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DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY DETERMINATION OF COPPER (II) AT GLASSY CARBON ELECTRODE IN THE PRESENCE OF BIS(BENZYLIDENE)ETHYLENEDIAMINE AS A NOVEL COMPLEXING AGENT

(Penentuan Kuprum(II) Menggunakan Voltammetri Perlucutan Anodik Denyut Pembezaan Dengan Elektrod Karbon Berkaca Serta Kehadiran Bis(Benzilidina)Etilinadiamina Sebagai Agen Pengkompleks)

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Abstract

This paper reports on the application of synthesized Schiff base bis(benzylidene)ethylenediamine (BBE) to increase the detection sensitivity of copper (II) at 0.01 V vs Ag/AgCl using glassy carbon electrode. Aliquot of 2.0×10^{-3} M of BBE in DMF solution containing BR buffer pH 6 was introduced into the voltammetric cell followed by the addition of Cu(II) ions and then further proceeded to differential pulse anodic-stripping scan from -1.4 V to +0.3 V vs Ag/AgCl. The optimum parameters obtained were; scan rate; 25 mV/s, accumulation time; 200 sec and accumulation potential; -0.6 V. Under the optimal conditions, the detection limit of 0.4 µgL^{-1} and a linear response in the range of 1-10 µgL^{-1} were obtained. The effects of interfering ions such as Cd(II), Cr(III), Fe(II), Pb(II) and Zn(II) were also investigated. The practical applicability of this technique was illustrated by the determination of Cu(II) ions at 3µgL^{-1} concentration level in tap water with 94.43% of recovery.

Keywords: bis(benzylidene)ethylenediamine, copper ion, differential pulse anodic stripping voltammetry

Abstrak

Kertas ini melaporkan aplikasi sintesis Schiff base bis(benzilidena)ethylenadiamina (BBE) untuk meningkatkan kepekaan pengesanan kuprum(II) pada 0.01 V vs Ag/AgCl dengan menggunakan electrod karbon berkaca. Alikuot BBE (2.0 x10^{-3} M) dalam DMF dimasukkan ke dalam sel voltammetri yang mengandungi larutan buffer BR pada pH 6. Larutan Cu(II) kemudian ditambah dan di imbas menggunakan teknik voltammetri pelucutan anodik denyut pembezaan dari -1.4 V kepada +0.3 V vs Ag/AgCl. Parameter optimum ialah, kadar imabasan 25 mV/s, masa pengumpulan 200 saat dan keupayaan pengumpulan -0.6 V. Dibawah kondisi optimum ini, had pengesanan ialah 0.4 ugL^{-1} dan julat linear yang diperolehi ialah 1-10 ugL^{-1}. Kesan ion–ion lain seperti Cd(II), Cr(III), Fe(II), Pb(II) dan Zn(II) juga dikaji. Kaedah ini telah diaplikasikan bagi menentukan Cu(II) pada kepekatan 3ugL^{-1} dalam air paip dengan perolehan semula sebanyak 94.43%.

Kata kunci: Bis(benzylidene)ethylenediamine, ion kuprum, voltammetri pelucutan anodik denyut pembezaan

Introduction

Environmental pollution and human exposure to heavy metals are steadily increasing. The World Health Organization (WHO) estimates that about 25% of the diseases facing humans today occur due to long-term exposure to environmental pollution, including air, soil, and water pollution [1]. Environmental contaminations by trace metals such as copper, mercury, lead, zinc, and cadmium are a serious problem not only for ecosystem, but also for human health because they are non-degradable and their accumulation leads to various systemic diseases. Among heavy metals, copper is an essential element in the nutrition of plants, and animals and it is also fundamental in many metabolic processes since it is the third most abundant trace element in biological systems. However, excess of copper can cause various intoxications and may cause symptoms such as gastroenteritis and vomiting [2]. Numerous techniques, such as UV-Vis spectrophotometry [3], inductively coupled plasma mass spectrometry (ICP-MS) [4, 5], inductively coupled plasma optical emission spectrometry (ICP-OES), atomic absorption spectrophotometry (AAS) [6, 7] and atomic fluorescence spectrometry (AFS) [8], have been used for the detection of metal ions.

Among these techniques, electrochemical techniques have a great potential for environmental monitoring of toxic metal ions in drinking or waste water due to their excellent sensitivity, rapid analysis and low cost [9-11]. Adsorptive stripping voltammetry has been employed as a powerful technique for determination of ultratrace levels of metals. This method is an extremely sensitive technique that offers low detection limits and is based on adsorptive accumulation of metal ions and suitable complexing agent on the electrode surface [12].

Heavy metals show a great tendency to form complexes, especially with ligands containing nitrogen, sulfur, and oxygen. Previous study of electrochemical determination of copper has been performed with glassy carbon electrode modified with 1-aminoindan [2], phenanthroline derivatives [13, 14], luteolin and kaempferol [13-15] and dopamine [16]. However, most of these Cu(II) ion selective electrodes are affected by interfering heavy metal ions such as Cd(II), Co(II), Fe(II), Ni(II) and Pb(II)) and offer only limited sensitivity within a relatively short linear-range.

Bis(benzylidene)ethylenediamine (BBE) is a Schiff base ligand prepared by condensation of salicylaldehyde and ethylenediamine. It is a symmetrical molecule and exhibits chiral properties. The structure of its ligand is presented in Figure 1. Electrochemical techniques using Schiff bases ligands have been widely used for the determination of low concentrations of organic and inorganic compounds in a number of different matrices. Several authors have studied the electrochemical behaviour of Schiff base complex with metals ion and some of their applications [17-19].

To enhance the Cu(II) ions detection, the differential pulse stripping voltammetry technique was proposed based on the complexation of Bis(benzylidene)ethylenediamine with Cu(II) ions on the glassy carbon electrode surface. The peak currents of Cu(II) ions were evaluated within a wide concentration range, with high selectivity and sensitivity suitable for investigation of real samples. It was shown that the proposed technique can be used for the determination of Cu(II) ions even in the presence of some interfering ions.

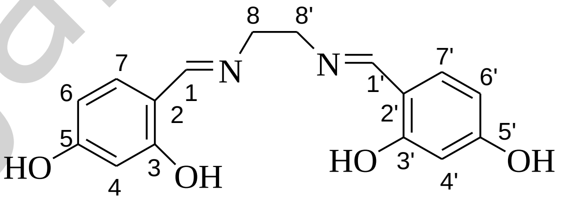

Figure 1. Structure of Bis(benzylidene)ethylenediamine

Materials and Methods

Reagents

2,4-dihydroxyabenzaldehyde (Fluka) and ethylenediamine (Merck) were used for synthesis. Britton Robinson (BR) buffers (pH 2-11) were prepared by mixing appropriate amount of boric acid (H_3BO_3), glacial acetic acid (CH_3COOH) and 85% orthophosphoric acid (H_3PO_4) in deionized water. Standard solutions Cu(II) were prepared by dissolving $CuSO_4.5H_2O$ in de-ionized water. Stock solutions of ligand were prepared by dissolving appropriate amount of ligand in dimethylformamide (DMF). The de-ionized water used throughout the present work was obtained from Barnstead Ultra Nanopure water system.

Instrument

0.2 mm Merck pre-coated silica gel TLC plates were used to monitor the Schiff base synthesis and visualized with UV light. The ^{1}H and ^{13}C NMR spectra (400 and 100 MHz respectively) were recorded on a Bruker Avance 400 instrument using deuterated solvents ($CDCl_3$, dimethylsulfoxide (DMSO) and methanol (CD_3OD)). IR spectra were measured on a Shimadzu 8000 or Perkin-Elmer series 1600 spectrometers using thin film technique (NaCl windows) for liquid samples or KBr pellet technique for solid samples. Melting points were measured on a Leica Galen III micro melting point apparatus and were not corrected. All electrochemical measurements were performed using EA163 potentiostat (Edaq). A conventional three-electrode cell configuration was used for the voltammetric measurements with glassy carbon working electrode (Metrohm), platinum wire auxiliary electrode, and silver-silver chloride (Ag/AgCl, 3M KCl) reference electrode.

Voltammetric Determination

The surface of the GC electrode was polished with 1.0 µm alumina water slurry using a polishing cloth. The electrode was rinsed and then sonicated in distilled water followed by methanol for 10 mins, respectively. 15 ml of BR buffer was placed into the voltammetric cell and the required amount of Cu(II) ions and 100µL of 0.001M of BBE dissolved in DMF were added. Appropriate accumulation potential and specified accumulation time were further used whilst stirring. Typically, the DPASV voltammetric parameters were as follows: pulse amplitude 25 mV, scan rate 10 mV/s. Prior to the voltammetric measurement pure nitrogen were purge into the solution whilst stirring at 400 rpm. Voltammograms were then recorded by scanning anodically from -1.2 V to +0.3 V.

Results and Discussion

Characterization of Bis(benzylidene)ethylenediamine by Cyclic Voltammetry

Cyclic voltammograms of BBE on GCE at 250 mV/s in BR buffer pH 5 showed two anodic waves at +0.73V and +1.06 V attributed to the oxidation of hydroxyl groups on aromatic systems as reported in [20]. One cathodic peak at -0.62 V is due to the reduction of C=N double bonds of BBE (see Figure. 2) [21].

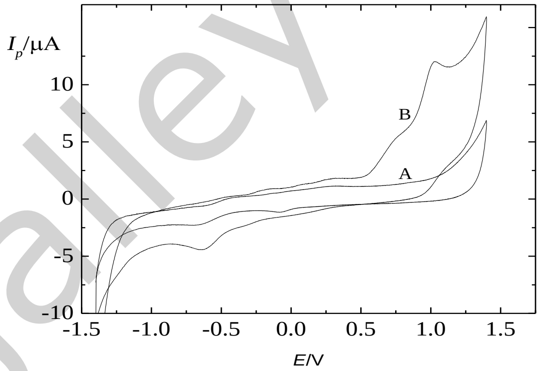

Figure 2. Cyclic voltammograms of 3 µgL^{-1} BBE (B) at GCE in 0.04 M BR buffer (A) pH 5.0. v = 250 mV/s.

Differential Pulse Anodic Stripping Characteristics of Copper(II)-BBE Complexes

Preliminary experiments were performed to identify the general features characterizing the behavior of Cu(II)-BBE complex. Figure 3 shows differential pulse anodic stripping voltammograms (DPASV) of the Cu(II) in BR buffer pH 6. Accumulation was carried out at -600mV for 180 sec. The stripping voltammogram was scanned positively between -1400 mV and +300 mV. The blank solution (a) (the BBE without metal ions) does not show any peak in this potential range. Cu(II) 3 µgL^{-1} shows a small peak at -0.03 V in the absence of the BBE (curve b). The solution containing Cu(II) ions (c=3 µgL^{-1}) with the BBE (c=2.0×10^{-3} M) shows sharp peak (curve c) at 0.0 V that corresponds to the oxidation of Cu(0) complex with BBE at pH 6 to Cu(II) complex. The performance of the newly developed Cu(II)-BBE is based on the preconcentration of Cu(II) from aqueous solution onto the surface of the GC electrode by forming complexes with the BBE. BBE acts as the ligand and Cu(II) as the central atom. The existence of two donating oxygen atoms and two donating nitrogen atoms is expected in the selective complexation behavior of Cu(II). The accumulated Cu(II) was reduced at 0.0 V and the products were then oxidized in the stripping stage. The mechanism can be described as follows:

$$(Cu^{2+})_{solution}+(BBE)_{solution} \longrightarrow (Cu^{2+}\text{-}BBE)_{complex}$$

(Complex formation)

$$(Cu^{2+}\text{-}BBE)_{complex}+2e \longrightarrow (Cu^{o}\text{-}BBE)_{adsorption}$$

(Reduction and adsorption step)

$$(Cu^{o}\text{-}BBE)_{adsorbed} \longrightarrow (Cu^{2+})_{solution} + BBE_{solution} + 2e$$

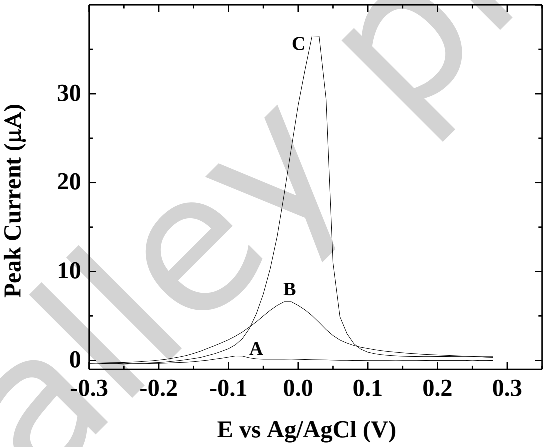

Figure 3. DPASV of Cu(II)-BBE (c=3 µgL^{-1}) in 0.04 M BR buffer pH 6. E_i= -1200 mV, E_f =300 mV, E_{acc}=-600 mV, t_{acc}=60s, υ = 10 mV/s and rest time 2s. (A): Blank BR buffer, (B): BR buffer + Cu(II) (c=3 µgL^{-1}, (C): BR buffer + Cu(II) (c=3 µgL^{-1}) + BBE (c=2.0×10-3 mol L^{-1}).

Effects of pH

The influence of pH on the response of the glassy carbon (GC) electrode was studied at 3 µgL-1 Cu(II) ion in the pH range of 2-11 in the presence of 2.0×10^{-3} M BBE (see Figure 4). The pH of the test solutions was adjusted by addition of BR buffer with appropriate pH. It was found that for pH lower than 4.0 no peak was observed. Above pH 5, there is an increase in the peak current, which reaches its maximum at pH 6. Further increase of pH above 7.0 results in the decrease of peak current and at pH 10 the peak disappeared. From figure 4, it can be observed that the peak potential is shifted toward more negative potential with increasing the pH value. This behavior indicated the transfer of protonation or deprotonation steps was involved in the oxidation process at the surface of GC electrode [22].

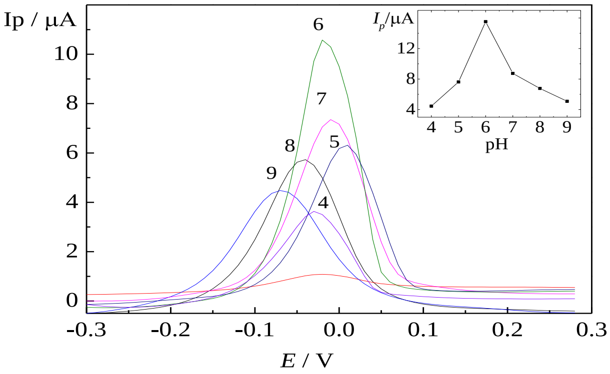

Figure 4. Dependence of DPASV peak current of copper(II)-BBE complex (Cu(II) (c= 3 µgL^{-1}) + BBE (c=2.0×10^{-3} mol L^{-1}) on pH of BR buffer. E_i= -1200 mV, E_f = 300 mV, E_{acc}=-600 mV, t_{acc}=180s, υ = 25 mV/s and pulse amplitude 25 mV.

Effect of Ligands Concentration

The use of BBE can greatly improve the sensitivity and selectivity of Cu(II) determination due to the complexation of Cu(II) with BBE via its functional groups. Figure 5 shows the increase in peak current with increasing concentration of BBE. At 3 µgL^{-1} of BBE, the maximum peak current was obtained. Afterwards, the peak decreased with decreasing concentration of BBE.

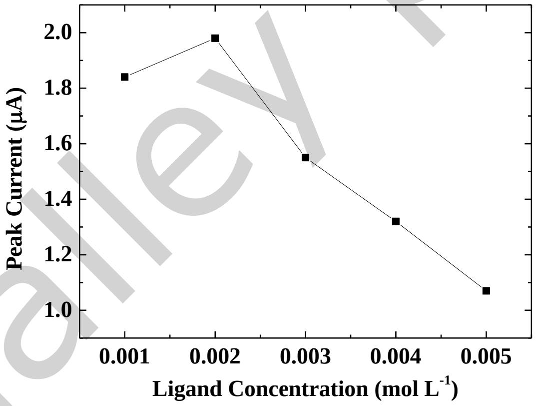

Figure 5. Dependence of DPASV peak current of Cu(II)-BBE complex (Cu(II), (c= 3 µgL^{-1}) + BBE (c=2.0×10^{-3} mol L^{-1}) on BBE concentration in BR buffer pH 6 E_i= -1200 mV, E_f = 300 mV, E_{acc}=-600 mV, t_{acc}=180s, υ = 25 mV/s and pulse amplitude 25 mV.

Effects of Accumulation Time

The influence of accumulation time on the stripping peaks of copper was investigated and the results are summarized in Figure 6. As expected for adsorption processes, the dependence of the peak current on the accumulation time is limited by the saturation of the electrode surface, resulting in the current decreasing at high accumulation times, as shown in Figure 6. Thus, a deposition time of 200 s was used throughout.

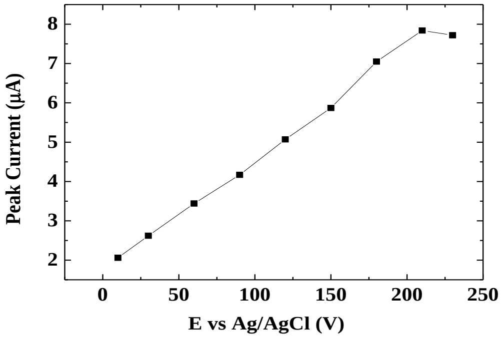

Figure 6. Dependence of DPASV peak current of Cu(II)-BBE complex (Cu(II) (c= 3 μgL^{-1}) + BBE (c=2.0×10^{-3} mol L^{-1}) in 0.04 M BR buffer pH 6, E_i= -1200 mV, E_f = 300 mV, v = 25 mV/s , pulse amplitude 25 mV.

Effect of Accumulation Potential

The effect of accumulation potential on the stripping peak currents of copper and complexes with BME was examined over the potential range of 0 to –1000 mV. The plots of stripping peaks current Cu(II) ions as a function of preconcentration potential are shown in Figure 7. As it is obvious, the peak currents of Cu(II) are independent of accumulation potential at the potential range of 0 to –1000 mV, and at potentials whose values are more negative than –800 mV, the sensitivity of reduction of Cu(II) decreased. The maximum peak current was achieved at –600 mV. At this potential, the Cu(II)-BBE was adsorbed on the surface of electrode and the response signals are reducted due to metal ion complexes during the anodic sweep.

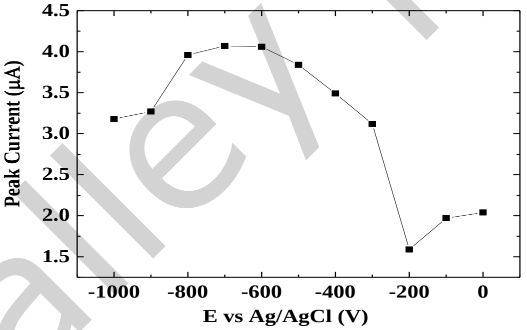

Figure 7. Dependence of DPASV peak current of Cu(II)-BBE (Cu(II) (c= 3 μgL^{-1}) + BBE (c=2.0×10^{-3} mol L^{-1}) in 0.04 M BR buffer on accumulation time. E_i= -1200 mV, E_f = 300 mV, E_{acc}= -600 t_{acc}=180s, v = 25 mV/s, pulse amplitude 25 mV.

Limit of Detection and Linearity Range

The optimum parameters selected have been applied to measure a calibration curve as shown in Figure 8. The calibration graph is: y=0.0308x+0.0597 (y=peak current, I_p/μA; x: the concentration of Cu(II), μA), correlation coefficient is 0.9953. A linear response in the 1-10 μgL^{-1} concentration range was obtained. The detection limit and quantification limit calculated were 0.4 μgL^{-1} and 1.63 μgL^{-1} respectively. The relative standard deviation of 3 measurements for 3 μgL^{-1} is 0.7%.

Interference Studies

The interferences of some metal ions on the determination of Cu(II) were investigated in the solution of 6 μgL^{-1} of Cu(II) by evaluating the interference effects of Zn(II), Cr(II), Pb(II) Cd(II) and Fe(II). These metal species were used because they might be expected to exhibit redox activity in the same potential range as copper(II). The results in Table 1 showed that most of these metal ions do not interfere with the determination of Cu(II) except for Zn(II). The peak current of Cu(II) decreased in the presence of high concentration of Zn(II) which is attributed to the fact that this metal can compete with Cu(II) for complexing with BBE.

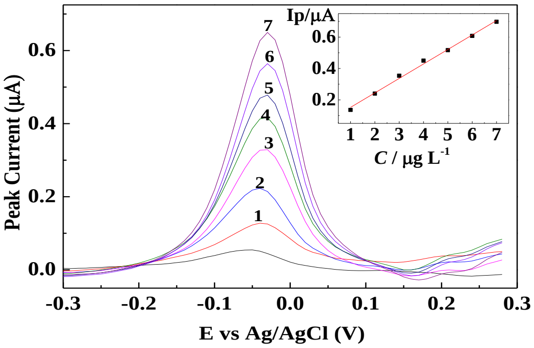

Figure 8. Linear plot and calibration curve of Cu(II)-BBE in 0.04 M BR buffer solution pH 6 with experimental parameters are: 0.002M BBE, E_i= -1200 mV/s, E_f = 300 mV/s, E_{acc}=-600 t_{acc}=180s vs Ag/AgCl (3M), v = 25 mV/s and pulse amplitude, 25 mV.

Table 1. Peak current change of interfering ions in determination of 6 μgL^{-1} of Cu(II)

Interfering ions	**Peak Current Change (%)**
Zn(II)	-20.73
Cr(II)	2.04
Pb(II)	-5.77
Cd(II)	11.27
Fe(II)	-0.9

Real Sample

The practical applicability of the newly developed method was verified by the determination of Cu(II) in tap water. Tap water from the water pipeline in the C10 building of Faculty of Science of Universiti Teknologi Malaysia, Johor Bharu spiked with appropriate amounts of stock solutions of Cu(II) was used as the model sample. The analysis was performed by standard addition method. The procedure for the DPASV determination was as follows: 9.0 mL of a model water sample was diluted up to 10.0 mL with 0.004M of BR buffer for the direct determination of Cu(II) in tap water. DPASV voltammogram was recorded. The amount added was 3.0 μgL^{-1} and the result obtained was 3.2 μgL^{-1} ± 0.09 M with good recoveries of 94.43% and RSD of 3.9% (n=4). There were no significant differences between the obtained and the added concentrations indicating that Cu(II)-BBE electrode can be successfully used for the determination of Cu(II) in natural samples under the optimized conditions.

Conclusion

The proposed method is suitable for direct determination of Cu (II) by differential pulse anodic stripping voltammetry (DPASV). The voltammetric response was linear in the concentration range of 1-10 μgL^{-1} for

180 s preconcentration time at accumulation potential of -600 mV/s. The proposed method also exhibits a very low detection limit up to 0.4 μgL^{-1}.

Acknowledgement

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