. NG solution used in modification was 1 mM concentration in 10 ml acetonitrile (MeCN) + 40 ml PBS, pH 7, mixture and the PBS was prepared by mixing of 0.05 mM Na_2HPO_4 and 0.05 mM KH_2PO_4 and then adjusting of pH by addition of NaOH or HCl. $CuSO_4·5H_2O$ solutions were prepared at different concentrations (ranging from 1.0×10^{-12} M to 1.0×10^{-6} M) in BR buffer solution, pH 5, which was prepared from $H_3PO_4 + CH_3COOH + H_3BO_3$ according to preparation conditions in the literatures [31,32] and then adjusting of pH by addition of 0.2 M or 1 M NaOH.

2.2. Electrodes and apparatus

A traditional three-electrode cell system was used in all electrochemical and spectroelectrochemical experiments. In our experiments, GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA from GAMRY Instruments (PA, USA) electrochemical analyzer with BAS (Bioanalytical Systems, West Lafayette, IN, USA) Model MF-2012 and Tokai GC-20 GC electrodes were used. Ag/Ag^+ (10 mM $AgNO_3$) (BAS Model MF-2042) for non-aqueous medium and an Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous medium were used as reference electrodes. Pt wire (BAS Model MW-1032) was used as counter electrode. Jenway 3010 pH meter was used for the measurement of pH values. CV experiments were performed using a GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA equipped with a BAS model C3 cell stand. Electrochemical characterization was performed with the same electrochemical devices and software used for the modification. Characterizations of the modified surfaces were recorded by CV and EIS. EIS experiments were carried out with a GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA in conjunction with EIS 300 software. The DPV technique for Cu(II) determination was applied with a GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA with PV 220 software.

2.3. Preparation and modification of the working electrodes

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 µm alumina slurry on micro cloth pads (Buehler, USA). After the initial polishing, the GC electrodes were resurfaced with 0.05 µm alumina slurry. First, in the following order, the GC electrodes were sonicated in water then in 1:1 (v/v) isopropyl alcohol (IPA) and MeCN (IPA + MeCN) mixture for 10 min each [31–35].

Following polishing, the electrochemical modification of the GC electrode were performed with NG in 10 ml MeCN + 40 ml PBS, pH 7, mixture in the 0.0 mV and +1400 mV potential ranges with a sweep rate of 100 mV s^{-1} and 30 cycles.

3. Result and discussions

3.1. Modification of NG onto GC surface and surface characterization

Surface modification experiment was performed with NG in the 0.0 mV and +1400 mV potential ranges with a sweep rate of 100 mV s^{-1} and 30 cycles (Fig. 3).

As it is clear from the Fig. 3, NG molecule is binded to the GC electrode surface after second cycle. This is an evidence a monolayer binding of NG molecule to the electrode surface. The surface is stable after the second cycle. A bulk molecule like polyphenol was used in the modification process and 30 cycles have been applied to fill the any pin holes exist on the electrode surface. Although five cycles is enough for the modification of NG molecule, 30 cycles has been employed for filling the pin holes completely. This application does not from a multi-layer on the electrode surface. The electrooxidation mechanism would be discussed with recent papers [28,35].

Surface characterizations after the modification process were carried out by CV and EIS. In the characterizations with CV, 1 mM ferrocene solution in 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) was performed in the −100 and +400 mV potential range in Fig. 4(a) and 1 mM $Fe(CN)_6^{3-}$ in BR buffer solution, pH 2.0, was performed from +600 to 0.0 mV potential range in Fig. 4(b) using 100 mV s^{-1} sweep rate. The voltammograms of modified electrode were compared with surface voltammograms of the bare GC electrode.

The electrode surface was negatively charged after the modification process. Thus, negatively charged ferrocene and $Fe(CN)_6^{3-}$ ions are repelled by the negatively

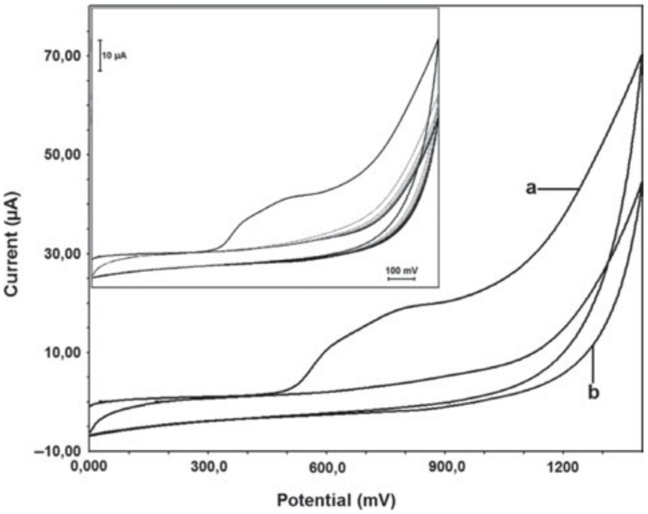

Fig. 3. Cyclic voltammogram of 1 mM NG in PBS, pH 7, vs. Ag/AgCl/(3 M KCl), 1st (a) and 30th (b) potential scan cycle. Potential sweep rate is 100 mV s^{-1}.

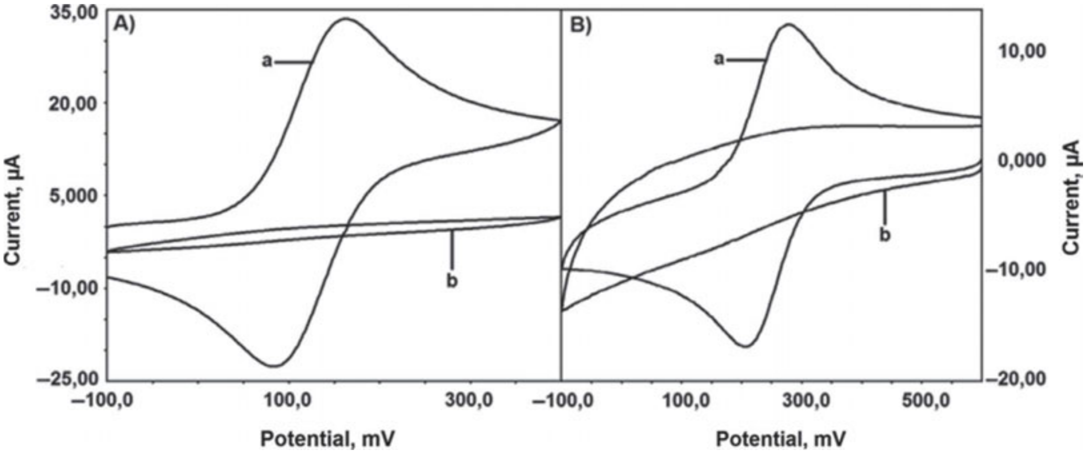

Fig. 4. Overlaying the bare GC and NG/GC voltammogram (a) 1 mM ferrocene redox probe solution vs. Ag/Ag$^+$ (10 mM) in MeCN + 0.1 M TBATFB, (A) Bare GC and (B) NG/GC, (b) 1 mM Fe(CN)$_6^{3-}$ redox probe solution vs. Ag/AgCl/(3 M KCl) in BR buffer solution, pH 2.0, (A) Bare GC and (B) NG/GC. Sweep rate was 100 mV s^{-1}.

charged electrode surface. Consequently, no electron transfer occurs. In this part of the manuscript the fact about polyphenol adsorption and formation of polymeric films at the carbon electrodes in presence of polyphenols is completely missing. The polymeric (adsorbed) film of polyphenols is usually formed onto electrode surface in aqueous medium at potentials higher than +1.1 V (vs. Ag/AgCl).

Impedance measurements were carried out in 1 mM Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ mixture (in 0.1 M KCl) in the range from 100.000 to 0.05 Hz frequency using EIS and the Nyquist plots were recorded. The Nyquist plot of modified electrode was compared with the EIS data of the bare GC electrode (Fig. 5).

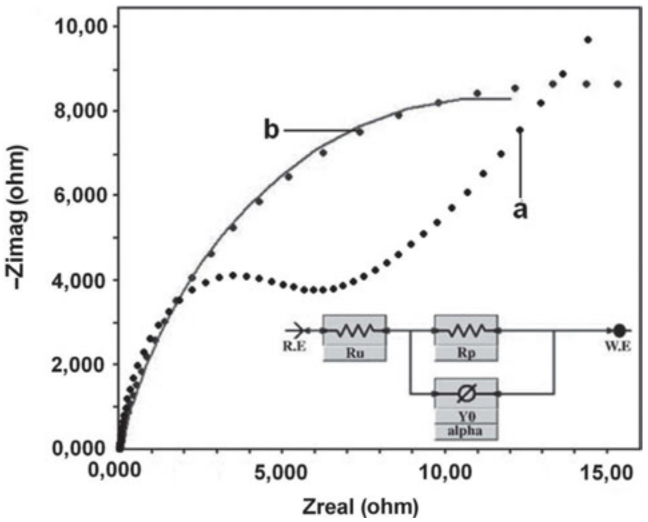

Fig. 5. Nyquist plots of 1 mM of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ in 0.1 M of KCl of bare GC (a), and NG/GC electrode (b). Frequency range is from 100.000 to 0.05 Hz the modulation amplitude is 10 mV. Inset: Equivalent circuit applied for calculations.

3.2. Detection of Cu(II) on grafted NG/GC electrode by DPV

The complex formation of Cu(II) ions with modified surface was investigated using DPV technique after the characterization of NG/GC surface by CV and EIS technique. In DPV experiments, the potential range was from −400 to 0.0 mV, the potential sweep rate was 50 mV s^{-1}, pulse amplitude was 25 mV, the pulse period was 0.05 s and sample period was 1.0 s. For the optimum conditions, the pH of Cu(II) solution and modified NG/GC electrode incubation time were investigated. For this aim, 1.0×10^{-6} M Cu(II) solutions were prepared in BR buffer solution at 2–12 pH range. The modified electrodes were incubated into these Cu(II) solutions and then Cu(II) ions were determined by DPV. pH 5 was found to be the optimum value for determination of Cu(II) ions. Cu(II) cannot be determined due to the precipitation of Cu(II) as hydroxide at higher pH value. The optimum incubation time was determined by incubating NG/GC electrode in Cu(II) solutions in BR buffer solution, pH 5.0, for various time periods (30, 60, 90, 120, 150, 180 min). As the incubation time increased, DPV signals also increased up to 120 min incubation time in Fig. 6.

Above this time, the steady state was achieved. For most Cu(II) complex with NG, the optimum conditions are as follows: BR buffer solution, pH 5.0, incubation time 120 min Cu(II)-NG complex [28] was investigated using DPV technique. The DPVs of Cu(II)-NG complex are shown in Fig. 7.

3.3. Calibration curve

Under the optimized experiment conditions, for the determination of Cu(II) varying standard solutions from 1×10^{-12} M to 1×10^{-6} M was prepared and the calibration

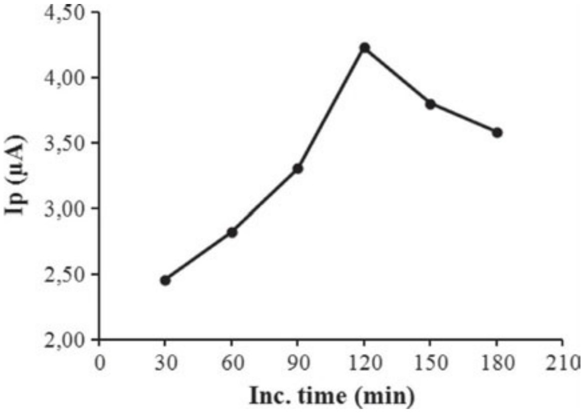

Fig. 6. Ip-Inc. time plot. Time periods: 30, 60, 90, 120, 150, 180 min in BR buffer solution, pH 5.

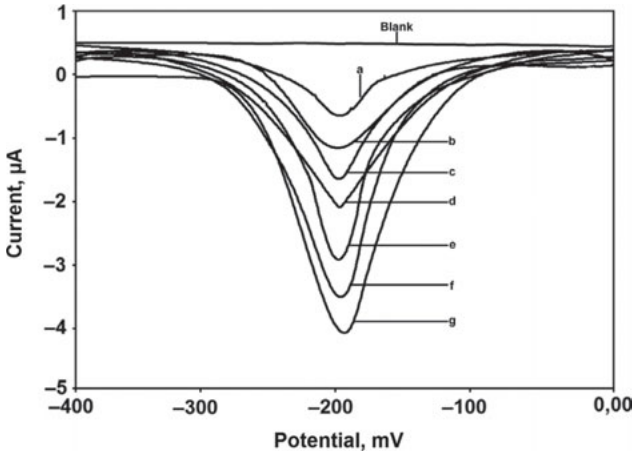

Fig. 7. Differential pulse voltammograms of different concentrations of $CuSO_4 \cdot 5H_2O$ (a) 1×10^{-12} M, (b) 1×10^{-11} M, (c) 1×10^{-10} M, (d) 1×10^{-9} M, (e) 1×10^{-8} M, (f) 1×10^{-7} M, (g) 1×10^{-6} M and the blank (BR buffer, pH 5.0) solution on NG/GC. The measurements were performed in BR buffer solution, pH 5.0, vs. Ag/AgCl/(3 M KCl). Sweep rate was 50 mV s^{-1}.

curve was drawn. The modified NG/GC electrodes were incubated into these Cu(II) solutions and then Cu(II) ions were determined by DPV. Peak currents from the obtained voltammograms were used to form a calibration curve (Fig. 8).

The calibration curve is linear in the range from 1×10^{-12} M to 1×10^{-6} M Cu(II) ions under the optimum conditions of the general procedure. According to following equation for Cu(II) determination is $Ip = 0.588\ C - 2.978$, Ip is the peak current and C is Cu(II) concentration. The correlation coefficient (R^2) is 0.997.

3.4. Interference effects

The interferences of some ions on the determination of Cu(II) were investigated. The NG/GC electrode was incubated in a mixture of (cation ions: Fe^{2+}, Fe^{3+}, Cd^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}, anion ions: NO_3^-, SO_4^{2-}, CO_3^{2-} and Cl^-, (1.0×10^{-6} M each one)). The voltammogram of NG/GC electrode was taken using differantial pulse technique after 120 min duration. The DPVs after incubation in solution of Cu(II) ions with the interference ions were compared. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±2% related to the determination of Cu(II) ions. The ions normally present in water do not interfere under the experimental conditions used. This modified electrode can be used successfully for the determination of Cu(II) ions in the presence different interference.

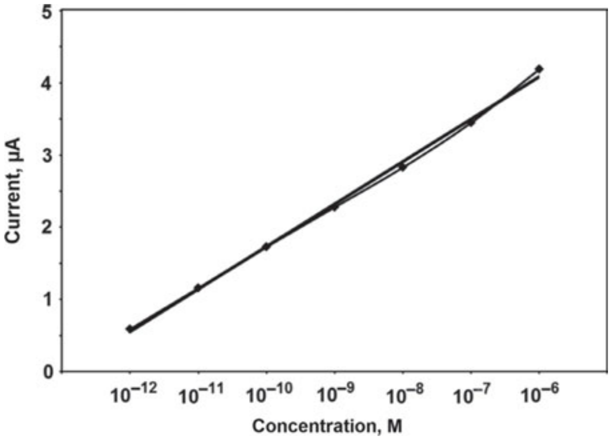

Fig. 8. Linear relationship between peak currents and different concentrations of Cu(II) ions.

3.5. Determination of Cu(II) ions in lake water sample

The proposed method was successfully applied for the determination of Cu(II) ions in Beyşehir lake water

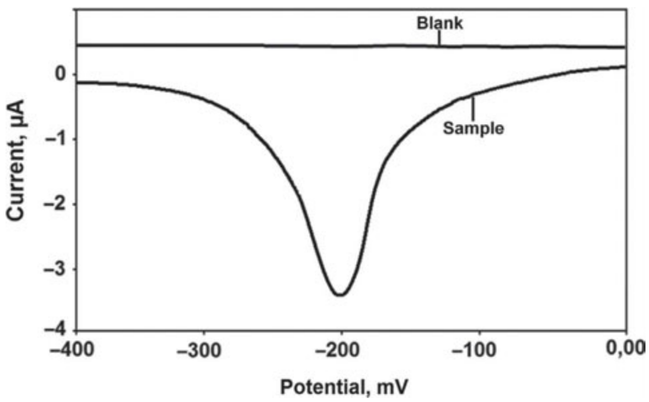

Fig. 9. Differantial pulse voltammogram of Cu(II) ions in lake water sample and the blank (ultra pure water) solution onto the NG/GC electrode. The measurement was performed in BR buffer, pH 5.0, potential is referred vs. Ag/AgCl/(3 M KCl).

sample in Konya, Turkey without any pretreatment. For the determination of Cu(II), a homogeny mixture was prepared by sonicating the mixture of 10 ml BR buffer solution, pH 5.0, and 10 ml water sample taken from Beyşehir lake for 10 min.

NG modified GC electrode was incubated for 2 h in the prepared mixture. The voltammogram of incubated NG/GC electrode was taken by differential pulse technique in BR buffer solution (pH 5.0) (Fig. 9).

After the grafting of the Cu(II) ions in lake water sample to the NG/GC electrode surface, peak current value was measured by DPV. And then, obtained peak current value was used to detection of Cu(II) ions concentration in lake water sample by interpolating using the calibration curve. The concentration of Cu(II) ions in the real sample is found to be 0.327 µM ml^{-1} from calibration curve.

4. Conclusions

Although Cu(II) ions has been determined for years using various techniques, there are few studies for the determination of Cu(II) ions with a sensor electrode using electrochemical technique. The main advantages of this proposed method are: (i) the electrochemical modification of NG on the GC electrode in aqueous media at neutral pH is reported, (ii) NG/GC electrode is developed for determination of Cu(II) ions for the first time, (iii) the polyphenol structure has a significant role in formation of complexes with Cu(II) ions, (iv) the proposed method is simple, sensitive and quick, (v) the determination of Cu(II) ions is carried out in lake water sample without any preconcentration, (vi) it is cheap with no need of using expensive reagents or equipment, and (vii) it has a low detection limit.

Acknowledgements

This study was financially supported by the Research Foundation of Selçuk University, Konya-TURKEY (BAP-09401118).

References

[1] M.J. Yonone-Lioy and P.J. Lioy, Assessment of human exposure to copper: A case study using the NHEXAS database, J. Exposure Sci. Environ. Epidemiol., 16 (2006) 397–409.

[2] T.W. Lin and S.D. Huang, Direct and simultaneous determination of copper, chromium, aluminum, and manganese in urine with a multielement graphite furnace atomic absorption spectrometer, Anal. Chem., 73 (2001) 4319–4325.

[3] G. Pethes, Element Analysis of Biological Materials, IAEA, Vienna, 1980, p. 3.

[4] X. Wen, Q. Yang, Z. Yan and Q. Deng, Determination of cadmium and copper in water and food samples by dispersive liquid–liquid microextraction combined with UV–vis spectrophotometry, Microchem. J., 97 (2011) 249–254.

[5] B. Buke, U. Divrikli, M. Soylak and L. Elci, On-line preconcentration of copper as its pyrocatechol violet complex on Chromosorb 105 for flame atomic absorption spectrometric determinations, J. Hazard. Mater., 163 (2009) 1298–1302.

[6] Ç.A. Şahin, İ. Tokgöz and S. Bektaş, Preconcentration and determination of iron and copper in spice samples by cloud point extraction and flow injection flame atomic absorption spectrometry, J. Hazard. Mater., 181 (2010) 359–365.

[7] C.S. Nomura, C.S. Silva, A.R.A. Nogueira and P.V. Oliveira, Bovine liver sample preparation and micro-homogeneity study for Cu and Zn determination by solid sampling electrothermal atomic absorption spectrometry, Spectrochim. Acta Part B., 60 (2005) 673–680.

[8] S.L.C. Ferreira, A.S. Queiroz, M.S. Fernandes and H.C. dos Santos, Application of factorial designs and Doehlert matrix in optimization of experimental variables associated with the preconcentration and determination of vanadium and copper in seawater by inductively coupled plasma optical emission spectrometry, Spectrochim. Acta Part B., 57 (2002) 1939–1950.

[9] A.D. Mulazimoglu, I.E. Mulazimoglu and E. Ozkan, Preconcentration and determination of copper and zinc with 1-nitroso-2-naphthol complexes on Dowex MWC-1 resin using ICP-AES, E-J. Chem., 6 (2009) 1176–1180.

[10] L.A. Escudero, S. Cerutti, R.A. Olsina, J.A. Salonia and J.A. Gasquez, Factorial design optimization of experimental variables in the on-line separation/preconcentration of copper in water samples using solid phase extraction and ICP-OES determination, J. Hazard. Mater., 183 (2010) 218–223.

[11] Z. Ajtony, N. Szoboszlai, E.K. Susko, P. Mezei, K. Gyorgy and L. Bencs, Direct sample introduction of wines in graphite furnace atomic absorption spectrometry for the simultaneous determination of arsenic, cadmium, copper and lead content, Talanta, 76 (2008) 627–633.

[12] A. Ali, H. Shen and X. Yin, Simultaneous determination of trace amounts of nickel, copper and mercury by liquid chromatography coupled with flow-injection on-line derivatization and preconcentration, Anal. Chim. Acta, 369 (1998) 215–223.

[13] A. Zeng, E. Liu, S. Tan, J. Zhang and J. Gao, Stripping voltammetric analysis of heavy metals at nitrogen doped diamond-like carbon film electrodes, Electroanalysis, 14 (2002) 1294–1298.

[14] A. Mohadesi and M.A. Taher, Voltammetric determination of Cu(II) in natural waters and human hair at a meso-2,3-dimercaptosuccinic acid self-assembled gold electrode, Talanta, 72 (2007) 95–100.

[15] L.W. Potts, Quantitative Analysis. Theory and Practice, Harper and Row, New York, 1987, p. 656.

[16] J. Kuhnau, The flavonoids. A class of semi-essential food components: Their role in human nutrition, World Rev. Nutr. Diet., 24 (1976) 117–191.

[17] D. Nematollahi and M. Malakzadeh, Electrochemical oxidation of quercetin in the presence of benzenesulfinic acids, J. Electroanal. Chem., 547 (2003) 191–195.

[18] D. Nematollahi and R.A. Rahchamani, Electro-oxidation of catechols in the presence of benzenesulfinic acid. Application to electro-organic synthesis of new sulfone derivatives, J. Electroanal. Chem., 520 (2002) 145–149.

[19] M.H. Pournaghi-Azar and H. Nahalparvari, Preparation and characterization of electrochemical and electrocatalytic behavior of a zinc pentacyanonitrosylferrate film-modified glassy carbon electrode, J. Electroanal. Chem., 583 (2005) 307–317.

[20] Z. Üstündağ and A.O. Solak, EDTA modified glassy carbon electrode: Preparation and characterization, Electrochim. Acta, 54 (2009) 6426–6432.

[21] J. Pinson and F. Podvorica, Attachment of organic layers to conductive or semiconductive surfaces by reduction of diazonium salts. Chem. Soc. Rev., 34 (2005) 429–439.

[22] H.R. Zare, M. Namazian and N. Nasirizadeh, Electrochemical behavior of quercetin: Experimental and theoretical studies, J. Electroanal. Chem., 584 (2005) 77–83.

[23] A.O. Solak, L.R. Eichorst, W.J. Clark and R.L. McCreery, Modified carbon surfaces as “Organic Electrodes” that exhibit conductance switching, Anal. Chem., 75 (2003) 296–305.

[24] A.K. Timbola, C.D. de Souza, C. Giacomelli and A. Spinelli, Electrochemical oxidation of quercetin in hydro-alcoholic solution, J. Braz. Chem. Soc., 17 (2006) 139–148.

[25] P. Janeiro and A.M. Oliveira-Brett, Solid state electrochemical oxidation mechanisms of morin in aqueous media, Electroanalysis, 17 (2005) 733–738.

[26] E. Brillas, R. Sauleda and J. Casado, Destruction of aromatic contaminants in an Fe/O_2 battery, Electrochem, Solid-State Lett., 1 (1998) 168–171.

[27] İ.E. Mülazımoğlu and A.O. Solak, A novel apigenin modified glassy carbon sensor electrode for the determination of copper ions in soil samples, Anal. Methods, 3 (2011) 2534–2539.

[28] S.P. Wong, L.P. Leong and J.H.W. Koh, Antioxidant activities of aqueous extracts of selected plants, Food Chem., 99 (2006) 775–783.

[29] S. Quideau, D. Deffieux, C. Douat-Casassus and L. Pouysegu, Plant polyphenols: Chemical properties, biological activities, and synthesis, Angew. Chem. Int. Ed., 50 (2011) 586–621.

[30] J. Peterson and J. Dwyer, Taxonomic classification helps identify flavonoid-containing foods on a semiquantitative food frequency questionnaire, J. Am. Diet Assoc., 98 (1998) 677–685.

[31] I.E. Mülazımoğlu, A. Demir Mülazımoğlu and E. Yılmaz, Determination of quantitative phenol in tap water samples as electrochemical using 3,3′-diaminobenzidine modified glassy carbon sensor electrode, Desalination, 268 (2011) 227–232.

[32] 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, 256 (2010) 64–69.

[33] 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, E-J. Chem., 6 (2009) 965–974.

[34] I.E. Mülazımoğlu, Covalent modification of a glassy carbon surface by electrochemical oxidation of 3,3′-diaminobenzidine, Asian J. Chem., 22 (2010) 8203–8208.

[35] M. Zatloukalova, V. Kren, R. Gazak, M. Kubala, P. Trouillas, J. Ulrichova and J. Vacek, Electrochemical investigation of flavonolignans and study of their interactions with DNA in the presence of Cu(II), Bioelectrochemistry, 82 (2011) 117–124.