Determination of heavy metals in corn (*Zea Mays* L.) using silver nanoparticles/graphene/nafion modified glassy carbon electrode

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Abstract. Silver nanoparticles (AgNP)/graphene/Nafion modified glassy carbon electrodes were fabricated for the determination of trace amounts of cadmium (Cd^{2+}) and lead (Pb^{2+}) via anodic stripping voltammetry (ASV). The electrode modifiers and the ASV parameters were optimized. The fabricated electrode was characterized by field emission scanning electron microscopy and energy dispersive x-ray spectroscopy. A linear relationship between anodic peak current and heavy metal concentration was obtained in the range of 25 parts per billion (ppb) to 250 ppb. The limit of detection of the modified electrode is 25 ppb for both Cd^{2+} and Pb^{2+}, while the limits of quantitation are 155.7 ppb for Cd^{2+} and 159.5 ppb for Pb^{2+}. Real sample analysis using corn plant and soil samples was performed to show the utility of the fabricated electrode in sensing applications. Trace amounts of Cd^{2+} and Pb^{2+} were found in the said samples.

Key words: anodic stripping voltammetry, heavy metals, silver nanoparticles, graphene, Nafion.

INTRODUCTION

Heavy metal pollution is one of the main environmental problems of third world countries as well as industrialized countries. Due to anthropogenic activities such as smoking, mining, industrial processing, automobile exhausts, and application of organic manure and fertilizers, heavy metals accumulate in the air, soil, and water sources (Ganeshamurthy et al., 2008). Soil pollution is a serious problem since plants easily absorb heavy metals through their roots and accumulate them in their leaves, stems, and fruits. Consumption of food from plants such as crops, fruits, and vegetables with high levels of heavy metals has detrimental effects on human health (Baghaie & Fereydoni, 2019). Heavy metals can cause severe ailments such as kidney damage and cancer, lung and neurological damage, neurological effects, behavioral changes, loss of motor response, and disturbance in the cardiovascular and central nervous systems, bone marrow depression, hemolysis, hepatomegaly, melanosis, polyneuropathy, and encephalopathy (Jarup, 2003).

Corn (*Zea Mays* L.) is one of the most important crops in the Philippines. It is the best substitute staple food during rice shortages and is one of the primary sources of animal feeds. A study (Ibrahim, 2015) has shown that corn absorbs heavy metals like nickel (Ni), copper (Cu), iron (Fe), lead (Pb), and zinc (Zn) from soil and accumulates them in the grain, stem, silk, and stalk. Another study determined high levels of Pb on roots, leaves and seeds of corn grown on dumpsite soil (Cortez & Ching, 2014). Due to the adverse effects of heavy metals on human health, there is a need to detect heavy metals in corn.

There are different methods of detecting heavy metals viz., UV-Vis spectroscopy, atomic fluorescence spectroscopy, inductively coupled plasma mass spectroscopy (ICP-MS), surface enhanced Raman spectroscopy (SERS), ion chromatography, and atomic absorption spectroscopy (AAS). Although effective, these methods are considered to be complicated and expensive (March et al., 2015). A relatively low-cost and simpler alternate method (Bohrill et al., 2019) is anodic stripping voltammetry (ASV).

Anodic stripping voltammetry is an electrochemical method which offers a simple, low cost, and highly sensitive technique to determine various compounds, which gives it an upper hand (Zhai et al., 2015). It utilizes three electrodes; a working electrode, a counter electrode, and a reference electrode. The working electrode acts as the sensor and is usually modified to further increase its sensitivity. One of the common modifiers used is graphene which has a very unique set of physical and chemical properties such as large surface area and high conductivity (Er et al., 2017; Palisoc et al., 2017a). Other modifiers commonly used are gold nanoparticles (Palisoc et al., 2017b; Palisoc et al., 2017c; Palisoc et al., 2019b; Palisoc et al., 2019c), silver nanoparticles (AgNP) (He et al., 2017; Palisoc et al., 2018a), and bismuth nanoparticles (Palisoc et al., 2019a; Palisoc et al., 2020). Nanomaterials are usually used because of their remarkable properties, high adsorption and reactive capacity due to active sites and abundant functional groups on the nanomaterials' surface (Kurbanoglu et al., 2017), high surface-to-volume ratio, as well as enhanced sensitivity (Maduraiveeran & Jin W, 2017). The aforementioned nanomaterials are common in electrochemical detection for their unique physical and chemical properties like high-efficiency electrochemical sensing and quantum conductance (Hamidi-Asl et al., 2016). Silver nanoparticles, in particular, have excellent conductivity and biocompatibility, and electrocatalytic properties that can accelerate electron transfer and sensor stabilization (Zhai et al., 2015). Nafion has been widely used as an electrode modifier due to its anti-fouling capabilities, as well as its impressive optical quality, ability to load metal ions, and its simple handling (Zhai et al., 2015).

In this study, AgNP/graphene/Nafion modified glassy carbon electrodes (GCE) were fabricated for the detection and assessment of cadmium (Cd^{2+}) and lead (Pb^{2+}) accumulation in Philippine corn via ASV.

MATERIALS AND METHODS

AgNP/Graphene/Nafion modified glassy carbon electrode was fabricated by using the drop-coating method. The AgNP and graphene concentrations were each varied at 1 mg, 2 mg, and 3 mg. The modified GCEs were then used as the working electrode for detecting Pb^{2+} and Cd^{2+} in standard and real sample solutions via anodic stripping voltammetry.

Glassware and equipment

The following are the glassware and equipment that were used in this study: beaker, graduated cylinder, petri dish, Transferpette micropipette, teflon tape, glass slide, crucibles, Bosch SAE 200 electronic balance, Rocker Ultrasonic cleaner soner bath, AUTOLAB potentiostat, AA-6300 Shimadzu Atomic Absorption Spectrophotometer, glassy carbon electrode, and a voltammetric cell.

Chemicals and Reagents

Silver nanopowder (< 100 nm particle size), sodium chloride, lead chloride, cadmium chloride, copper chloride, mineral oil, nitric acid, concentrated hydrochloric acid, methanol, ethanol, 0.3 and 0.05-micron alumina slurry were purchased from Sigma Aldrich (Sigma-Aldrich Pte Ltd, Singapore). Graphene nanopowder (multilayer graphene; average flake thickness: 60 nm) was purchased from Graphene Supermarket (Calverton, NY, USA). Nafion (15-wt%) was purchased from Fuel Cell Earth (Woburn, MA, USA).

Preparation of AgNP/Graphene/Nafion casting solution

A Bosch SAE 200 electronic balance was used to measure the concentrations of AgNP and graphene. A 10 mL graduated cylinder was then used to measure ten weight-percentage (10-wt%) of Nafion. Since 15% Nafion was utilized, it was diluted with ethanol. Ethanol (4.667 mL) was added to 0.333 mL of 15% Nafion. The diluted Nafion was kept constant while the AgNP and graphene concentrations were each varied at 1 mg, 2 mg, and 3 mg.

Fabrication of the modified GCE

The bare GCE was polished with alumina slurry. This is to ensure an even surface for an even distribution of the casting solution. The alumina slurry was placed on a glass slide to serve as a surface to smoothen the GCE. The GCE was polished with 0.3-micron alumina slurry followed by 0.05-micron alumina slurry. Once the tip of the GCE was smoothened, the GCE was placed in a petri dish with nitric acid and was sonicated for 15 minutes. It was then rinsed with running water for 5 minutes and was sonicated in ethanol for 15 minutes. After the sonication, the electrode was rinsed with deionized water and was allowed to dry in air.

The AgNP/Graphene/Nafion solution was deposited onto the bare GCE via the using a Transferpette micropipette. The modified GCE was air dried at room temperature for at least two (2) hours.

Characterization of the modified GCE

The AgNP/Graphene/Nafion modified glassy carbon electrode was characterized using field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) point analysis.

Anodic Stripping Voltammetry

An AUTOLAB potentiostat was used to perform anodic stripping voltammetry (ASV). A three-electrode voltammetry setup was utilized wherein Ag/AgCl served as the counter electrode, Pt wire as the reference electrode, and the AgNP/Graphene/Nafion modified GCE as the working electrode. Deionized water (100 mL) with 0.5844 g of

NaCl was used as the electrolyte solution. It was sparged with nitrogen to prevent oxygen from interfering with the scans.

Preparation of Stock Solution for Optimization of ASV Parameters

For the optimization of the parameters, 10 parts per million (ppm) stock solutions of Pb and Cd was prepared. The analyte solution is composed of 0.1 M NaCl, 1.6307 mg of $CdCl_2$, and 1.3389 mg of $PbCl_2$. The solutions were all diluted with 100 mL deionized water.

Preparation of stock solution for Calibration curve

For the calibration curve, 25, 50, 75, 100, 150, 200, and 250 ppb stock solutions of Pb and Cd were prepared. A 10-ppm solution was first prepared and was then diluted to obtain the desired concentration. All stock solutions were diluted with deionized water.

Real Sampling

Three corn plant (Zea mays) samples from a local farm were used for this study. Sample 1 was obtained nearest to a road used by cars and tractors. Sample 2 was obtained in between the nearest and farthest from the said road, and Sample 3 was obtained farthest from the road (sample 3). This was done to test if being closer to a source of pollution such as vehicle exhaust would affect heavy metal concentrations in plants, thus, the samples were not washed prior to testing. After one week of air drying, the samples were segregated and blenderized. There were a total of eighteen (18) samples that were tested. All the samples were subjected to acid digestion. All the samples, except the soil, were ashed beforehand. One gram (1 g) of soil and 2 g each of silk, leaf, stem, crop, and root were used in the real sampling. Using the AgNP/graphene/Nafion modified electrode, Cd^{2+} and Pb^{2+} were determined in the corn plant's silk, crop, leaf, stem, root, and the soil sample where it was planted on.

The fifteen (15) samples (silk, leaf, stem, crop, and root) were placed in crucibles and were ashed in a furnace with a temperature of 450 °C for 5 to 6 hours or until the samples have turned to white ash. Nitric acid (1.5 mL) was added to each sample and was allowed to evaporate to dryness over a hot plate. Once dried, the samples were placed in a 450 °C furnace for 15 mins. Hydrochloric acid (1 mL) was then added to each sample. The samples were then diluted with 100 mL of deionized water. The analyte was filtered with filter paper to remove larger particles and sodium chloride (0.5844 g) was added to the filtered analyte to form the analyte solution.

Determination of Pb^{2+} and Cd^{2+}

Anodic stripping voltammetry was performed to determine the concentraions of Pb^{2+} and Cd^{2+} in the samples of this study. The optimal electrode and optimized parameters were used todetermine the heavy metal concentrations in each of the samples. The calibration curves of Pb^{2+} and Cd^{2+} were used to compute for the concentrations present in the sample. Statistical analysis was performed via histograms for the optimization of the ASV parameters and linear regression for the calibration curves.

RESULTS AND DISCUSSION

Optimization of the electrode modifiers

The modifiers of the electrode were optimized by the amounts of AgNP and graphene at 1 mg, 2 mg, and 3 mg while the concentration of the Nafion solution (4.667 mL ethanol and 0.333 mL Nafion) was held constant. The resulting electrodes were then used for the simultaneous detection of 10 ppm of Cd^{2+} and Pb^{2+} in an electrolyte solution via anodic stripping voltammetry. The deposition potential, deposition time, and accumulation time were held constant at -1 V s^{-1}, 60 s, and 15 s, respectively.

Fig. 1 shows the comparison of the current peaks for varying amounts of AgNP and graphene for the simultaneous detection of Cd^{2+} and Pb^{2+}. It can be observed from the figure that for 1 mg AgNP, the anodic current peaks of Cd^{2+} and Pb^{2+} decrease with increasing amounts of graphene, while for 3 mg AgNP, the anodic current peaks of Cd^{2+} and Pb^{2+} are almost constant with varying amounts of graphene. Since the electrode fabricated with 2 mg AgNP and 1 mg graphene manifested the highest anodic current peaks of Cd^{2+} and Pb^{2+}, it was considered as the optimized electrode.
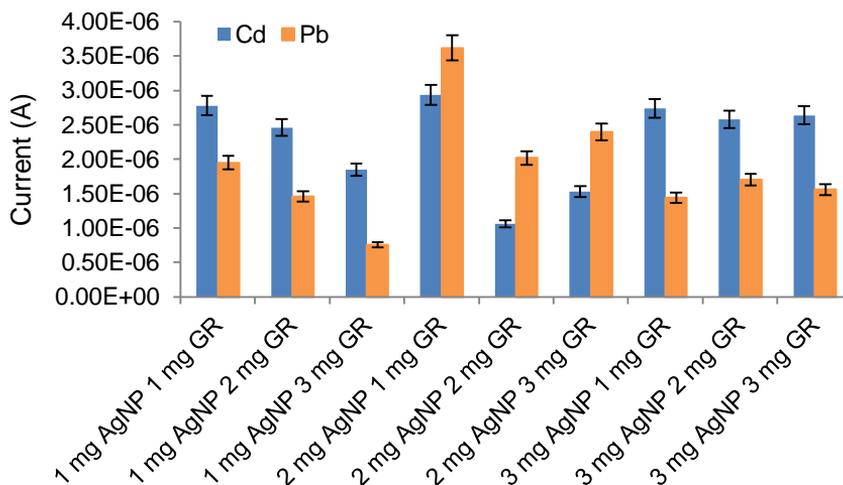

Figure 1. Anodic current peaks for varying amounts of AgNP and graphene for the simultaneous detection of Cd^{2+} and Pb^{2+}.

Optimization of ASV Parameters

The deposition potential was varied at -1.05 V, -1.0 V, -0.95 V, -0.9 V, -0.85 V and -0.8 V while the deposition time and accumulation time were held constant at 60s and 30s, respectively. Fig. 2 shows the comparison of the anodic current peaks for varying deposition potential. From the figure, it can be noted that as the deposition potential increased, the anodic peak current also increased. However, when it reached -0.95 V, the peaks started to plateau and decrease. Thus, the optimized deposition potential is -0.90 V since it showed the highest anodic current peak.

The deposition time was varied at 30, 40, 50, 55, and 60 s while deposition potential was held constant at -0.9 V, and accumulation time at 30 s. As seen in Fig. 3, as the accumulation time increased, the anodic peak current also increased. However, at 60 s,

the anodic peak current significantly decreased. Thus, the optimized deposition time is 55 s because it showed the highest anodic current peak.
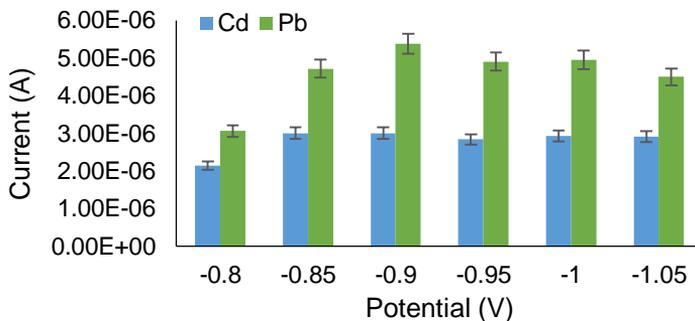

Figure 2. Anodic peak currents for varying deposition potential for the simultaneous detection of Cd^{2+} and Pb^{2+}.
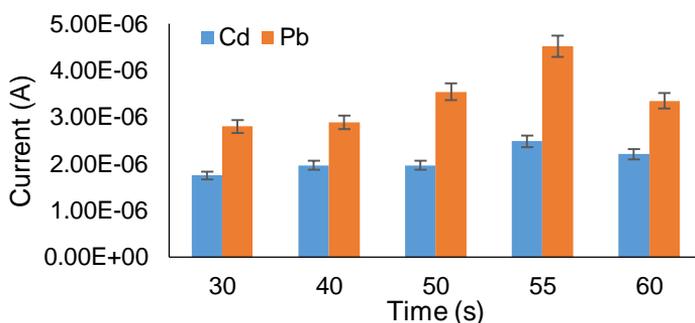

Figure 3. Anodic peak currents for varying deposition time for the simultaneous detection of Cd^{2+} and Pb^{2+}.
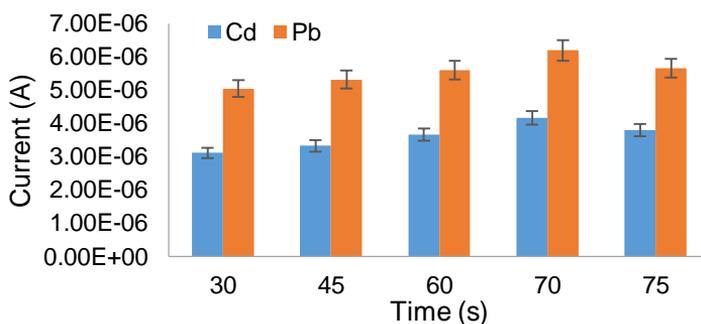

Figure 4. Anodic peak currents for varying resting time for the simultaneous detection of Cd^{2+} and Pb^{2+}.

The accumulation time was varied at 30, 45, 60, 65, 70, and 75 s while the deposition potential was held constant at -0.9 V, and deposition time at 55 s. As seen in Fig. 4, as the accumulation time increased, the anodic peak current increased as well. However, at 75 s, the anodic peak currents started to decrease. Thus, 70 s is the optimized resting time since it gave the highest anodic current peak.

Characterization of the modified electrode

Field emission scanning electron microscopy and energy dispersive X-ray spectroscopy were used to verify the presence of AgNP and graphene on the electrode surface, as well as to characterize the morphology of the modified electrode surface.

Fig. 5 shows the scanning electron micrograph of the modified electrode surface. The image confirms the dendritic shape of the silver nanoparticles and the sheet like structure of graphene. It also shows that AgNP was dispersed uniformly on the modified GCE surface. The SEM image is in agreement with previous studies (Song et al., 2013; Molina et al., 2016).
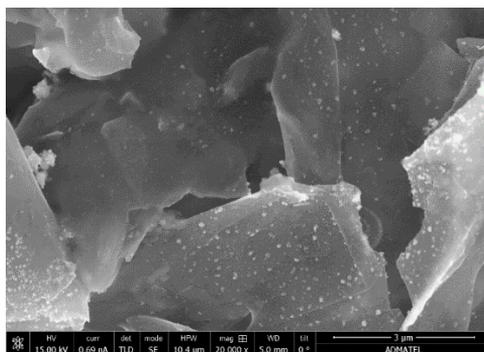
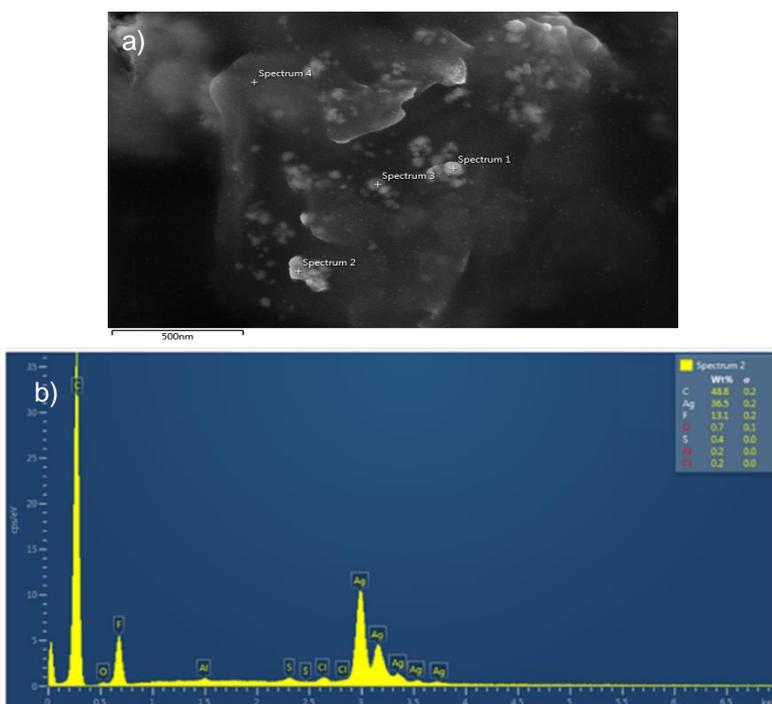**Figure 5.** FESEM image of AgNP/Graphene/ Nafion modified GCE.

Figure 6. (a) FESEM point analysis micrograph and (b) the corresponding EDX spectrum of AgNP/Graphene/Nafion modified GCE.

Fig. 6 shows the FESEM point analysis micrograph and the corresponding EDX spectrum of the modified electrode. As seen in the figure, the EDX spectrum confirms the presence of AgNP and graphene on the GCE surface. Aluminum found in the spectrum is attributed to the alumina slurry used in polishing the bare GCEs. Alumina

slurry is the common polishing reagent for carbon electrodes. It has been found that even after sonication, the aluminum layer still remains (Kiema et al. 2013). Fluorine (F), Sulfur (S), and Oxygen (O) found in the spectrum are from Nafion's composition.

Calibration Curve

Using the prepared stock solutions, the calibration curves for Pb^{2+} and Cd^{2+} concentrations were obtained (Fig. 7). The calibration curve of each of the said heavy metals were obtained by plotting the heavy metal concentrations against their respective anodic current peaks. With an R^2 value close to 1 for both heavy metals, it can be stated that the current peaks and the heavy metal concentration have a strong linear relationship.
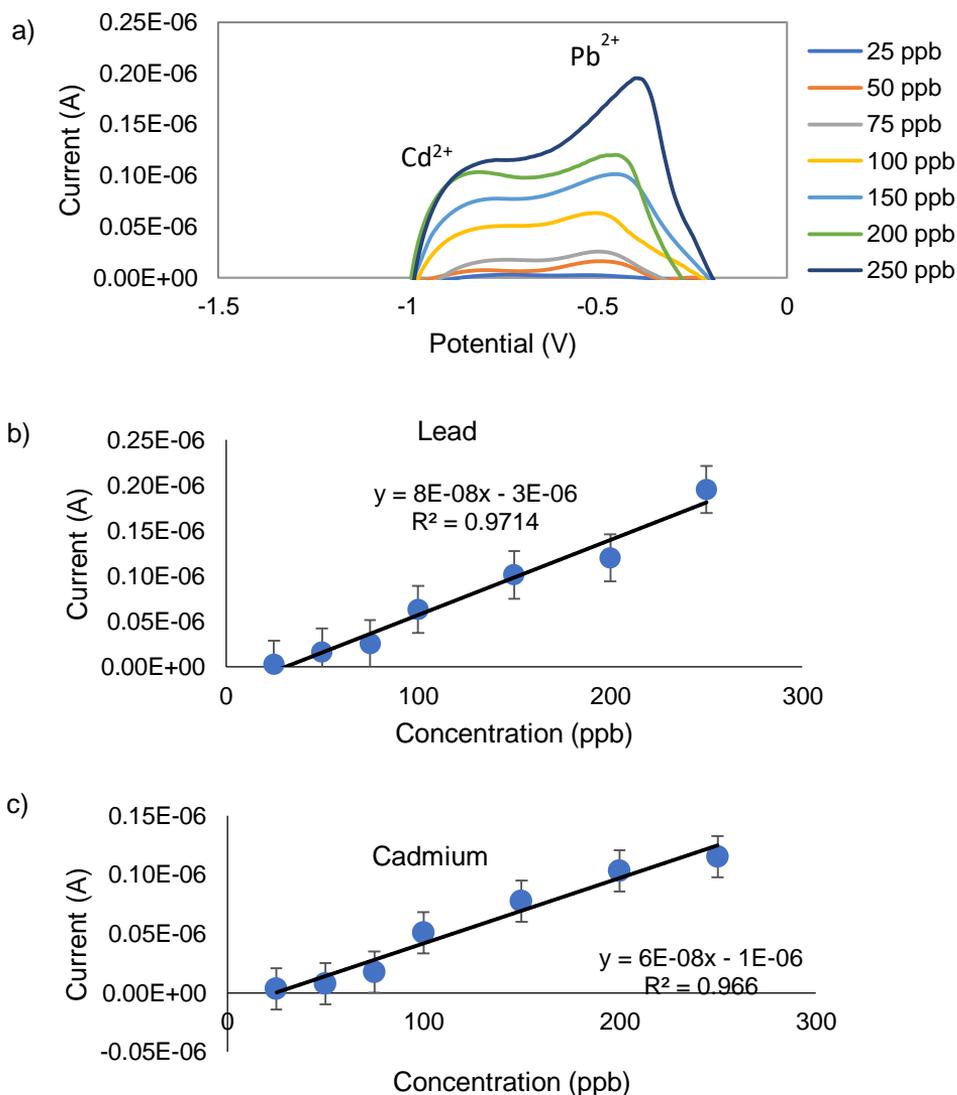

Figure 7. (a) Anodic stripping voltammograms for varying concentrations of Cd^{2+} and Pb^{2+}. Calibration curves for (b) Pb^{2+} and (c) Cd^{2+}.

Limit of Detection and Limit of Quantitation

The limit of detection (LOD) and limit of quantitation (LOQ) for both Cd^{2+} and Pb^{2+} were computed to determine the lowest concentration that the AgNP/graphene/Nafion modified GCE can detect. The limit of detection of the modified electrode was determined to be 25 ppb for both Cd^{2+} and Pb^{2+}. The limits of quantitation are 155.7 ppb for Cd^{2+} and 159.5 ppb for Pb^{2+}. These values were computed using the line equations obtained from the calibration curves.

Table 1 shows the performance comparison of the AgNP/Graphene/Nafion modified glassy carbon electrode with other works. From this, it can be concluded that the modified electrode in this study has a lower LOD than most of the electrodes presented in the table.

Table 1. Comparison of the AgNP/Graphene/Nafion modified GCE with other works

Electrode	Modifier	Method	Limit of Detection	Reference
Indium Tin Oxide	$[Ru(NH_3)_6]^{3+}$/Nafion	ASV	Pb – 500 ppb Cd – 500 ppb	(Palisoc et al., 2015)
Glassy Carbon	AuNP/$[Ru(NH_3)_6]^{3+}$/ Nafion	ASV	Pb – 45 ppb Cd – 200 ppb	(Palisoc et al., 2017b)
Glassy Carbon	Chitosan/carbon nanotubes	SWASV	Pb – 600 ppb Cd – 800 ppb	(Wu et al., 2017)
Glassy carbon	$[Ru(bpy)_3]^{2+}$/graphene/ Nafion	DPV	Pb – 48 ppb Cd – 49 ppb	(Palisoc et al., 2017a)
Carbon Paste	Coconut Shell powder	ASV	Cd – 105 ppb	(Rajawat et al., 2014)
Multilayer Graphene paste	Activated carbon from coconut husk	ASV	Pb – 44 ppb Cd – 56 ppb	(Palisoc et al., 2018b)
Graphene paste	Bismuth nanoparticles	ASV	Pb & Cd – 100 ppb	(Palisoc et al., 2019a)
Graphene paste	Gold nanoparticles	ASV	Pb–256 ppb Cd – 267 ppb	(Palisoc et al., 2019b)
Glassy Carbon	AgNP/Graphene/Nafion	DPV	Cd –25 ppb Pb – 25 ppb	This work

Real Sampling

Using the optimized modified electrode and optimized ASV parameters for obtaining the highest possible anodic peak currents for Pb^{2+} and Cd^{2+}, ASV was performed for the real sample analysis.

Table 2 shows the Cd^{2+} and Pb^{2+} concentrations present in the three different plant and soil locations. It can be observed that soil 3, root 1, stem 3, leaves 1, corn 2, and silk 3 have the highest concentration of the two heavy metals for their respective parts. The plant part that accumulated the most Pb^{2+} concentration was stem 3 with 142.375 ppb; while the part that absorbed the least amount of Pb^{2+} was leaves 3, with only 51.25 ppb. For Cd^{2+}, the highest concentration was also found to be in stem 3, with 261.67 ppb. The lowest Cd^{2+} concentration was found in root 2, with only 22.92 ppb.

It has been observed that the soil and the plant samples had an increase in heavy metal content as it got planted further away from the road, leading to location 3 having most of the highest concentrations for both metals. This may be due to the environment enclosing location 3, such as smaller roads accessible to the locals. According to Peralta-Videa (Peralta-Videa et al., 2009), the main source of Cd^{2+} intake is due to anthropogenic activities such as smoking. It can also be noted that Cd^{2+} utilizes the same biosorption pathway as calcium when absorbed by plants, which means it could easily be absorbed and stored in stems. For the concentration of Pb^{2+}, Peralta-Videa also mentioned that plants do not have channels for the uptake of Pb^{2+}. However, there have been observations that Pb^{2+} enters through the roots and builds up in the plant's phloem, which would most likely end up accumulating in the plant's leaves as it grows. This would explain the presence of Pb^{2+} in leaves 1 and 3. The minimal uptake of Pb^{2+} is also in agreement with previous studies (Mirecki et al., 2015; Wang et al., 2017).

According to the World Health Organization (WHO), the maximum amount of lead and cadmium that a person is allowed to consume is 50 ppb and 5 ppb, respectively (Palisoc et al., 2017). The corn 2 and corn 3 samples had lead contents of 88 and 67.125 ppb, respectively. This is way beyond the acceptable WHO limits and are therefore deemed toxic for human consumption.

Table 2. Concentrations of Cd^{2+} and Pb^{2+} and in the soil, corn grain, silk, leaves, stem and roots using ASV (ND-Not detected)

Samples	Cadmium (ppb)	Lead (ppb)
Soil 1	113.17	121.13
Soil 2	35.17	ND
Soil 3	221.6	162.5
Root 1	39.3	107.75
Root 2	22.92	ND
Root 3	ND	ND
Stem 1	ND	ND
Stem 2	ND	ND
Stem 3	261.67	142.38
Leaves 1	ND	109.88
Leaves 2	ND	ND
Leaves 3	ND	51.25
Corn 1	ND	ND
Corn 2	ND	88
Corn 3	ND	67.13
Silk 1	25.13	ND
Silk 2	50.3	ND
Silk 3	57.5	ND

CONCLUSIONS

A AgNP/Grahphene/Nafion modified glassy carbon electrode has been successfully fabricated via the drop-coating method. It was determined that 2mg AgNP and 1mg graphene were the optimum modifier amounts for detecting Cd^{2+} and Pb^{2+} since they obtained the highest anodic peak current for the detection of lead and cadmium. Characterization of the modified electrode by FESEM and EDX showed that the silver nanoparticles and graphene have successfully been deposited on to the electrode surface. The limit of detection for the modified electrode was found to be at 25 ppb for both Cd^{2+} and Pb^{2+}. The limit of quantitation was found to be at 155.7 ppb for Cd^{2+} and 159.5 ppb for Pb^{2+}. In future studies, it is suggested to use other nanomaterials as modifiers of the GCE to obtain a lower LOD. Moreover, using a standard method such as inductively coupled plasma mass spectroscopy is recommended to verify the ASV results.

REFERENCES

Baghaie, A.H. & Fereydoni, M. 2019. The potential risk of heavy metals on human health due to the daily consumption of vegetables. *Environmental Health Engineering and Management* **6**, 11–16.

Borrill, A., Reily, N. & Macpherson, J. 2019. Addressing the practicalities of anodic stripping voltammetry for heavy metal detection: a tutorial review. *Analyst* **144**, 6834–6849.

Cortez, L.A. & Ching, J. 2014. Heavy Metal Concentration of Dumpsite Soil and Accumulation in Zea mays (corn) Growing in a Closed Dumpsite in Manila, Philippines. *International Journal of Environmental Science and Techenology* **5**, 77–80.

Er, E., Çelikkan, H. & Erk, N. 2017. A novel electrochemical nano-platform based on graphene/platinum nanoparticles/nafion composites for the electrochemical sensing of metoprolol. *Sensors and Actuators B-Chemistry* **238**, 779–787.

Ganeshamurthy, A.N., Varalakshmi, L.R. & Sumangala, H.P. 2008. Environmental risks associated with heavy metal contamination in soil, water and plants in urban and periurban agriculture. *Journal of Horticultural Sciences* **3**, 1–29.

Hamidi-Asl, E., Dardenne, F., Pilehvar, S., Blust, R. & Wael, K.D. 2016. Unique Properties of Core Shell Ag@Au Nanoparticles for the Aptasensing of Bacterial Cells. *Chemosensors* **4**, 1–11.

He, D., Rauwel, E., Malpass-Evans, R., Carta, M., McKeown, N., Gorle, D.B., Kulandainathan, M.A. & Marken, F. 2017. Redox reactivity at silver microparticle–glassy carbon contacts under a coating of polymer of intrinsic microporosity (PIM). *Journal of Solid State Electrochemistry* **21**, 2141–2146.

Ibrahim, K.N. 2015. Heavy Metal Concentration (Pb, Cu, Fe, Zn, Ni) in Plant Parts of *Zea Mays* L. Cultivated in Agricultural Area Near Alor Gajah, Melaka, Malaysia. *American Journal of Environmental Engineering* **5**, 8–12.

Jarup, L. 2003. Hazards of heavy metal contamination. *British Medical Bulletin* **68**, 167–182.

Kiema, G.K., Aktay, M. & Mcdermott, M.T. 2003. Preparation of reproducible glassy carbon electrodes by removal of polishing impurities. *Journal of Electroanalytical Chemistry* **540**, 7–15.

Kurbanoglu, S., Ozkan, S.A. & Merkoçi, A. 2017. Nanomaterials-based enzyme electrochemical biosensors operating through inhibition for biosensing applications. *Biosensors and Bioelectronics* **89**, 886–898.

Maduraiveeran, G. & Jin, W. 2017. Nanomaterials based electrochemical sensor and biosensor platforms for environmental applications. *Trends in Environmental Analytical Chemistry* **13**, 10–23.

March, G., Nguyen, T.D. & Piro, B. 2015. Modified Electrodes Used for Electrochemical Detection of Metal Ions in Environmental Analysis. *Biosensors* **5**, 241–275.

Mirecki, N., Sunic, L., Agic, R. & Ilic, ZS. 2015. Transfer factor as indicator of heavy metals content in plants. *Fresenius Environmental Bulletin* **24,** 4212–4219.

Molina, J., Cases, F. & Moretto, L. 2016. Graphene-based materials for the electrochemical determination of hazardous ions. *Analytica Chimica Acta* **946**, 9–39.

Palisoc, S., Chua, R. & Natividad, M. 2020. Highly sensitive determination of heavy metals in Upland and Lowland Rice using AgNP/BiNP/MWCNT/Nafion modified glassy carbon electrode via anodic stripping voltammetry. *Materials Research Express* **7**, 1–14.

Palisoc, S., Natividad, M., Malabuyo, Y.A. & Pereja, R.C. 2019a. Determination of heavy metals in root crops using bismuth nanoparticles modified graphene paste electrode. *Agronomy Research* **17**, 245–260.

Palisoc, S., Leoncini, J. & Natividad, M. 2019b. Trace level determination of cadmium and lead in coffee (Coffea) using gold nanoparticles modified graphene paste electrode. *Agronomy Research* **17**, 229–239.

Palisoc, S., Bentulan, J.M. & Natividad, M. 2019c. Determination of trace heavy metals in canned food using Graphene/AuNPs/[Ru(NH$_3$)$_6$]$^{3+}$/Nafion modified glassy carbon electrodes. *Journal of Food Measurement and Characterization* **13**, 169–176.

Palisoc, S., Lee, E., Natividad, M. & Racines, L. 2018a. Silver Nanoparticle Modified Graphene Paste Electrode for the Electrochemical Detection of Lead, Cadmium and Copper. *International Journal of Electrochemical Science* **13**, 8854–8866.

Palisoc, S., Estioko, L.C. & Natividad, M. 2018b. Voltammetric Determination of Lead and Cadmium in Vegetables by Graphene Paste Electrode Modified with Activated Carbon from Coconut Husk. *Materials Research Express* **5**, 1–10.

Palisoc, S., Uy, D.J., Natividad, M. & Lopez, T.B. 2017a. Determination of heavy metals in mussel and oyster samples with tris (2,2′-bipyridyl) ruthenium (II)/graphene/Nafion® modified glassy carbon electrodes. *Materials Research Express* **4**, 1–13.

Palisoc, S., Causing, N. & Natividad, M. 2017b. Gold nanoparticle/hexaammineruthenium/Nafion® modified glassy carbon electrodes for trace heavy metal detection in commercial hair dyes. *Analytical Methods* **9**, 4240–4246.

Palisoc, S., Valeza, N.C. & Natividad,M. 2017c. Fabrication of an Effective Gold Nanoparticle/Graphene/Nafion® Modified Glassy Carbon Electrode for High Sensitive Detection of Trace Cd^{2+}, Pb^{2+} and Cu^{2+} in Tobacco and Tobacco Products. *International Journal of Electrochemical Science* **12**, 3859–3872.

Palisoc, S., Natividad,M., Martinez, N., Ramos, R. & Kaw, K. 2015. Fabrication and electrochemical study of [Ru(NH$_3$)$_6$]$^{3+}$/Nafion modified electrodes for the determination of trace amounts of Pb^{2+}, Cd^{2+}, and Zn^{2+} via anodic stripping voltammetry. *e-Polymers* **16**, 117–123.

Peralta-Videa, J.R., Lopez, M.L., Narayan, M., Saupe, G. & Gardea-Torresdey, J. 2009. The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain. *The International Journal of Biochemistry and Cell Biology* **41**, 1665–1677.

Rajawat, D.S., Kumar, N. & Satsangee, S.P. 2014. Trace determination of cadmium in water using anodic stripping voltammetry at a carbon paste electrode modified with coconut shell powder. *Journal of Analytical Science and Technology* **5**, 1–8.

Song, Y.Z., Ma, K., Zhu, F.X. & Xu, J. 2013. Synthesis of Silver Nanoparticles Using Cefopernazone as a Stabilizing Reagent and Its Catalysis for Sodium Sulfide. *International Jouranl of Electrochemical Science* **8**, 3628–3635.

Wang, S., Wu, W., Liu, F, Liao, R. & Hu, Y. 2017. Accumulation of heavy metals in soil-crop systems: a review for wheat and corn. *Environmental Science and Pollution Research* **24**, 15209–15225.

Wu, K., Lo, H., Wang, J., Yu, S. & Yan, B. 2017. Electrochemical detection of heavy metal pollutant using crosslinked chitosan/carbon nanotubes thin film electrodes. *Materials Express* **7**, 15–24.

Zhai, H., Liang, Z., Chen, Z., Wang, H., Liu, Z., Su, Z. & Zhou, Q. 2015. Simultaneous detection of metronidazole and chloramphenicol by differential pulse stripping voltammetry using a silver nanoparticles/sulfonate functionalized graphene modified glassy carbon electrode. *Electrochimica Acta* **171**, 105–113.