Highly sensitive determination of heavy metals in upland and lowland rice using AgNP/BiNP/MWCNT/nafion modified glassy carbon electrode via anodic stripping voltammetry

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Abstract

It is of prime importance to determine the presence of trace heavy metals, especially cadmium ($\text{Cd}^{2+}$) and lead ($\text{Pb}^{2+}$) in rice to ensure food safety as it is the staple source of the daily caloric intake of Asians. This work utilized anodic stripping voltammetry (ASV) for the determination of heavy metals due to its portability for in situ measurements. A glassy electrode modified with silver nanoparticles (AgNP), bismuth nanoparticles (BiNP), multiwalled carbon nanotubes (MWCNT) and Nafion was fabricated to serve as the working electrode. The morphology of the fabricated electrode was characterized using scanning electron microscopy and x-ray diffraction, its elemental composition was determined by energy dispersive spectroscopy, its chemical bonds were identified using Fourier transform infrared spectroscopy, and its electrochemical behavior was measured via cyclic voltammetry. The electrode showed high stability at 50 continuous scans. The optimal deposition time, accumulation time and scan rate were determined to be 80 s, 60 s and 100 mV s$^{-1}$, respectively. The detection limit for Cd$^{2+}$ and Pb$^{2+}$ were determined to be 25.12 ppb and 20.55 ppb, respectively. Rice samples were analyzed and the transfer factor of the heavy metals were determined at each isolated part. The ASV results were validated with atomic absorption spectroscopy.

1. Introduction

Rice ($Oryza sativa$) is the main Asian staple food crop, particularly, in the Philippines. It is also the main source of livelihood of more than 5 million farmers all over the country [1]. $Oryza sativa$, is a cereal food crop that belongs to the grass family (Family: Poaceae) of the plant kingdom.

The risk of contamination from leaching pollutants from the field is a major consideration since rice is the most consumed carbohydrate source in the country. With the extended time of submergence in water, the crop has a high risk of seepage of pollutants, particularly of heavy metals if the water used for irrigation is near mining sites, or even particulates emitted from engines via vehicles and factories.

Some heavy metals are essential as micronutrients to the body (e.g. Iron, Copper, Zinc); however, elevated amounts of such metals overwhelm the natural processes of the body, inducing toxicity to the body [2]. Lead (Pb$^{2+}$) and cadmium (Cd$^{2+}$) even in trace amounts are toxic, hence they are banned and/or regulated by the World Health Organization (WHO) alongside Arsenic (As), Beryllium (Be), Chromium (Cr), Mercury (Hg), and Nickel (Ni). These heavy metals are mostly produced as mine tailings as they are used for extraction and refining of different metal ores. Bioaccumulation, which is the exponential deposition of minute quantities of toxic chemicals in the body due to a lack of mechanism to excrete such chemicals, is a major concern when it comes to the presence of heavy metals in the produce that humans consume [3].

Anodic stripping voltammetry (ASV) is a desired heavy metal detection method due to its selectivity and cost-efficiency compared to atomic absorption spectroscopy (AAS), high resolution inductively coupled mass spectrometry (HR-ICP-MS), etc. This work fabricated an AgNP/BiNP/MWCNT/Nafion® modified glassy
carbon electrode that served as the working electrode in ASV measurements for the highly sensitive detection of heavy metals in upland and lowland rice.

2. Methodology

2.1. Preparation of electrodes
To modify the electrode, a glassy carbon electrode was polished using 0.3 \( \mu m \) and 0.05 \( \mu m \) alumina slurry sequentially against a glass slide until a lustrous finish was attained. The electrode was then wrapped with Polytetrafluoroethylene (PTFE) tape, making sure that the polished tip was exposed. The electrode was then submerged in a petri dish, half-filled with ethanol, and sonicated for 30 min to remove the alumina slurry at the tip of the electrode; after which it was then allowed to air-dry for 24 h at room temperature.

2.2. Preparation of modifiers
The casting solutions were prepared by dissolving 1 mg, 2 mg and 3 mg each of AgNP, BiNP and MWCNT in 5 ml 1% solution of Naion in methanol and was homogenized using a sonicator.

2.3. Optimization of ASV parameters
Using the optimized electrode, different parameters were adjusted to enhance the anodic current. The first step was the determination of the optimized time for deposition or pre-treatment time. Holding the rest time (accumulation time) constant, the deposition time was varied from 20 to 120 s with 10 s increments. With the optimized deposition time determined, the accumulation time was then varied from 20 to 60 s at 10 s increments. With both deposition and accumulation time optimized, the scan rate was varied from 10 mV s\(^{-1}\) to 90 mV s\(^{-1}\) at 10 mV s\(^{-1}\) increments.

2.4. Real sampling
The rice samples were obtained from different parts of Luzon, making the bulk of the so-called Rice Granary of the Philippines. From there, the rice plants were divided into 3 different parts, the grain, the husk, and the stem. As with the acquisition of the rice plants, a soil sample was also obtained from the rice field were the rice plant was acquired. With the divided rice plant, 1 gram of the different samples was placed on a ceramic crucible and dry ashed in a furnace at approximately 500 \( ^\circ \)C, taking note not to exceed 700 \( ^\circ \)C as this is near the boiling point of elemental Cd. The time at which the ashing was completed were varying as different organic structures have different rates of ashing time. The ashing was considered to be completed if the remaining sample was around light gray to white in color and is powder in consistency. The ashed samples was then acid digested with 5 ml aqua regia in 1:3 HNO\(_3\)/HCl ratio. The samples were allowed to sit in the acid for about 24 h to complete the reaction process. The samples were then heated to boil out the remaining acid from the sample. After the acid was evaporated, the remaining sample was then diluted with deionized water and filtered out to make an electrolyte of the sample. The addition of NaCl provides a molarity of 0.1 M for the electrolyte. The samples were then ready for ASV analysis. The resulting voltammogram, with the determination of its anodic peaks was used to determine the concentration of Pb\(^{2+}\) and Cd\(^{2+}\) using the calibration curve obtained from the previous step.

3. Results and discussion

3.1. Morphological characterization
Scanning electron microscopy (SEM) was utilized to evaluate the surface morphology of the fabricated modified electrode. The SEM micrographs are shown in figure 1.

Figure 1(A), shows a micrograph of the AgNP used in modifying the electrode. On the average, the particle size was less 250 nm. The elemental composition of the powder used was measured using Energy Dispersive Xray (EDX). Figure 2 shows the percentage elemental composition of the AgNP powder. The data revealed that there was a high purity of Ag present in the powder. The presence of Si in the EDX could be an error due to possible Raman scattering \[^{\text{4}}\], as shown by the less intense spike from the EDX graph. The presence of Cl, however, could be an inherent trace element in the produced powder. Lastly, the presence of Al was from the alumina slurry used for cleaning the surface of the glassy carbon electrode that adhered onto the modifier.

Figure 3(A), shows the SEM micrograph of the BiNP used as a modifier for the electrode. The particle size of the powder was approximately 500 nm. The EDX profile of the BiNP as shown in figure 3(B) shows the high purity of the powder. The presence of carbon was from the glassy carbon used as the substrate of the BiNP during...
the scanning of the powder. The presence of Al was from the alumina slurry used to clean the tip of the electrode prior to coating with the modifier.

Figure 4(A) shows the micrograph of MWCNT used as modifier for the electrode. The micrograph shows the presence of the MWCNT which adhered onto the surface of the electrode as evidenced by the presence of a network of tendril-like structures. The carbon detected was both from the MWCNT and the surface of the glassy carbon used. The presence of the Al was from the alumina slurry and the Cl was from the inherent trace material from the powder.

To verify the crystal structure of the MWCNT, the Xray diffraction pattern of the sample was evaluated. With the denoising and baselining of the XRD pattern, figure 5 was obtained. From the XRD data collected, the
Figure 3. EDX profile of the BiNP.

Figure 4. EDX profile of the MWCNT.
number of carbon nanotube walls were calculated as prescribed by Roslan et al [5]. The ratio was calculated to be 4.09 which is approximately 4, confirming the presence of multiple walls in the CNT used.

Figure 6(A) shows the surface morphology of the modified electrode. The SEM micrograph, upon comparison with figures 3(A) and 2(A), shows the presence of BiNP which are the larger particles and AgNP which are the smaller particles. In addition, the tendril-like structures are MWCNT, upon comparison with with figure 4(A). The EDX profile collected verifies the adherence of the modifiers in the specified AgNP/BiNP/MWCNT ratios used in the study. The presence of the Al was also from the alumina slurry used to polish the surface of the electrode.

The functional groups present in the glassy carbon rod was also detected using FTIR as shown in figure 7. The first two peaks detected at 3459.724 and 3414.368 cm\(^{-1}\) indicate the presence of O–H bonds in the sample. The small peak at 2925.53 cm\(^{-1}\) indicates the presence of aldehyde. The peaks at 2362.409 and 2337.339 cm\(^{-1}\)
3.2. Cyclic voltammetry

Figure 8 shows the cyclic voltammogram which describes the electrochemical property of the electrode. The anodic peak present at the forward scan of the electrode shows the presence of both Ag and Bi on the electrode surface, with the half reaction \(\text{Ag}^{+} + e \rightarrow \text{Ag} \) and \(\text{Bi}^{+} + e \rightarrow \text{Bi} \), respectively [7]. The overlapping of the anodic peaks of Ag and Bi produced a higher current response. Unlike a bismuth film electrode (BiFE) which disperses Bi particles evenly across the surface of the electrode through electrodeposition, the adherence of BiNP via drop coating method creates adsorption sites on which the heavy metals attach to. Furthermore, these adsorption sites produce a larger signal, lowering the limit of detection [8]. However, the particle size of AgNP causes instability due to agglomeration. This instability can be seen in the reverse scan of the CV with the appearance of 2 cathodic peaks. The first cathodic peak during the reverse scan represents the ionization of Ag and Bi to Ag\(^{2+}\) and Bi\(^{2+}\). The second cathodic peak shows the instability of the AgNP due to agglomeration by further ionizing Ag\(^{+}\) onto Ag\(^{2+}\) with the half reaction \(\text{Ag}^{+} \rightarrow \text{Ag}^{2+} + e \) [9].
Additional scans were also employed to evaluate the stability of the fabricated modified electrode (figure 9). The anodic peak still maintained a decent current of 274.5 μA compared to the initial anodic current peak of 335.9 μA. From the equation of the trendline, the slope at which the anodic current decays are at $-1.2489 \mu$A per scan, confirming the stability of the fabricated electrode even after several usage. The decay of the anodic peak is also reflected with the first cathodic peak, with a response of 0.698 μA per scan. The second cathodic peak, however, exhibited a low Pearson coefficient (R2) of 0.0011, which is insignificant to the response of the modified electrode, further confirming that the presence of the second peak is a product of side reaction from the initial cathodic peak.

3.3. Optimization of ASV parameters

3.3.1. Deposition time

The deposition time during ASV was first optimized. The deposition time range used was between 30 s to 120 s in 10 s increments, as shown in figure 10. The broken lines represent the Gaussian curve fitted with each peak, with the red representing Cd$^{2+}$ and navy blue representing Pb$^{2+}$. 

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Figure 9. Stability analysis of the modified electrode.

Figure 10. Optimization of the deposition time.
In order to evaluate the optimum deposition time, the anodic peaks of Cd and Pb\(^{2+}\) were plotted as shown in figure 11. The Cd peaks during the optimization showed a steady increase as the deposition time was increased. On the other hand, the response of Pb\(^{2+}\) during the optimization plateaued at the 50 s mark, with minimal decrease after 80 s. From these, 80 s was chosen to be the optimal deposition time to compensate for the insignificant decrease of response after 80 s.

3.3.2. Accumulation time

With the deposition time optimized, the next step was to optimize the accumulation time. From the voltammograms shown in figure 12, there was no obvious trend as the accumulation time was varied.

In order to further optimize the accumulation time, a histogram of the anodic peaks was made, as shown in figure 13. The histogram revealed minimal changes, notwithstanding the decrease in the anodic peaks of both Cd\(^{2+}\) and Pb\(^{2+}\) between 20 to 30 s. At 40 s, however, the anodic peaks of both Cd\(^{2+}\) and Pb\(^{2+}\) increased, with minimal variation until the 60 s mark. Since this step of the ASV did not involve any hydrodynamic condition as stirring was turned off during this step, only diffusion along the electrode surface could be factored in. Hence, 60 s was used as the optimized accumulation time in order to have a leeway for additional deposition of trace heavy metals.

![Figure 11. Optimization of the deposition time.](image1)

![Figure 12. Optimization of the accumulation time.](image2)
3.3.3. Scan rate

The scan rate was determined from 10 to 90 mV s\(^{-1}\) at 10 mV s\(^{-1}\) increments, as shown in figure 14. From the voltammogram, the peak separation of the individual peaks of Cd\(^{2+}\) and Pb\(^{2+}\) decreases as the scan rate.
The scan rate is the determining factor of the resolution of the ASV to ascertain the selectivity of the working electrode as evidenced by its ability to determine the presence of different heavy metals in the analyte.

To further determine the optimal scan rate for ASV, the anodic peaks of Cd\(^{2+}\) and Pb\(^{2+}\) were plotted in figure 15. There is a significant correlation of a linear increase in anodic peak signal as the scan rate increases. With this correlation, the optimal scan rate was determined to be 100 mV s\(^{-1}\).

### 3.4. Calibration curve

The standard solutions for a known concentration of Cd\(^{2+}\) was plotted against the anodic peak of each concentration, as shown in figure 16. A linear correlation was established between the anodic peak current and

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| LOD and LOQ of the fabricated modified electrode. |
|-----------------|-----------------|
|                  | Cd              | Pb              |
| Limit of Detection (LOD) | 25.12 ppb | 20.55 ppb |
| Limit of Quantification (LOQ) | 76.12 ppb | 62.26 ppb |

Figure 16. Calibration curve for Cadmium.

Figure 17. Calibration curve for lead.
| Electrode                        | Modifiers                                                                 | Method | Heavy Metals Detected | Cadmium | Lead    | References |
|---------------------------------|---------------------------------------------------------------------------|--------|-----------------------|---------|---------|------------|
| Glassy carbon electrode         | Crosslinked Chitosan and Carbon Nanotubes Film                           | SWASV  | Cd, Pb, and Cu        | 800 ppb | 600 ppb | [11]       |
| Carbon paste electrode          | Coconut Shell Powder                                                      | ASV    | Cd                    | 105 ppb | —       | [12]       |
| Pencil graphite electrode       | Bismuth Film                                                              | ASV    | Cd and Pb             | 11 ppb  | 11.5 ppb | [13]       |
| Pencil graphite electrode       |                                                                           | DPV    | Pb                    | —       | 8.9 ppm | [14]       |
| Glassy carbon electrode         | Tris (2,2′-bipyridyl)ruthenium(II), Graphene, and Nafion                  | DPV    | Cd, Pb, and Cu        | 49 ppb  | 48 ppb  | [15]       |
| Glassy carbon electrode         | Gold Nanoparticles, Hexammoneruthenium, and Nafion                        | ASV    | Cd and Pb             | 45 ppb  | 200 ppb | [16]       |
| Indium Tin oxide electrode      | [Ru(NH₃)₆]³⁺ and Nafion                                                  | ASV    | Cd, Pb, and Zn        | 500 ppb | 500 ppb | [17]       |
| Graphene paste electrode        | Coconut Husk Activated Carbon                                            | ASV    | Cd and Pb             | 56 ppb  | 44 ppb  | [18]       |
| Graphene paste electrode        | Silver Nanoparticles                                                      | ASV    | Cd, Pb, and Cu        | 17 ppb  | 12 ppb  | [19]       |
| Glassy carbon electrode         | AgNP/BiNP/MWCNT/Nafion*                                                 | ASV    | Cd and Pb             | 25 ppb  | 21 ppb  | This work  |
the concentration of the trace heavy metal under consideration. This calibration curve is used to determine the response of the electrode at the level of concentration and to determine the equation to be used in order to quantify the concentration of Cd$^{2+}$ in the real sample. The calibration curve for Cd$^{2+}$ provided a good linear response with a Pearson coefficient of 0.9442. This value validates the linear response of the electrode with increasing concentration in a simultaneous scan of Cd$^{2+}$ and Pb$^{2+}$. A calibration curve was also plotted for the anodic current peaks of Pb$^{2+}$ at different standard concentrations, as shown in figure 17. There is a linear response between anodic current peak of Pb$^{2+}$ and the concentration of the standard concentrations of the trace heavy metal. The plot also showed a good linear correlation with a Pearson coefficient of 0.9367.

The limit of detection (LOD) and limit of quantification (LOQ) of Cd$^{2+}$ and Pb$^{2+}$ in this study are shown in table 3. Based on the calculated values of LOD and LOQ, the fabricated electrode showed a high sensitivity to simultaneous detection of Cd$^{2+}$ and Pb$^{2+}$, at around 25.12 to 20.55 ppb, with high confidence level at the concentration of 76.12 to 62.26 ppb.

The comparison of the LOD and LOQ in this study was compared to that of previous studies in detecting Cd and Pb in trace concentration, as shown in table 2. The modified electrode was able to detect at a level beyond the detection limit of other analytical techniques, like AAS. Although the study exhibited a higher detection limit compared to some of the previous work shown, the stability of the electrode produced, and the simplicity of modification compared to previous studies maintains the novelty of the study.

### 3.5. Real sampling

The electrode produced was then used in detection of Cd and Pb in different variety of rice gathered from multiple locations along Central and Northern Luzon. Organic, lowland rice was collected from Capas in Tarlac, and Organic, upland rice was collected from Daraitan in Rizal. While others were collected from Pozorrubio in Pangasinan, Nueva Ecija and Paniqui in Tarlac. The concentration levels of Cd and Pb were calculated based from the anodic peak signals of the heavy metal, as shown in table 3. The transfer factor of each heavy metal was also calculated. A transfer factor higher than 1 indicated a high absorption of the heavy metal in the isolated part. The transfer factor of Pb in the rice stalk obtained from Paniqui was not determined because of the limit of the electrode. The transfer factor was not calculated for the rice from Daraitan as there were no soil sample acquired.

### 3.6. Atomic absorption spectrometry

The summary of the obtained concentration of the rice plant samples from ASV and AAS is shown in table 4. Based from the data gathered, the concentration of Cd from the samples was undetectable using AAS. This is due to the limitation of the spectrum produced by the AAS and the innate limit of detection of the technique itself,
which is around 100 ppb. The discrepancy of the detected concentration of Cd and Pb from the ASV versus that of the AAS was due to known interference of Cu in detection of both Cd and Pb in voltammetry [20]. Such interference can be mitigated with the use of ferrocyanide which complexes with the Cu ions [21].

4. Conclusion

A modified electrode of AgNP/BiNP/MWCNT/Nafion®-GCE was fabricated by determining the highest anodic peak of Cd and Pb detected with concentration matrix of AgNP, BiNP and MWCNT. With the selected electrode modification, the morphology electrode was characterized using SEM, EDX, XRD and FTIR. The SEM confirmed the presence of AgNP, BiNP and MWCNT on the surface of the electrode, with the confirmation of EDX at each micrograph. The multiplicity of the carbon nanotube walls was determined from the XRD of the MWCNT. The FTIR confirmed the presence of functional groups on the structure of the glassy carbon electrode. The electrochemical property of the electrode was also analyzed using cyclic voltammetry. It showed the adherence of both AgNP and BiNP onto the surface due to the high anodic peak response. Agglomeration of the AgNP resulted in instability of Ag⁺ ions to form Ag²⁺, which further proved by the stability test of the electrode. The electrode also showed high stability at 50 scans. The deposition time, accumulation time and scan rate were optimized, which was determined to be 80 s, 60 s, and 100 mV s⁻¹, respectively. Calibration curve of Cd and Pb was also constructed, with a high linear correlation. From the calibration curve, the LOD of Cd and Pb was determined to be 25.12 ppb and 20.55 ppb, respectively, and the LOQ of Cd and Pb at 76.12 ppb and 62.26 ppb was also determined. Different rice samples were analyzed for their Cd and Pb content, based from the anodic peak response of their voltammograms. Different parts of the plant also have different transfer factors. The rice samples were then tested with AAS and was compared to the concentration obtained from ASV. The discrepancy of the values obtained from AAS was due to known interference of Cu in ASV scans.

The fabrication of AgNP/BiNP/MWCNT/Nafion®-GCE provided a highly sensitive method of determination of Cd and Pb. Rice plant have different absorption and accumulation of heavy metal in different parts of the plant.

To progress this study, possible steps to prevent agglomeration could be established in order to stabilize the AgNP used. Further investigation on interference of different ions could also be established to isolate the metals which one is interested in detecting.

| Table 4. ASV and AAS comparison. |
|----------------------------------|
|                                  |
| Concentration (ppb)              |
|                                  |
| ASV                              |
| Cd                               |
| Pb                               |
| AAS                              |
| Cd                               |
| Pb                               |

| Capas, Tarlac                    |
|----------------------------------|
| Grain                            |
| 116.18                           |
| 255.26                           |
| −28.20                           |
| 102.30                           |
| Husk                             |
| 146.68                           |
| 281.48                           |
| −32.90                           |
| 59.50                            |
| Stalk                            |
| 187.30                           |
| 693.17                           |
| −32.30                           |
| 426.30                           |
| Soil                             |
| 144.89                           |
| 255.87                           |
| −33.10                           |
| 132.90                           |

| Pozorrubio, Pangasinan           |
|----------------------------------|
| Grain                            |
| 129.33                           |
| 124.64                           |
| −31.60                           |
| 53.40                            |
| Husk                             |
| 126.48                           |
| 311.73                           |
| −33.80                           |
| 59.50                            |
| Stalk                            |
| 102.31                           |
| 382.73                           |
| −32.00                           |
| 108.50                           |
| Soil                             |
| 104.62                           |
| 168.32                           |
| −33.60                           |
| 96.20                            |

| Nueva Ecija                      |
|----------------------------------|
| Grain                            |
| 151.05                           |
| 313.75                           |
| −32.50                           |
| 59.50                            |
| Husk                             |
| 259.44                           |
| 396.22                           |
| −24.80                           |
| 71.80                            |
| Stalk                            |
| 96.18                            |
| 238.05                           |
| −14.90                           |
| 188.00                           |
| Soil                             |
| 95.03                            |
| 357.66                           |
| −25.50                           |
| 96.20                            |

| Paniqui, Tarlac                  |
|----------------------------------|
| Grain                            |
| 184.15                           |
| 490.06                           |
| −20.30                           |
| 84.00                            |
| Husk                             |
| 85.52                            |
| 198.06                           |
| −29.10                           |
| 77.90                            |
| Stalk                            |
| 219.72                           |
| −4.81                            |
| −30.40                           |
| 84.00                            |
| Soil                             |
| 218.65                           |
| 191.57                           |
| −28.90                           |
| 71.80                            |

| Daraitan, Rizal                  |
|----------------------------------|
| Grain                            |
| 154.48                           |
| 480.13                           |
| −32.20                           |
| 71.80                            |
| Husk                             |
| —                               |
| 309.80                           |
| −33.60                           |
| 548.80                           |
| Stalk                            |
| 213.74                           |
| 756.23                           |
| −33.60                           |
| 84.00                            |

which is around 100 ppb. The discrepancy of the detected concentration of Cd and Pb from the ASV versus that of the AAS was due to known interference of Cu in detection of both Cd and Pb in voltammetry [20]. Such interference can be mitigated with the use of ferrocyanide which complexes with the Cu ions [21].
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