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Voltammetric Determination of Copper and Zinc in Water using a Ruthenium Bipyridyl/Nafion-modified Indium Tin Oxide-coated Glass Electrode

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Abstract: *Chemically-modified Indium Tin Oxide (ITO) coated glass substrates were fabricated by depositing Nafion thin films doped with tris (2,2'-bipyridyl) ruthenium(II) dichloride hexahydrate via drop coating deposition technique. The Nafion volume concentration in the film is 1% (v/v) and the mediator concentration is 5 mg per 1 mL Nafion. The chemically-modified electrodes were characterized by cyclic voltammetry (CV) and were used as working electrodes to detect varying concentrations of copper (Cu^{2+}) and zinc (Zn^{2+}) in a 0.1 M NaCl supporting electrolyte solution via Anodic Stripping Voltammetry (ASV). Cu^{2+} and Zn^{2+} ions were successfully determined by ASV. The limits of detection for Cu^{2+} and Zn^{2+} were 0.1 ppm and 0.7 ppm, respectively. The modified electrodes were used to determine the presence of Cu^{2+} and Zn^{2+} in different real water samples. The presence of Cu^{2+} was successfully determined in deep well, lake, and tap water samples, while the presence of Zn^{2+} was successfully determined in sea and tap water samples. Atomic Absorption Spectroscopy (AAS) results confirm the presence of Cu^{2+} and Zn^{2+} in the samples.*

Keywords: Nafion, Ruthenium bipyridyl, Indium Tin Oxide, Anodic Stripping Voltammetry, Copper, Zinc

1. INTRODUCTION

One of the many environmental issues faced by many developing countries is water pollution, especially the one caused by trace metals. Trace metals of different kinds from varying sources eventually seep into different bodies of water, causing different forms of harm on biota. Certain transition metals such as lead (Pb) and arsenic (As) are lethal to the human health when ingested by the body. The tiniest amounts of lead can severely harm the body in many ways, especially the nervous system [1]. Arsenic causes different types of cancer to humans when ingested from contaminated water and food [2]. While other trace metals such as copper (Cu) and zinc (Zn) are essential to the human body and living organisms, these very same metals become hazardous to living organisms when ingested in excess quantities. Copper is important for structural and catalytic properties of various enzymes for different biological processes [3]. The human body can tolerate up to 10 mg of copper on a daily basis [4]. However, when copper is consumed in excessive quantities, this leads to different neurological disorders, such as Wilson's disease, which is a genetic disorder of the liver involving the abnormal metabolism of copper [5]. Zinc is another vital nutrient for various bodily enzymes [6]. The human body can tolerate up to 12-15 mg of zinc on a daily basis [7]. However, zinc consumed in excessive quantities is toxic to brain cells [8]. Determining and quantifying the presence of these metals in water is important to determine its safety for consumption.

Different trace metal analysis techniques such as Atomic Absorption Spectroscopy (AAS) [9,10] and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) [11,12] and Anodic Stripping Voltammetry (ASV) [9-14] were used to determine the presence of these metals in water. ASV is the most recommended technique for the determination of Cu^{2+} and Zn^{2+} in this study. It is because the other electrochemical techniques are relatively costly, have higher limits of detection, can only be performed inside a laboratory, and usually require complicated methodologies [13]. Unlike other detection methods, ASV is low in cost, highly sensitive [13], relatively easier to perform, more accurate, and is relatively more convenient in performing trace metal analysis [14].

ASV involves the accumulation of metal ions onto the electrode

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surface from the solution at a negative potential and then the stripping of the metal ions back to the solution with gradual potential increase [15]. In a typical ASV experiment, the most commonly used working electrode, where the metal ions are accumulated during the deposition step, is the Hanging Mercury Drop Electrode due to its wide potential window towards negative values [10]. However, its use was restricted since mercury poses various hazards to living organisms and their surrounding environment [16]. In this study, the working electrode was Indium Tin Oxide (ITO) modified with Ruthenium bipyridyl-doped Nafion or $[Ru(bpy)_3]^{2+}$/Nafion. Nafion is an ion-exchange polymer that has both hydrophilic (sulfonic acid) and hydrophobic (tetrafluoroethylene) sections [17]. Nafion is also known for its inertness, good chemical stability, and excellent proton conductivity [18]. Because of its excellent proton conductivity, Nafion has been used in heavy metal sensor applications [19,20]. Also, doping Nafion with a redox mediator such as hexaamineruthenium $[Ru(NH_3)_6]^{3+}$ or tris(2,2'-bipyridyl)ruthenium $[Ru(bpy)_3]^{2+}$ or with a nanomaterial such as graphene or carbon nanotubes enhances electrode sensitivity by accelerating electron transfer processes that would otherwise proceed slowly with bare electrodes [21-23]. $[Ru(bpy)_3]^{2+}$ is an organometallic compound that facilitates electron transfer processes in its excited state [24]. The redox mediator that is immobilized in a polymer membrane bridges the gap between the electrode surface and the analyte [25]. This results to the enhancement of the sensitivity and the stability of the working electrode.The drop-coating deposition technique works by depositing the coating solution onto the substrate in incremental amounts and allowing them to evaporate to form thin films [26]. This technique is a straightforward process and does not require any specific piece of equipment [27].

Sensitivity is an indication of an instrument's response to small changes in analyte concentration, which is influenced by the slope of the calibration curve and the instrument's precision [28]. The two types of sensitivity are calibration sensitivity and analytical sensitivity. Calibration sensitivity is dependent on the slope of the calibration curve of the analyte; a steeper slope means higher calibration sensitivity [28]. Analytical sensitivity is dependent on the precision of the instrument. Assuming equal calibration curve slopes, a higher precision of measurements points out to higher analytical sensitivity [28].

In this study, $[Ru(bpy)_3]^{2+}$-modified Nafion was deposited onto Indium Tin Oxide (ITO) glass substrates via drop coating deposition method. The modified electrodes were used for the sequential determination of copper (Cu^{2+}) and zinc (Zn^{2+}) at varying concentrations. The modified electrodes were also used to determine the presence of Cu^{2+} and Zn^{2+} in deep well, lake, sea, and tap water samples.

2. EXPERIMENTAL

2.1. Reagents and solutions

Nafion solution (10%) was purchased from Fuel Cell Earth (Wakefield, MA, USA). Tris(2,2'-bipyridyl)ruthenium(II) $[Ru(bpy)_3]^{2+}$ dichloride was purchased from Sigma-Aldrich (Sigma-Aldrich Pte Ltd, Singapore). Laboratory-grade heavy metals, Copper(II) chloride was purchased from Sigma-Aldrich, Zinc(II) chloride and Sodium chloride were purchased from Uni-Chem Chemical Reagents (Strahinjića Bana 44, 11000 Beograd, Serbia). Stock solutions of heavy metals were prepared with deionized distilled water.

2.2. Instruments

BOSCH SAE200 electronic balance (BOSCH-Wägesysteme GmbH, Jungingen, Germany) was used to weigh 2.5 mg $[Ru(bpy)_3]^{2+}$ and 0.584 g of NaCl. A Transferpette®S micropipette was used to transfer incremental amounts of the casting solution onto the surface of ITO substrates (Sigma-Aldrich Pte Ltd., Singapore). All glasswares were put in BANDELIN SONOREX ultrasonic bath (BANDELIN electronic GmbH & Co. KG, Berlin, Germany) for cleaning. BST8-STAT potentiostat/galvanostat (MTI Corporation, Richmond, CA, USA) was used in the ASV set-up to obtain voltammograms.

2.3. Preparation of substrates

ITO substrates (7.5 cm x 2.5 cm) were cut into 1.0 cm x 2.5 cm strips using a diamond glass cutter for electrode fabrication. The newly cut strips were then sonicated in acetone and ethanol for 5 minutes.

2.4. Preparation of casting solution

A stock solution of the casting solution was prepared by adding 2.5 mg of tris(2,2'-bipyridyl) ruthenium(II) dichloride hexahydrate powder and 0.5 mL of 10% Nafion solution. The two substances were mixed with 4.5 mL methanol. The resulting solution was then sonicated for 30 minutes.

2.5. Fabrication procedure

From the stock casting solution, 100 µL of the prepared solution was pipetted onto the surface of the ITO substrates. The substrates were then dried in an ambient temperature for 12 hours.

2.6. Voltammetric procedure

The three-electrode set-up was used in this study with the Nafion/$[Ru(bpy)_3]^{2+}$-modified ITO glass electrode was used as the working electrode, the Saturated Calomel Electrode (SCE) as the reference electrode, and the Platinum coil electrode as the counter electrode. The voltammetry cell was filled with 100 mL of 0.1 M NaCl solution. The heavy metal samples were added to the electrolyte solution. The supporting electrolyte solution was stirred with a ceramic magnetic stirring bar and was sparged with nitrogen gas. Sequential determination of Cu^{2+} and Zn^{2+} was performed at ten different concentrations starting from 0.1 ppm and 0.7 ppm, respectively. In every voltammetry experiment, a potential of +1.0 V was applied for 60.0 s for the cleaning step, -1.1 V for another 60.0 s for the deposition step. The stirring was then stopped and the potential was maintained for 15.0 s for the equilibration step, and then ramped to +0.5 V for 16.1 s for the stripping step.

2.7. Real Sample Analysis

Four different water samples were obtained from different locations: the deep well water was obtained from Laguna; the sea water was obtained from the shore of Manila Bay; the lake water was obtained near the shore of Laguna de Bay; the tap water was obtained from the Condensed Matter Laboratory. From each water sample, 100 mL of the water sample was obtained, added with 0.5844 g NaCl, and then used for ASV analysis.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

The newly fabricated ITO electrodes were characterized using cyclic voltammetry (CV). The cyclic voltammetric scanning of the modified ITO electrodes was performed in ten continuous cycles.

During the entire 10-scan cycle, it can be observed that the oxidation and reduction peak currents were close with each other (Fig. 1). This implies that the electrode is stable. The electrode's calculated reversibility was 0.64. This demonstrates the success of electron transport due to the presence of the redox mediator $[Ru(bpy)_3]^{2+}$. The presence of a redox mediator facilitates electron transfer processes from the analyte of interest towards the electrode surface. Thus, electrons can easily transfer from the substrate to the electrolyte and vice-versa.

3.2. Anodic Stripping Voltammetry

Each metal was sequentially detected using anodic stripping voltammetry (ASV) to obtain their limits of detection and calibration curves. The voltammograms (Figs. 2 and 4) were obtained by performing five voltammetric scans and getting the average of the five trials. The calibration curves (Figs. 3 and 5) were obtained by plotting the maximum reduction currents against the concentrations of the heavy metals.

Anodic stripping voltammetry experiments were successful in determining the presence of both Cu^{2+} and Zn^{2+} in 0.1 M NaCl electrolyte solution. The limits of detection for Cu^{2+} and Zn^{2+} were 0.1 ppm and 0.7 ppm, respectively. The Pearson correlation coefficients (R^2) of copper and zinc were observed to be close to 1, which is indicative of a linear relationship between the reduction current and the heavy metal concentration.

3.3. Sensitivity

Table 1 displays the calibration sensitivity of the modified electrode towards copper and zinc in terms of Amperes per part-per-million. The calibration curve of copper was observed to be steeper than that of zinc. So the calibration sensitivity of the modified electrode towards copper is higher than that towards zinc. This implies that the modified electrode has a more sensitive response to copper than to zinc.

Table 2 displays the analytical sensitivity of the modified electrode towards different concentrations of Cu^{2+} and Zn^{2+}. No trend was observed in the analytical sensitivity of the modified electrode with increasing analyte concentrations. However, at each analyte concentration, the analytical sensitivity of the modified electrode towards copper at different concentrations tends to be greater than that towards zinc at different concentrations. This implies that the modified electrode has higher analytical sensitivity towards copper than that towards zinc.

3.4. Real Samples Analysis

The modified electrodes were used as working electrodes to determine the presence of Cu^{2+} and Zn^{2+} in deep well, lake, sea, and tap water samples using ASV. The presence of Cu^{2+} was successfully determined in deep well, lake, and tap water samples, while the presence of Zn^{2+} was successfully determined in sea and tap water samples. The determination of Cu^{2+} and Zn^{2+} in environmental water samples proved to be difficult because of the presence of contaminants that accumulate onto the electrode surface, which

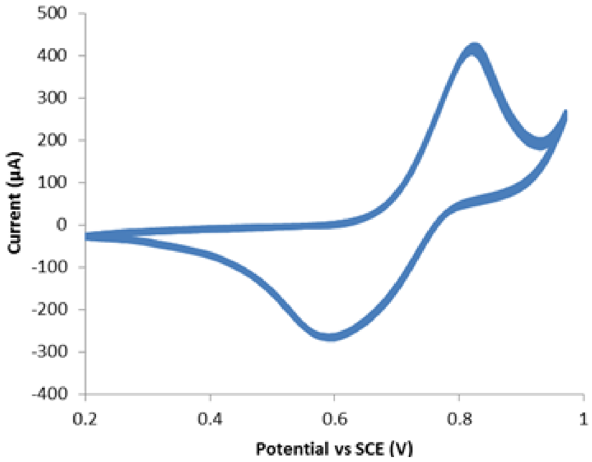

Figure 1. Cyclic voltammograms of Nafion/$[Ru(bpy)_3]^{2+}$-modified ITO electrodes

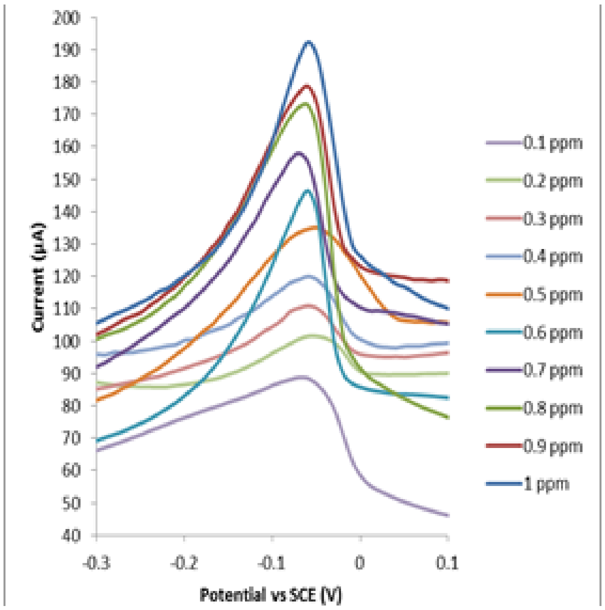

Figure 2. Voltammograms of different concentrations of copper at a 0.1 M NaCl supporting electrolyte

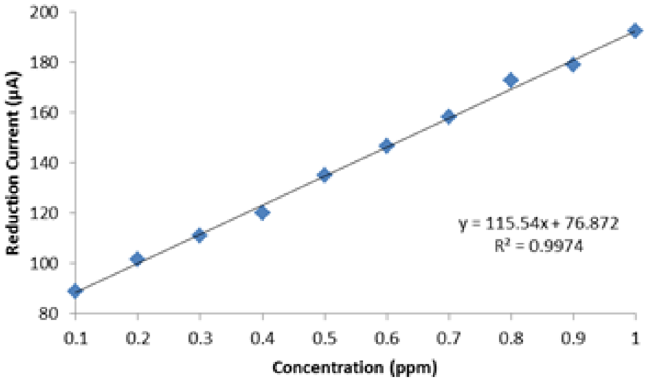

Figure 3. Calibration curve of different concentrations of copper at a 0.1 M NaCl supporting electrolyte

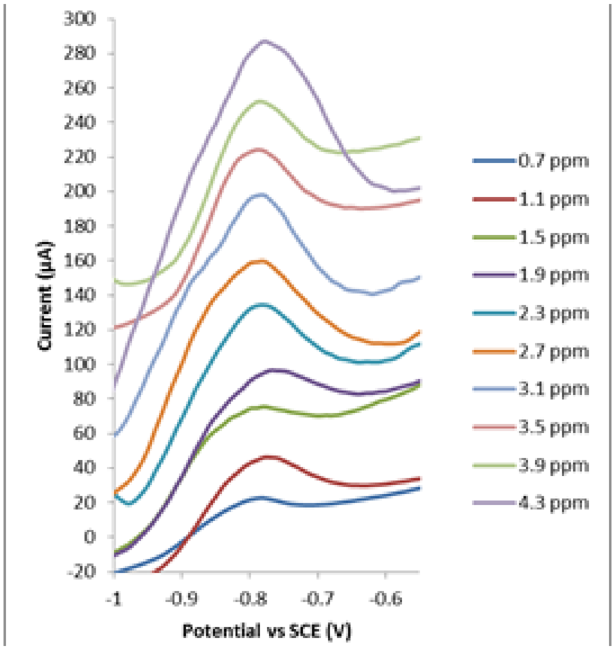

Figure 4. Voltammograms of different concentrations of zinc at a 0.1 M NaCl supporting electrolyte

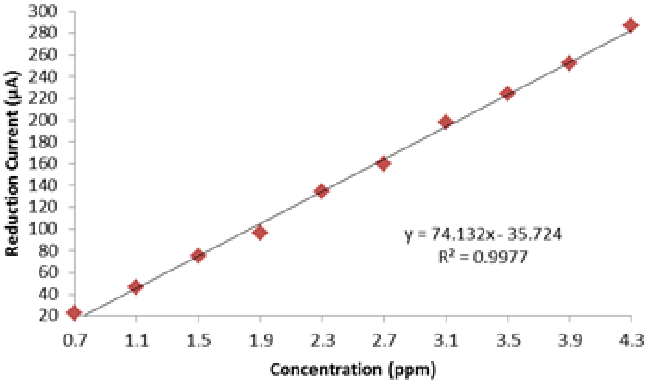

Figure 5. Calibration curve of different concentrations of zinc at a 0.1 M NaCl supporting electrolyte

interferes with the stripping process of the metal ions from the electrode surface back into the solution.

Both Cu^{2+} and Zn^{2+} are susceptible to forming intermetallic bonds with each other and with other metals, with Zn^{2+} having the higher likelihood of forming intermetallic and organometallic bonds with other atoms. Additionally, the water samples were not freshly obtained and some of the heavy metals had already settled to the bottom of the container, hence, the sample was no longer homogeneous.

Table 3 shows the calculated concentrations of Cu^{2+} and Zn^{2+} based on the equation of the line from the calibration curve. The concentrations of the trace metals were calculated using the peak currents, the slope of the calibration curve, and its y-intercept.

Table 4 shows the Cu^{2+} and Zn^{2+} concentrations of the different water samples obtained by AAS. Both Cu^{2+} and Zn^{2+} ions were observed to be present in all water samples. However, the concentrations of Cu^{2+} in sea water and of Zn^{2+} in deep well and lake water samples were below the electrode's limit of detection. Thus, the presence of Cu^{2+} was confirmed only in deep well, lake, and tap water samples and the presence of Zn^{2+} was confirmed only in sea and tap water samples.

Table 1. Calibration Sensitivity of the modified electrode towards copper and zinc

Trace Metal	Calibration Sensitivity (A/ppm)
Cu^{2+}	0.0001
Zn^{2+}	0.00007

Table 2. Analytical Sensitivity of the modified electrode towards different copper and zinc concentrations

Concentration (ppm)		Analytical Sensitivity (A/ppm)	
Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}
0.1	0.7	27.93	35.71
0.2	1.1	56.50	11.53
0.3	1.5	67.11	31.67
0.4	1.9	66.67	2.31
0.5	2.3	4.24	3.78
0.6	2.7	48.08	13.23
0.7	3.1	100.00	1.89
0.8	3.5	4.74	12.94
0.9	3.9	4.98	13.81
1	4.3	28.49	16.06

Table 3. Calculated Concentrations of Cu^{2+} and Zn^{2+} based on the ASV calibration curve

Water Sample	Peak Current (μA)		Concentration (ppm)	
	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}
Deep Well	4.7691 ± 0.5315	-	0.6241	-
Lake	24.8776 ± 3.0746	-	0.4500	-
Sea	-	17.2772 ± 8.1735	-	0.7150
Tap	15.0052 ± 0.7780	-1.3511 ± 2.4747	0.5355	0.4637

Table 4. Cu^{2+} and Zn^{2+} AAS concentrations in different water samples

Water Sample	Cu^{2+} Concentration (ppm)	Zn^{2+} Concentration (ppm)
Deep Well	0.3077	0.3042
Lake	0.3548	0.4254
Sea	0.0396	2.4609
Tap	0.1713	18.2716

4. CONCLUSIONS

In this study, the deposition of Nafion/[Ru(bpy)$_3$]$^{2+}$ thin films on ITO glass electrodes via drop coating deposition technique were proven to be successful. The fabricated electrodes were successfully able to detect Cu^{2+} and Zn^{2+} ions in a 0.1 M NaCl solution via anodic stripping voltammetry. The heavy metal concentration and the reduction current displayed a linear correlation with each other. The lowest amount of copper and zinc that can be detected by the fabricated electrode was 0.1 ppm and 0.7 ppm, respectively. The modified electrodes were successful in determining the presence of Cu^{2+} in deep well, lake, and tap water samples, and the presence of Zn^{2+} in sea and tap water samples.

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