Utilizing of 2-Amino-3-hydroxypyridine Modified Glassy Carbon Electrode to Detect Copper(II) Ions

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In this paper, 2-amino-3-hydroxypyridine modified glassy carbon electrode was used for the electrochemical analysis of trace copper(II) ions by square wave voltammetry technique. The modification of the glassy carbon electrode by 2-amino-3-hydroxypyridine solution was performed in the potential range between -150 mV and +600 mV by 30 cycles at 100 mV s^{-1} potential scan rate in non-aqueous media by cyclic voltammetry. The surface characterizations of this sensor electrode were performed by cyclic voltammetry. A lower detection limit would be reached in the presence of Britton-Robinson buffer solution at pH 5 for determination of Cu(II) ions by square wave voltammetry. The voltammetric response of the electrode was linear within the Cu(II) ion concentration range from 1.0×10^{-12} M to 1.0×10^{-6} M and the detection limit of 1.0×10^{-12} M. The modified electrode offered an excellent way, with a high stability, simple, rapid, low cost and reusability, for selective determination of Cu(II) ions in Acigöl lake (in Afyonkarahisar, Turkey) water sample.

Key Words: 2-Amino-3-hydroxypyridine, Sensor electrode, Copper(II) ions, Surface modification, Surface characterization.

INTRODUCTION

Electrochemical modified electrodes have a broad range of applications in modern electrochemistry. Over the past two decades, they have been widely applied in electro-catalytic reactions[1-3] and as electrochemical sensors[4-7]. Electrochemical, chemical, catalytic and kinetic properties can be achieved by modifying selectively the electrode surfaces. Modification of carbon surfaces is an important goal in electrochemistry and materials science in order to achieve specific surface functionality[8,9]. New methods for covalent attachment of various compounds to carbon electrode surfaces have been recently developed[10,11].

Copper is an essential element that is used in a variety of industrial materials[12] and human diet[13]. But it is also toxic after the intake of large quantities of copper in human diet[13]. Because copper is used widespread in many industries, so the pollution of soluble copper compounds in drinking water poses the greatest threat to humans. Thus its determination in water samples is essential and important using simply and reliable method.

The purposes of this study were to perform the electrochemical modification of 2-amino-3-hydroxypyridine onto the glassy carbon electrode surface using cyclic voltammetry, to characterize modified 2-amino-3-hydroxypyridine/glassy carbon electrode by cyclic voltammetry, to determine the interaction of this modified electrode with Cu(II) by square wave voltammetry and to apply this modified electrode in Acigöl lake water sample for the determination of Cu(II) ions.

EXPERIMENTAL

2-Amino-3-hydroxypyridine and the other chemicals used were purchased for electrochemical experiments from Fluka, Riedel de Haën and Sigma-Aldrich chemical companies and so no further purification was performed. CuSO$_4$·5H$_2$O 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$_3$PO$_4$ + CH$_3$COOH + H$_3$BO$_3$ according to preparation conditions in the literatures and then adjusting of pH by addition of 0.2 M or 1 M NaOH solution.

Electrochemical measurements were performed with GAMRY Reference PCI4/750 series potentiostat/galvanostat/ZRA from GAMRY Instruments (PA, USA), using a standard cell with three electrodes. The working electrode with a geometric area of 0.071 cm^2 was a glassy carbon electrode BAS (Bioanalytical Systems, West Lafayette, IN, USA) Model MF-2012. Solutions were thoroughly deoxygenated by purging with purified argon gas (99.99 %) for 10 min prior to the electrochemical experiments. Argon blanket was maintained over the solutions to supply an inert atmosphere during electrochemical measurements. All electrochemical experiments were carried out inside a BAS model C$_3$ cell stand (in, USA) at room temperature (25 ± 1 ºC). Prior to use in electrochemical experiments, the glassy carbon electrodes were cleaned

according to procedure in the literatures[14]. In all experiments, the electrodes were kept in acetonitrile when they were not in use. Electrode surfaces were sonicated with acetonitrile before and after each treatment.

RESULTS AND DISCUSSION

The polished and cleaned glassy carbon electrode surface was modified in 1 mM solution of 2-amino-3-hydroxypyridine prepared in 100 mM tetrabutylammonium tetrafluoroborate (NBu_4BF_4) (in CH_3CN) by cyclic voltammetry technique. The modification of the glassy carbon electrode by 2-amino-3-hydroxypyridine was performed in the potential range from -150 mV to +600 mV by 30 cycles at 100 mV s^{-1} scan rate[15]. The cyclic voltammogram of 2-amino-3-hydroxypyridine modified glassy carbon electrode surface is shown in Fig. 1. The cyclic voltammogram of 2-amino-3-hydroxypyridine onto the glassy carbon electrode surface indicated one irreversible oxidation peak (at E_{pa} = +241.7 mV) (Fig. 1). After the modification the sensor electrode was used for the determination of Cu(II) ions in Acigöl lake water sample.
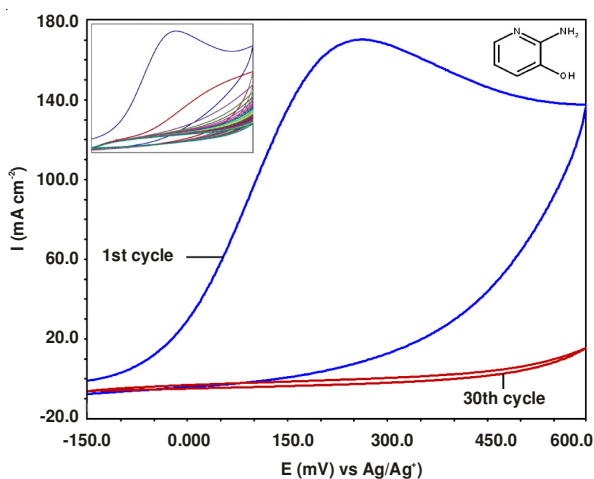

Fig. 1. Cyclic voltammogram of 1 mM 2-amino-3-hydroxypyridine in 100 mM NBu$_4$BF$_4$ (in CH$_3$CN) *vs.* Ag/Ag$^+$/(10 mM AgNO$_3$). Potential scan rate is 100 mV s^{-1}

The modified electrodes were characterized by cyclic voltammetry. In the characterizations with cyclic voltammetry, 1 mM ferrocene redox probe solution in 100 mM NBu_4BF_4 was carried out the potential range from -200 mV to +400 mV in non-aqueous media (Fig. 2A) and 1 mM $Fe(CN)_6^{3-}$ redox probe solution in BR buffer solution (pH 2) was performed the potential range from +600 mV to -100 mV in aqueous media (Fig. 2B) at scan rate of 100 mV s^{-1}.

After the modification and the characterization of 2-amino-3-hydroxypyridine/glassy carbon surface by cyclic voltammetry, the complex formation of Cu(II) ions with this modified electrode surface was investigated using square wave voltammetry technique. In square wave voltammetry experiments, we used the potential range from -400 mV to 0.0 mV for Cu(II) ions solution vs. Ag/AgCl/3 M KCl reference electrode, frequency 100 Hz, step potential 1.5 mV, amplitude 50 mV, equilibration time 15 s. As soon as we described basic electrochemical behaviour of the analyzed Cu(II) ions measured

on the surface of 2-amino-3-hydroxypyridine/glassy carbon electrode using square wave voltammetry, we decided to optimize parameters [pH of Cu(II)] solution and incubation time) of voltammetric method used. Firstly, 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 square wave voltammetry. pH 5 was found to be the optimum value for determination of Cu(II) ions. Cu(II) can't be determined due to the precipitation of Cu(II) as hydroxide at higher pH value. And then, the optimum incubation time was determined by incubating 2-amino-3-hydroxypyridine/glassy carbon electrode in Cu(II) solutions in BR buffer solution, pH 5, for various time periods (30, 60, 90, 120, 150, 180 min). As the incubation time increased, square wave voltammetry signals also increased up to 120 min incubation time. Above this time, the steady state was achieved. Based on the results obtained, we selected the most suitable conditions for the determination of Cu(II) ions as follows: BR buffer solution, pH 5.0, incubation time 120 min. Grafting onto the 2-amino-3-hydroxypyridine/glassy carbon electrode surface of Cu(II) ions was investigated by square wave voltammetry technique.
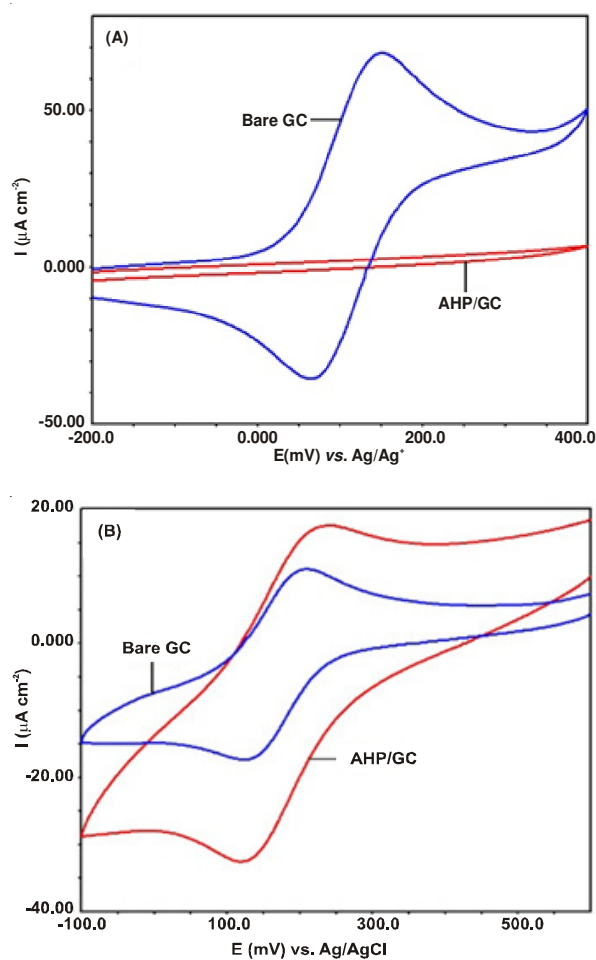

Fig. 2. Cyclic voltammograms and electrochemical impedance spectra of 2-amino-3-hydroxypyridine/glassy carbon (A) 1 mM ferrocene vs. Ag/Ag$^+$ (10 mM) in 100 mM NBu$_4$BF$_4$ (in CH$_3$CN), (B) 1 mM Fe(CN)$_6$$^{3-}$ redox probe solution *vs.* Ag/AgCl/3 M KCl reference electrode in BR buffer solution, pH = 2, with a Pt working electrode. Scan rate is 100 mV s^{-1}

In this part of the research, interference affects of some anions and cations were examined during the quantitative determination of Cu(II) ions. To examine the interference affect a solution of Cd^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Pb^{2+} and Zn^{2+} cations and NO_3^-, SO_4^{2-}, CO_3^{2-} and Cl^- anions was prepared in the order of 1×10^{-6} M. 2-Amino-3-hydroxypyridine/glassy carbon electrode was immersed 120 min in this solution and then square wave voltammogram was taken in BR buffer solution (pH = 5). The tolerance limit is defined as the ion concentration causing a relative error smaller than ±2 % related to the determination of Cu(II) ions. Tested cations and anions did not show any negative effects on Cu(II) determination. It is concluded that Cu(II) ions were determined in the presence of interfering cations and anions that have no any negative effect.

After the electrochemical modification and electrochemical characterizations by cyclic voltammetry, the electrode was used in the practical studies keeping in mind that 2-amino-3-hydroxypyridine/glassy carbon electrode surface modified in non-aqueous media. 2-Amino-3-hydroxypyridine/glassy carbon electrode was firstly incubated for a period of 120 min in 10 mL buffer solution and 10 mL water sample mixture and then the square wave voltammetry technique for Cu(II) ions determination was performed in BR buffer solution, pH 5 (Fig. 3A) The proposed method was successfully used for the determination of Cu(II) ions in Acigöl Lake water sample in Dazkiri region in Afyonkarahisar, Turkey without any pretreatment.

Determination of Cu(II) ions in real samples has crucial importance due to using of the technique for routine analysis. That also means if the method optimized above will not be suitable for analysis of real samples, we couldn't use it in the following experiments. A series of $CuSO_4 \cdot 5H_2O$ from 1×10^{-12} M to 1×10^{-6} M was prepared for the calibration curve of the determination of Cu(II) ions in water sample at optimum conditions. Firstly, the glassy carbon electrode surface was modified 2-amino-3-hydroxypyridine solution by cyclic voltammetry and then the square wave voltammetry technique was used in order to investigate formation of Cu(II) complex following the incubation of these electrodes in the prepared Cu(II) ions and BR buffer mixture solution for 120 min. A calibration curve, Cu(II) concentration *versus* peak current obtained from the voltammograms was drawn and given in Fig. 3B. The values of the peak current are linear with the concentration of Cu(II) ions in the range from 1.0×10^{-12} M to 1.0×10^{-6} M with the correlation coefficient (R^2) as 0.998 under the optimum conditions of the general procedure. According to following equation for Cu(II) ions determination is Ip= 3.6925C-19.684, Ip is the peak current and C is Cu(II) concentration.

After the grafting of the Cu(II) ions in lake water sample to the 2-amino-3-hydroxypyridine/glassy carbon electrode surface, peak current value was measured by square wave voltammetry. 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 9.5×10^{-7} M for 15.43 µA peak current value from calibration curve.
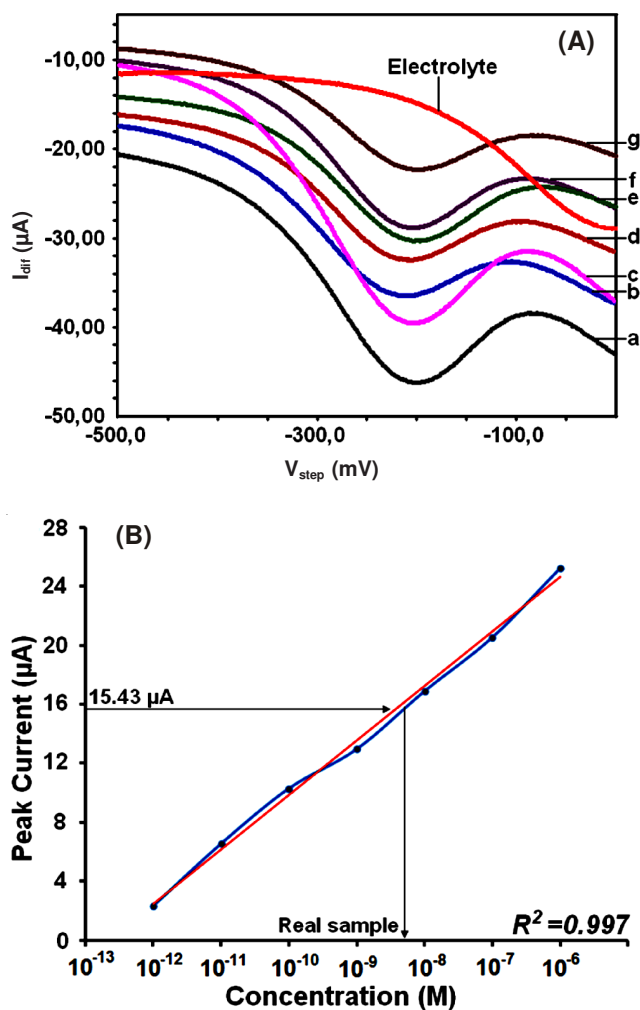

Fig. 3. A) Square wave voltammograms of bare glassy carbon electrode surface and different concentrations of $CuSO_4 \cdot 5H_2O$ onto the 2-amino-3-hydroxypyridine/glassy carbon electrode surface a) 1×10^{-6}, b) 1×10^{-7}, c) 1×10^{-8}, d) 1×10^{-9}, e) 1×10^{-10}, f) 1×10^{-11} and g) 1×10^{-12} the measurements were performed in BR buffer solution, pH 5.0, *vs.* Ag/AgCl/(3 M KCl). Frequency 100 Hz, step potential 1.5 mV, amplitude 50 mV, equilibration time 15 s. (Electrolyte: BR buffer solution, pH 5) B) Standard calibration curve for the Cu(II) ions

Conclusion

In this study, it was examined whether 2-amino-3-hydroxypyridine/glassy carbon electrode prepared by modification of 2-amino-3-hydroxypyridine solution could be used in the determination of Cu(II) ions after the modification in non-aqueous media. The proposed method is simple, sensitive and quick, the determination of Cu(II) ions is carried out in lake water sample without any pretreatment, it is cheap with no need of using expensive reagents or equipment. In some studies natural samples have been used for Cu(II) determination. However, the low detection limit of our study is the advantage of this study.

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