

# Determination of Cadmium ( $\text{Cd}^{2+}$ ) and Zinc ( $\text{Zn}^{2+}$ ) via Anodic Stripping Voltammetry with $[\text{Ru}(\text{NH}_3)_6]^{3+}$ /Nafion<sup>®</sup> Modified Electrodes

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Indium tin oxide (ITO) substrates were modified with  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ -doped Nafion<sup>®</sup> thin film using the drop-coating method. The redox mediator was successfully immobilized within the thin film. The modified electrodes were used to detect cadmium and zinc ions in de-ionized water via anodic stripping voltammetry (ASV). The effect of varying the concentration of the mediator  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  on the signals from the heavy metal was also studied. Redox mediator concentration was varied to control the properties of the modified electrodes. Different concentrations of the heavy metal were tested using ASV. The conducting properties of ITO electrodes were enhanced with the deposition of Nafion<sup>®</sup> attaining minimal interference. The ASV tests yielded higher oxidation current peaks for the modified electrodes in contrast to unmodified electrodes. The oxidation peaks increased monotonically with the concentration of immobilized mediator.

## KEYWORDS

Nafion<sup>®</sup>, Drop Coating, Anodic Stripping Voltammetry, Heavy Metal, Electrochemistry

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## INTRODUCTION

Trace elements of some heavy metals (HMs) play a very important role in human nutrition. Some are beneficial at low concentrations, but are lethal at high concentrations (Aragay and Merkoçi 2012). Cadmium is a heavy metal that is widely distributed and used in various industries; zinc is a vital element in human nutrition. Although these elements are naturally occurring and are essential in human life, they are potentially very toxic (Esmacili et al. 2014, Wang et al. 2013). Concerns about their long-term exposure and toxic effects on human health have increased with increasing industrial use and the associated environmental pollution (OmPrakash et al. 2011).

Heavy metals and their ions by definition are metals having atomic weights between 63.5 and 200.6  $\text{g mol}^{-1}$  and a specific gravity greater than 5  $\text{g cm}^{-3}$  (Zhu et al. 2012). In recent years, the heavy metal contamination of water sources have posed serious impacts on the environment and human health. Industry, traffic and even domestic waste are sources of heavy-metal contaminations that pollute the soil, water and atmosphere (Morton-Bermea et al. 2009, Meng et al. 2008). It is therefore necessary to be able to accurately and closely monitor the concentrations of various heavy metals especially in water sources because of the adverse effects they have on human health and the environment.

Although numerous methods are already established for detecting heavy metals, such as atomic absorption spectroscopy, atomic emission spectroscopy, mass spectroscopy and x-ray fluorescence spectroscopy (Ghica et al. 2009, Xu et al. 2008),

electrochemical techniques are sometimes preferred over spectroscopic techniques due to some advantages related to their cost, simplicity and the possibility of on-site application (Aragay and Merkoçi 2012, Kim et al. 2013, Kang et al. 2014). Anodic stripping voltammetry (ASV) is a very sensitive electroanalytical method (Settle 1997). ASV costs less than spectroscopic methods and the miniaturization allows in situ monitoring. ASV samples also require minimal pre-treatment and are generally unaffected by high salt content. The limitation of using ASV, however, is the limited number of metals it can detect when using a mercury-based working electrode. The aim of this work was to fabricate an indium tin oxide (ITO)-based modified electrode for the detection of cadmium and zinc ions.

A redox mediator is often used in reactions of compounds that react very slowly with the bare electrodes, thus resulting in low detection capabilities. It serves as an intermediate oxidizing/reducing agent that acts as a center for the hopping of electrons from the bulk solution to the electrode and vice versa as it switches from its two states as given by the reaction  $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+} + e^- \leftrightarrow [\text{Ru}^{\text{II}}(\text{NH}_3)_6]^{2+}$ .

## MATERIALS AND METHODS

Nafion<sup>®</sup> modified electrodes was fabricated via the drop-coating technique. The concentration  $\text{Ru}(\text{NH}_3)_6^{3+}$  redox mediator was varied at 5 mg, 10 mg, and 15 mg. The modified electrodes were used as the working electrodes for the electrochemical detection of cadmium ( $\text{Cd}^{2+}$ ) and zinc ( $\text{Zn}^{2+}$ ) in an analyte solution.

### Materials

Nafion<sup>®</sup> at 5% w solution was obtained from Fuel Cell Earth (Wakefield, Massachusetts, United States). Hexaammineruthenium(III) Chloride (98%) and ITO-coated rectangular glass slides with surface resistivity  $15\text{-}25 \Omega \text{ sq.}^{-1}$ ,  $\text{ZnCl}_2$  and  $\text{CdCl}_2$  powder were obtained from Aldrich (St Louis, Missouri, United States). All other chemicals and reagents used in the research were reagent-grade quality.

### Preparation of Substrates and Coating Solution

ITO substrates were cut to dimensions of 2.5 cm x 1.0 cm using a glass cutter. The substrates were then sonicated in ace-

tone and methanol for 10 minutes. Substrates were left to be air dried in a petri dish and was immediately used for drop coating.

The three concentrations of mediator were achieved by first preparing 5 mg, 10 mg, and 15 mg of  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ , carefully measured using a BOSCH SAE200 electronic balance. Each of the three masses was then dissolved in 6 mL of deionized water. 20  $\mu\text{L}$  of each solution were obtained using a Transferpette<sup>®</sup>S micropipette and mixed with 20  $\mu\text{L}$  of 5 wt% Nafion<sup>®</sup>, then diluted with 1.0 mL methanol in separate containers.

### Fabrication

Drop coating was carried out using the Transferpette<sup>®</sup>S micropipette. The solutions were systemically dropped to cover the ITO substrates and were air dried at an ambient temperature of  $26^\circ\text{C} \pm 1^\circ\text{C}$  for 24 hours.

### Anodic Stripping Voltammetry

The fabricated modified electrodes were used as the working electrodes for the three-electrode setup. The heavy metal concentration was varied at 100 ppm, 200 ppm, and 300 ppm to obtain the calibration curves. A fresh electrode was used for every set of runs.

The potential was held at  $-1.40\text{V}$  for 2 minutes during the preconcentration stage, with continuous stirring using a magnetic stirrer. The potential sweep for the stripping stage was ran from a potential of  $-1.4\text{V}$  to  $+0.2\text{V}$ . The cell potential was then sustained at  $+3.0\text{V}$  for 30 seconds to strip off any metal that had been previously adsorbed.

## RESULTS AND DISCUSSION

Results from the ASV (see Figures) show that the signals from both cadmium ( $\text{Cd}^{2+}$ ) and zinc ( $\text{Zn}^{2+}$ ) increased linearly with concentration. The linearity of the calibration curves obtained for the three electrodes yielded correlation values ( $r$ ) close to 1. Results were also obtained from getting the averages of three trials on the electrode coated with the three concentrations of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ -doped Nafion<sup>®</sup> casting solution. Peak currents were obtained at the potentials, against a calomel electrode, between  $-0.7\text{V}$  and  $-0.6\text{V}$ , which is characteristic for cadmium ( $\text{Cd}^{2+}$ ); and  $-0.84\text{V}$  to  $-0.80\text{V}$ , which is characteristic for zinc ( $\text{Zn}^{2+}$ ).

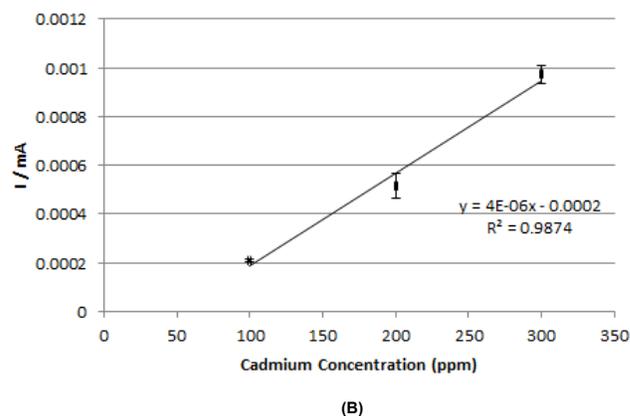
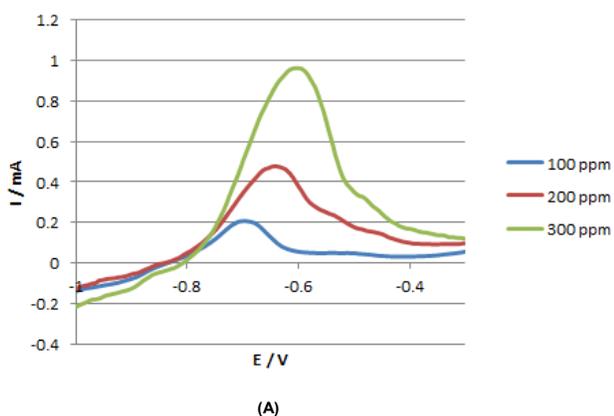


Figure 1. (A) Voltammogram and (B) calibration curve for cadmium for the 5mg  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  electrodes

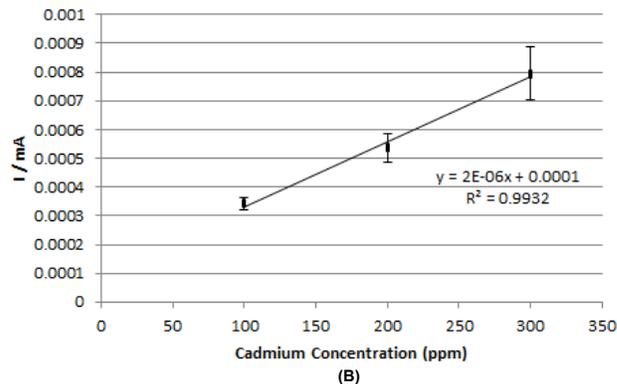
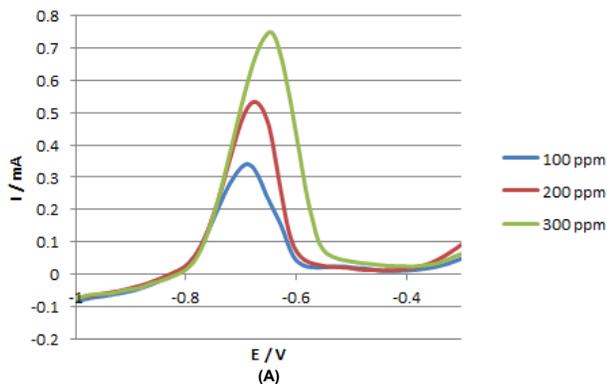


Figure 2. (A) Voltammogram and (B) calibration curve for cadmium for the 10mg  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  electrodes

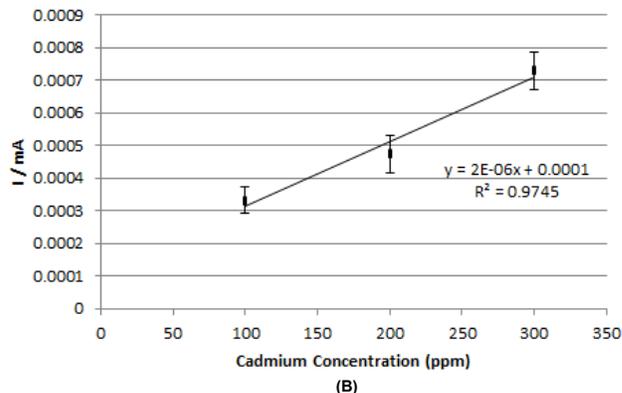
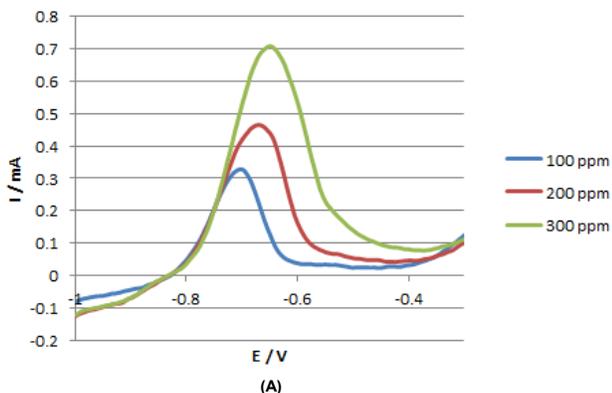


Figure 3. (A) Voltammogram and (B) calibration curve for cadmium for the 15mg  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  electrodes

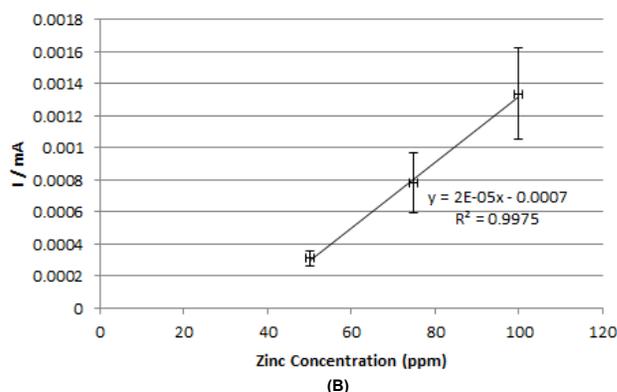
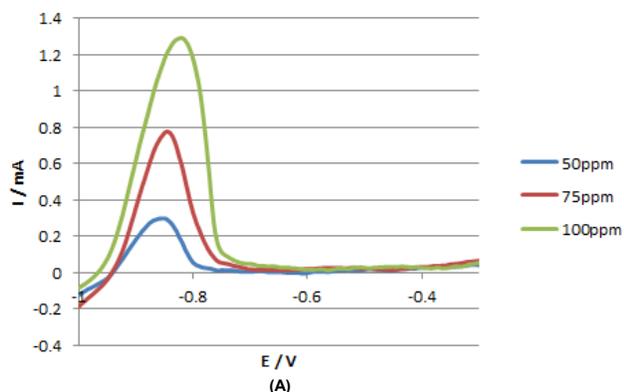


Figure 4. (A) Voltammogram and (B) calibration curve for zinc for the 5mg  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  electrodes

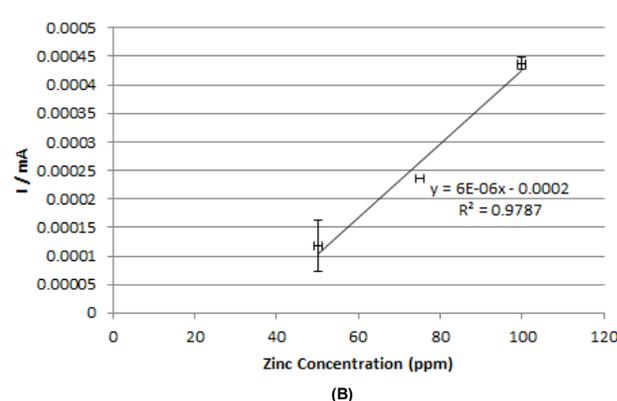
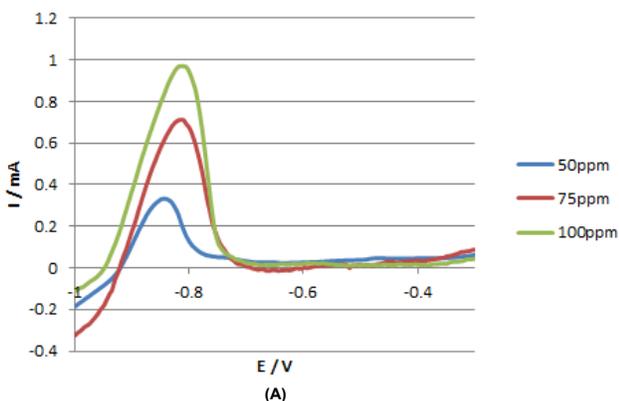
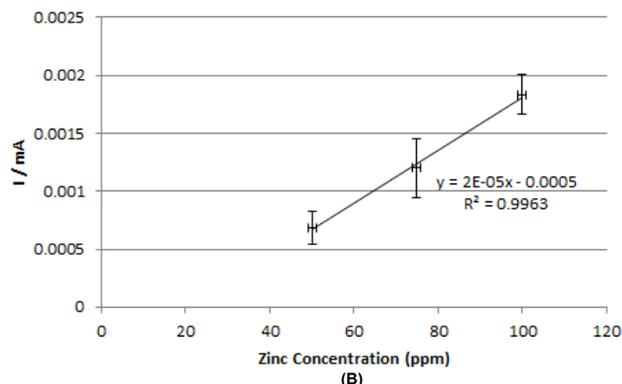
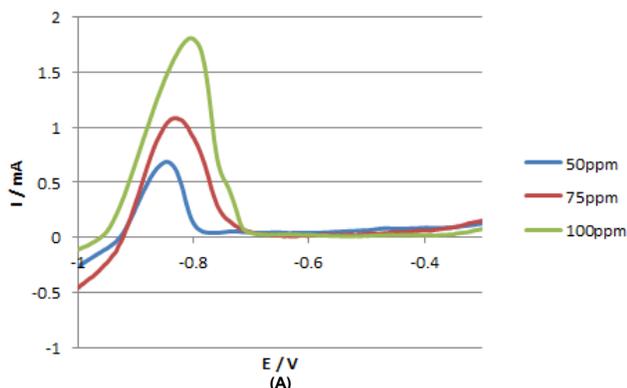


Figure 5. (A) Voltammogram and (B) calibration curve for zinc for the 10mg  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  electrodes



**Figure 6.** (A) Voltammogram and (B) calibration curve for zinc for the 15mg  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  electrodes

It can also be observed from the resulting voltammograms that the peak currents of both cadmium and zinc obtained from the three electrodes increased with mediator concentration. This increase can be attributed to the increase in the amount of redox centers, which facilitates the electron-hopping from the detecting species to the electrodes and vice versa.

## CONCLUSION

In this study,  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ -doped Nafion<sup>®</sup> thin film was successfully deposited on ITO substrates using the drop-coating method. The results from the electrochemical study showed that redox-active thin films were effectively fabricated. The peak currents increased monotonically with the concentration of the heavy metal present in the solution as well as with the concentration of the mediator,  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  due to the increase in the redox centers which enhanced the conducting property of the modified electrode. Also, all calibration curves obtained are linear and have a correlation factor near 1. This suggests that the fabricated modified electrodes can effectively be employed in various applications in heavy metal detection.

## ACKNOWLEDGEMENTS

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## CONFLICTS OF INTEREST

None

## CONTRIBUTIONS OF INDIVIDUAL AUTHORS

Shirley Tiong Palisoc and Michelle Tiamzon Natividad conceptualized the problem, developed the protocol, applied for funding, and procured the materials used in the study. Patricia Denise De Vera and Benjamin Simone B. Tuason did the experimental part and together with the other authors analyzed the results.

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