

## An environmental friendly electrode based on pyridine–imidazole modified glassy carbon electrode for anodic stripping voltammetry of copper detection

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The 2-(1-butyl-1*H*-imidazol-2-yl)pyridine was synthesized from the corresponding 2-pyridylcarboxaldehyde, glyoxal, and concentrated ammonia solution, subsequently alkylation with 1-iodobutane. It was obtained with yield of 63%. Electrochemical modification of glassy carbon electrode (GCE) surface via electrochemical oxidation of pyridine–imidazole ligand in 0.01 mol L<sup>-1</sup> hydrochloric acid solution (Py–Im/GCE) and applicability of electrode modified in this way for determination of copper(II) by anodic stripping voltammetry. Electrochemical surface modification was performed by cyclic voltammetry in the potential range between +1.4 and -1.4 V vs. Ag/Ag<sup>+</sup> (10.0 mM of AgNO<sub>3</sub>) at the scan rate of 100 mV s<sup>-1</sup> by 20 potential cycles. Some operational parameters including pyridine-imidazole ligand concentration, surface preconcentration potential, and preconcentration time were optimized. Under the optimum conditions, the sensitivity (the slope of the regression equation) of the Py–Im/GCE was 1.93 times higher than the bare GCE. The two linear ranges, 0.0075–0.1 mg L<sup>-1</sup> and 0.1–0.5 mg L<sup>-1</sup>, a detection limit of 0.029 mg L<sup>-1</sup> and a quantitation limit of 0.0098 mg L<sup>-1</sup>.

### 1. Introduction

Copper is one important elements in the environment. Copper is an essential trace element in biological systems and living organisms;<sup>1</sup> it serves as a cofactor in at least 30 important enzymes.<sup>2</sup> However, copper also causes the ischaemic heart disease, anaemia, and bone disorders.<sup>3</sup> Due to the low concentration of heavy metals in soil and food, several techniques have been employed for quantifying trace metals, such as spectroscopic methods especially graphite furnace atomic adsorption spectroscopy (GF–AAS) and inductively coupled plasma mass spectroscopy (ICP–MS). These methods have excellent sensitivities and good selectivities, but they also have various drawbacks such as time consuming and high cost of instrument are required.

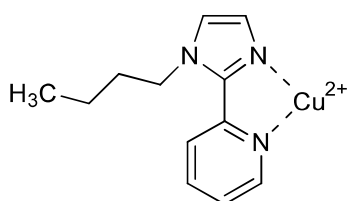
Electrochemical methods including anodic stripping voltammetry (ASV), and adsorptive cathodic stripping voltammetry (AdCSV) have shown different advantages such as faster analysis, higher selectivity and sensitivity, low cost, easy operation, and speciation analysis.

ASV, one of stripping voltammetry which is most widely used for determination of trace metals and speciation, consists of two steps: preconcentration step, trace metal ions in solution are accumulated on the working electrode surface by electro deposition at appropriate time, and stripping step (measurement), trace metal ion are stripped out from the working electrode surface into solution during an appropriate potential scan.

In recent years, because of these advantageous, there has been a growing interest in the use of chemically modified

electrodes (CME) for the great sensitivity enhancement obtained with the stripping voltammetric method. Several complexing agents have been studied for the adsorptive collection of complexes with copper ions.

The aim of this work was to develop a simple, and sensitive system for determination of Cu(II) ions by stripping voltammetry on glassy carbon electrode (GCE) surface modified with electrochemical oxidation of pyridine–imidazole ligand.



**Figure 1.** Structures of 2-(1-butyl-1*H*-imidazol-2-yl)pyridine (Py–Im)

2-(1-butyl-1*H*-imidazol-2-yl)pyridine (Py–Im) has two nitrogen atoms thus, it has been used to chelate heavy metal ions.<sup>4</sup> The Py–Im ligand showed excellent selectivity towards Cu(II) ions. Therefore, in this work, Py–Im-modified glassy carbon electrode it was used as an environmentally-friendly electrode to determine trace amounts of heavy metals (Cu(II)).

## 2. Materials and Methods

### 2.1 Materials

The reagents used for the synthesis of Py–Im derivative were an analytical reagent (AR) grade, purchased from Sigma–Aldrich Co., Ltd. and used without further purification. DMF was distilled from CaH<sub>2</sub> and stored over 4 Å molecular sieves. Copper(II) acetate monohydrate was purchased from Loba Chemie (Mumbai, India). Glacial acetic acid (100%) and hydrochloric acid fuming (37%) were purchased from Merck (Darmstadt,

Germany). Sodium acetate trihydrate was purchased from Ajax Finechem (New South Wales, Australia). All chemicals were used of analytical grade and were prepared in 18.2 MΩ cm<sup>-1</sup> distilled water. Chloroform-*d* (CDCl<sub>3</sub>) for NMR characterization was purchased from Sigma–Aldrich Co., Ltd. Thin layer chromatography (TLC) was purchased on Merck silica gel 60 F<sub>254</sub> aluminum sheets. Column chromatography was performed using Merck silica gel 60 (70–230 mesh.). NMR spectra were recorded on Bruker DPX–300 (300 MHz).

### 2.2 Apparatus

All electrochemical measurements were performed using Autolab/PGSTAT204 with FAR module potentiostat/ galvanostat (Metrohm Autolab B.V., KM Utrecht, The Netherlands) with the NOVA version 1.8 software connected to a computer. The three electrode systems consisted of a Py–Im modified glassy carbon electrode (GCE, 3.0 mm) as a working electrode, an Ag/AgCl as a reference electrode and a platinum wire as a counter electrode.

### 2.3 Synthesis of 2-(1-butyl-1*H*-imidazol-2-yl)pyridine (Py–Im)

A cold solution of 2-pyridine carboxaldehyde (100 mmol, 10 g) in ethanol (10 mL) was added to a cold solution of 40% aqueous glyoxal (20 mL) in ethanol (20 mL), and then cold concentrated aqueous NH<sub>3</sub> (10 mL) was added without delay. The reaction was stirred at 0 °C for 1 h, and the solution was then warmed up to room temperature for 8 h. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 15 mL), and dried with Na<sub>2</sub>SO<sub>4</sub>. The combined organic phase was concentrated under vacuum. The crude product was purified by column chromatography to afford the colourless solid 7.12 g (49%). The next step is alkylation reaction by mixing 2-(1-butyl-1*H*-imidazol-2-yl) pyridine (5 g, 34 mmol), butyl iodide (7.5 mL, 68 mmol), and KOH (11.6 g, 207 mmol) in DMF (20 ml). The reaction was

stirred at room temperature for overnight, 4.58 g (67%) of pale–yellow liquid was obtained.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.53–7.56 (m, 2H), 7.35–7.47 (m, 3H), 7.11 (d, 1H,  $J = 1.1$  Hz), 6.99 (d, 1H,  $J = 1.2$  Hz), 3.97 (t, 2H,  $J = 7.4$  Hz), 1.69–1.72 (m, 2H), 1.23–1.26 (m, 2H), 0.85 (t, 3H,  $J = 7.3$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  147.7, 131.1, 128.9, 128.6, 128.5, 128.4, 120.3, 46.5, 33.1, 19.7, 13.5.

#### 2.4 Fabrication of a Py–Im modified glassy carbon electrode (Py–Im/GCE)

GCE was polished with 1.5, 0.5, and 0.05  $\mu\text{m}$  alumina powder, rinsed with deionized water and dried in room temperature. The Py–Im/GCE was prepared by cyclic voltammetry, fifteen cycles of the potential sweep between +1.4 and –1.4 V were performed at a scan rate of 0.10  $\text{V s}^{-1}$  in a 10 mM Py–Im in 0.10 M HCl. Py–Im/GCE was then washed with water and dried at room temperature.

#### 2.5 Electrochemical measurement

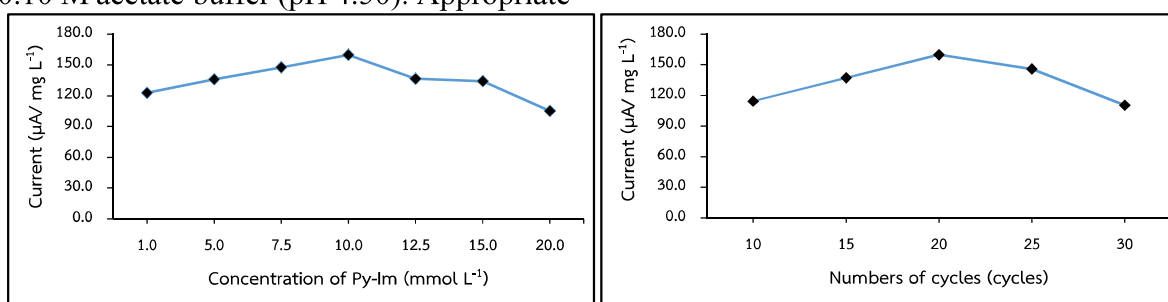
ASV measurement was performed in 0.10 M acetate buffer (pH 4.50). Appropriate

amounts of Cu(II) in two steps. The first step, accumulation, was carried out at –1.20 V for 60 s under stirring. Following the accumulation period, the stirring was stopped and after a 5 s equilibrium time. In the second step, stripping, the potential was scanned linearly from –0.20 to –1.20 V at 100 mV/s while the voltammogram was recorded.

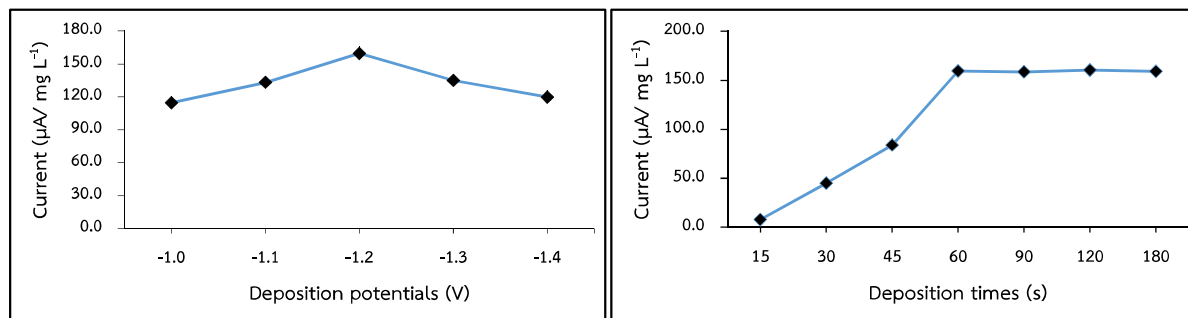
### 3. Results & Discussion

#### 3.1 Optimization of electrode modification

The effects of Py–Im concentration and numbers of cycles for the fabrication of the Py–Im film formation on the GCE surface were studied. The concentrations of Py–Im were investigated from 1.0 to 20.0 mM (Figure 2. (a)). When tested with Cu(II) the sensitivity of Cu(II) detection by the Py–Im/GCE initially increased with concentration from 1.0 to 10.0 mM, and then decreased when the concentrations of Py–Im more than 10.0 mM. This was probably because the Py–Im on GCE surface become too thick<sup>5</sup> and blocked the electron transfer.<sup>6</sup> Therefore, 10.0 mM of Py–Im was chosen for further study.



**Figure 2.** Effect of Py–Im concentration (a) and numbers of cycles for the fabrication of the Py–Im film formation on the GCE surface (b). The sensitivity is slope of the calibration curve at the concentration of Cu(II) between 0.05 and 0.5  $\text{mg L}^{-1}$ . (ASV operation conditions: 60 s preconcentration time, –1.20 V preconcentration potential, and square-wave potential scan between –1.20 and 0.20 V)



**Figure 3.** The effect of preconcentration potential (a) on the sensitivity of Cu(II) on the Py–Im/GCE and effect of preconcentration time (b) on the sensitivity of Cu(II) on the Py–Im/GCE. The sensitivity is slope of the calibration curve at the concentration of Cu(II) between 0.05 and 0.5 mg L<sup>-1</sup>. (ASV operation conditions: –1.20 V preconcentration potential and square-wave potential scan between –1.20 and 0.20 V)

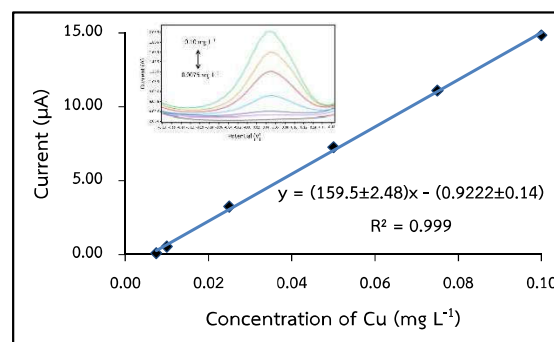
The numbers of cycles for the fabrication of the Py–Im film formation on the GCE surface were investigated from 10 to 30 cycles (Figure 2. (b)). When tested with Cu(II) the sensitivity of Cu(II) detection by the Py–Im/GCE initially increased with the numbers of cycles for the fabrication of the Py–Im film formation on the GCE surface 10 to 20 cycles.

This phenomenon indicated that the thickness of the Py–Im film on the GCE surface increased as the numbers of cycles increased. When the numbers of cycles higher than 20 cycles, the sensitivity of Cu(II) detection decreased which may be due to the Py–Im film at GCE surface becoming too thick. This caused inhibition of electron transfer on the surface. Therefore, the numbers of cycles chosen for further study was 20.

### 3.2 Effect of preconcentration potential, and preconcentration time

The effect of preconcentration potential was studied from –1.00 to –1.40 V (Figure 3. (a)). When tested with Cu(II) the sensitivity of Cu(II) detection by the Py–Im/GCE initially increased with the preconcentration potential from –1.00 to –1.20 V. Because at more negative deposition potentials, Cu(II) is reduced more completely.<sup>7</sup> However, when the

preconcentration potentials were more than –1.20 V, the sensitivity of Cu(II) detection decreased, because of the hydrogen evolution at the working electrode. Therefore, a preconcentration potential at –1.20 V was selected for further study. The effect of preconcentration time was studied from 15 to 180 s (Figure 3. (b)). When tested with Cu(II) the sensitivity of Cu(II) detection by the Py–Im/GCE initially increased with the preconcentration time from 15 to 60 s, and then constant or slightly changed, probably due to saturation of the electrode surface.<sup>8</sup>



**Figure 4.** The calibration curve between the anodic peak current and the concentration of Cu(II) in the range from 0.0075 to 0.10 mg L<sup>-1</sup>. The inset shows the anodic stripping voltammograms of Cu(II).

Therefore, 60 s of the preconcentration time was selected for further study.

### 3.3 Calibration curve, detection limit (LOD), and quantitation limit (LOQ)

The analytical performance of the Py–Im/GCE was studied between 0.0075 and 0.50 mg L<sup>-1</sup> under optimum conditions. The plot between the anodic peak currents and Cu(II) concentrations showed two linear ranges with different sensitivities, i.e., from 0.0075 to 0.10 mg L<sup>-1</sup> and 0.10 to 0.50 mg L<sup>-1</sup> (Figure 4). LOD was calculated from 3Sa/b and the LOQ from 10Sa/b where Sa is the standard deviation of the intercept and b is the slope of the calibration curve<sup>9</sup> and was calculated as 0.003 mg L<sup>-1</sup> and 0.009 mg L<sup>-1</sup>, respectively.

### 4. Conclusions

In this study, the Py–Im ligand was successfully synthesized for determination of Cu(II) by the formation of Cu<sup>2+</sup>–L<sub>(Py–Im)</sub> complexes. The Py–Im can be used as a modifier on glassy carbon electrode for Cu(II) detection by ASV. It provided high sensitivity and low detection limit. Moreover, the Py–Im/GCE electrode is environmentally friendly electrode. This proposed method could possibly be applied to determine of Cu(II) in food, soil, and serum.

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