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Silver/Bismuth/Nafion Modified Pencil Graphite Electrode for Trace Heavy Metal Determination

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A low–cost modified pencil graphite electrode (PGE) was developed for the determination of trace heavy metals in wastewater. Graphite rods (2HB) of 3 mm diameter from a commercial brand of pencils were modified by varying amounts of silver nanoparticles (AgNP) and bismuth (Bi) mixed in a solution of 1% Nafion® and isopropanol via the drop coating technique. The PGE modified by 3 mg AgNP and 2 mg Bismuth was deemed the best electrode as it yielded the highest anodic peaks as determined by anodic stripping voltammetry (ASV). By optimizing the ASV parameters, it was determined that the optimum accumulation time and deposition time are 120s and 15s, respectively. The calibration curve was used to determine the limits of detection which were 0.19 parts per billion (ppb) for Cd^{2+} and 0.30 ppb for Pb^{2+} while the limits of quantitation were 568 ppb for Cd^{2+} and 894 ppb for Pb^{2+}. The Pearson coefficients of the calibration plots of Cd^{2+} and Pb^{2+} are 0.9822 and 0.9569, respectively. Wastewater samples were collected and analyzed for trace heavy metals using the optimized electrode.

Keywords: anodic stripping voltammetry, pencil graphite electrode, bismuth, silver nanoparticles, Nafion®

1. INTRODUCTION

Cadmium and lead, as heavy metals, remain to be among the major industrial pollutants, and their detrimental effects to the plant and animal communities surrounding the polluted water and land sources are still experienced to this day. It is therefore imperative to measure the presence of these pollutants in our environment. There are several methods used for the analysis and detection of heavy metal contaminants. Anodic stripping voltammetry (ASV) is recognized as one of the more powerful methods to determine trace metal ions by using a pre-concentration step and electrochemical stripping measurements of the analytes. In addition to this, the said method is also advantageous because of its simplicity, better sensitivity, cost-effectiveness, high stability, and suitability to determine multiple analytes [1-3].

The use of pencil graphite electrodes (PGE) as the working electrode in ASV is advantageous due to the good stability of graphite over other forms of carbon. Pencil graphite electrodes are user-friendly and are easily disposable [4]. The surfaces of these electrodes do not require to be cleaned in between measurements thus saving time. In comparison to other electrodes, the researchers stated that pencil graphite electrodes exhibit more sensitivity, less background currents, and good reproducibility. Their surface areas can also be controlled, enabling the analysis of substances and samples with low concentration without requiring a deposition step. Aside from this, pencils are widely available, and come in various options depending on their graphite and clay content; they are also low in cost and easily reproducible, compared to other types of electrodes, such as glassy carbon electrodes (GCE). Graphite pencil electrodes can be modified in various ways: with nanostructures, polymers, or both together, with which the sensitivity, selectivity and redox capacity of the pencil electrode may improve [5-14].

Bismuth is a metal that has low thermal conductivity and exhibits natural diamagnetism [15]. In comparison to other heavy metals, it displays a lower toxicity which can be attributed to the insolubility of bismuth salts in water. It has been utilized in various fields for the production of materials such as electrodes, ceramics, magnets, and x-ray diagnostic media. Bismuth-modified electrodes are already comparable to their mercury counterparts in their properties. In addition to this, bismuth is also more advantageous because it is solid at room temperature, which allows for a wider scope for bismuth-based electrode configurations. Bismuth-modified electrodes have already been used in various real sample analyses, including in testing certain water sources, such as river, sea, rain and tap water, and in relation to this study, also in wastewaters as well [16-21].

Nanoparticles (NP) are used as electrode modifiers mainly due to their unique properties that aid in better electroanalysis; these properties include better mass transport, signal-to-noise ratio, and high surface area. Silver is considered the most ideal because silver has the highest electrical conductivity and stability among all metals, however, due to silver being expensive, silver nanoparticles (AgNP) serve as an alternative. These would then contain the benefits of silver, and as well as additional advantages provided by nanoparticles [22]. Electrodes modified with metallic nanoparticles are said to have many applications, mainly increased sensitivity due to a high surface area and surface free energy [23,24].

Nafion, also known as perfluorosulfonic ionomer, is stated to be a polymer with high corrosion resistance, excellent temperature stability, and good conductivity [25,26]. It is considered to be an excellent exchanger of cations and is also non-electroactive and insoluble in water. Furthermore, it has been used for various studies in analytical chemistry such as voltammetric analysis of heavy metals due to its good ion selectivity [27-36]. Nafion is used as an electrode modifier due to its capability to decrease surface interference and to better the mechanical stability thereby enhancing the sensitivity of the electrode.

In this study, the effectiveness of a fabricated pencil graphite electrode modified with silver nanoparticles (AgNP), bismuth (Bi), and Nafion® in the electrochemical detection of trace heavy metals in wastewater is determined.

2. METHODOLOGY

2.1. Chemicals and reagents

Bismuth nanopowder was purchased from Luoyang Tongrun Info Technology Co., Ltd. (Luoyang City, Henan, China). Silver nanopowder, sodium chloride, lead chloride, and cadmium chloride were purchased from Sigma-Aldrich (Sigma-Aldrich Pte Ltd, Singapore).

2.2. Glassware and equipment

A BOSCH SAE200 electronic balance (BOSCH-Wägesysteme GmbH, Jungingen, Germany) was used to measure the amounts of bismuth nanopowder, silver nanopowder, cadmium chloride, lead chloride, and sodium chloride. A Transferpette®S micropipette (Sigma-Aldrich Pte Ltd, Singapore) was used in drop coating the casting solutions onto the surface of the pencil graphite electrodes. All glassware were put into a BANDELIN SONOREX ultrasonic bath (BANDELIN electronic GmbH & Co. KG, Berlin, Germany) for cleaning. A BST8-stat potentiostat/galvanostat (MTI Corporation, Richmond, CA, USA) was used for the acquisition of the voltammograms. An AA-6300 Shimadzu atomic absorption spectrophotometer was used in atomic absorption spectroscopy (AAS) analysis.

2.3 Preparation of Pencil Graphite Electrodes

Commercially available 2HB pencils were cracked open to extract the graphite lead rod which was sliced into segments measuring 5 cm in length. One end of each segment was polished sequentially with sandpaper until no visible cracks could be seen. The lead segments were placed in a petri dish with ethanol and placed in a Bandelin Sonorex ultrasonicator bath for 15 minutes. These were left to air dry for two hours. Afterward, the lead rods were wrapped with Teflon tape with the polished tip exposed.

2.4 Fabrication of AgNP/Bi/Nafion Modified PGE

The modified electrodes were fabricated by depositing AgNP/Bi/Nafion® films on the PGEs using the drop coating method. The casting solution was prepared by diluting 5 ml of 15% Nafion® with 4.667 ml isopropanol to produce 1% Nafion solution. The solution was then mixed with silver nanoparticles and bismuth powder and ultrasonicated for 2 hours. To determine the best electrode, the amounts of both silver nanoparticles and bismuth powder in the casting solution were varied at 1 mg, 2 mg, and 3 mg. With a Transferpette® micropipette, the casting solutions were deposited on the prepared PGEs. The electrodes were then left to air dry for 2 hours.

2.5 Preparation of Stock Solutions

Solutions with 10 parts per million (ppm) of cadmium chloride ($CdCl_2$) and lead chloride ($PbCl_2$) were prepared. Cadmium chloride of mass 0.0016 g and 0.0013 g $PbCl_2$ were added to a solution of 0.5844 g NaCl and 100 ml deionized water. The stock solutions were sonicated for 15 minutes. To obtain the calibration curve, the prepared stock solutions were further diluted to produce 100 ppb, 250 ppb, 500 ppb, 750 ppb and 1000 ppb each of $CdCl_2$ and $PbCl_2$ solutions.

2.6 Anodic Stripping Voltammetry

Anodic stripping voltammetry was conducted with the use of the BST8 Potentiostat. For the three-electrode set-up, the counter electrode utilized in the study was a platinum coil while the reference electrode was the saturated calomel electrode. The AgNP/Bismuth/Nafion® modified pencil graphite electrode served as the working electrode. A sodium chloride solution was used as the electrolyte. The initial potential was set to -0.9V and the scan rate was set to 100mV/s. For the optimization of the ASV parameters, the accumulation time was varied from 15 seconds to 3 min, with 15 seconds interval and the deposition time was varied from 5 seconds to 45 seconds with 5 seconds interval.

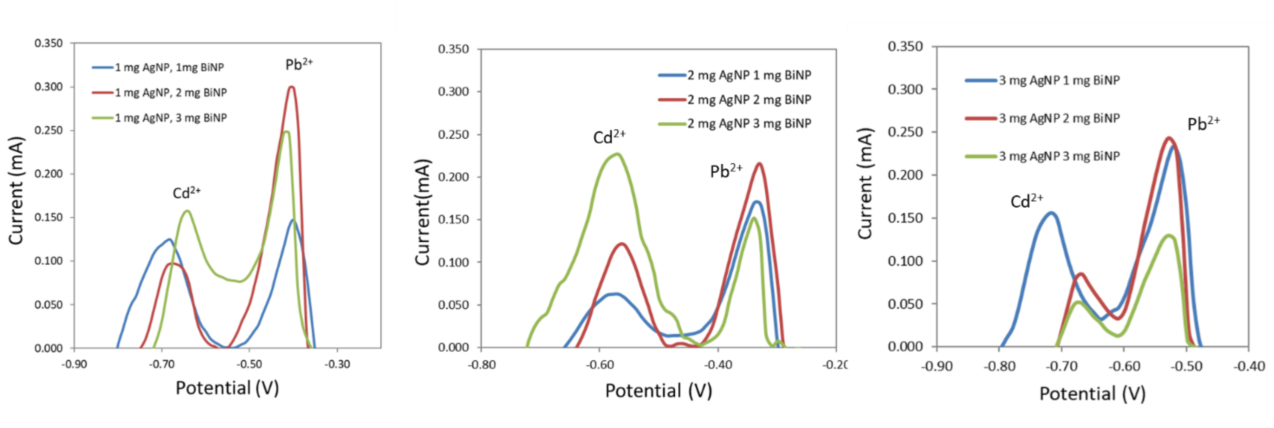
2.7 Real Sample Analysis of Wastewater

Wastewater obtained from a treatment plant was filtered using a filter paper and then sonicated for 15 minutes. The resulting filtrate was analyzed using ASV and AAS in order to determine its heavy metal content.

3. RESULTS AND DISCUSSION

3.1 Determination of the Best Modified PGE

The concentration of the silver nanoparticles was set at 1 mg, 2 mg, and 3 mg per 5 ml Nafion® solution. The amount of bismuth powder was varied from 1 mg to 3 mg for each of the three concentrations of the AgNPs. Anodic stripping voltammetry was utilized for the detection of Cd^{2+} and Pb^{2+} in the electrolyte solution. The accumulation time was set to 45 seconds, the deposition time to 15 seconds, the rest period to 15 seconds, and the scan rate to 100 mV/s. Figure 1 shows the voltammograms obtained from the ASV runs and Fig. 2 shows the comparison of anodic current peaks obtained for each electrode.



(a) (b) (c)

Figure 1. Voltammograms (a) for 1 mg AgNP with Bi varied at 1mg, 2mg, and 3 mg, (b) for 2 mg AgNP varying Bi varied at 1 mg, 2mg, and 3 mg, and (c) for 3 mg AgNP with Bi varied at 1 mg, 2 mg, and 3 mg for the simultaneous the detection of Cd^{2+} and Pb^{2+}.

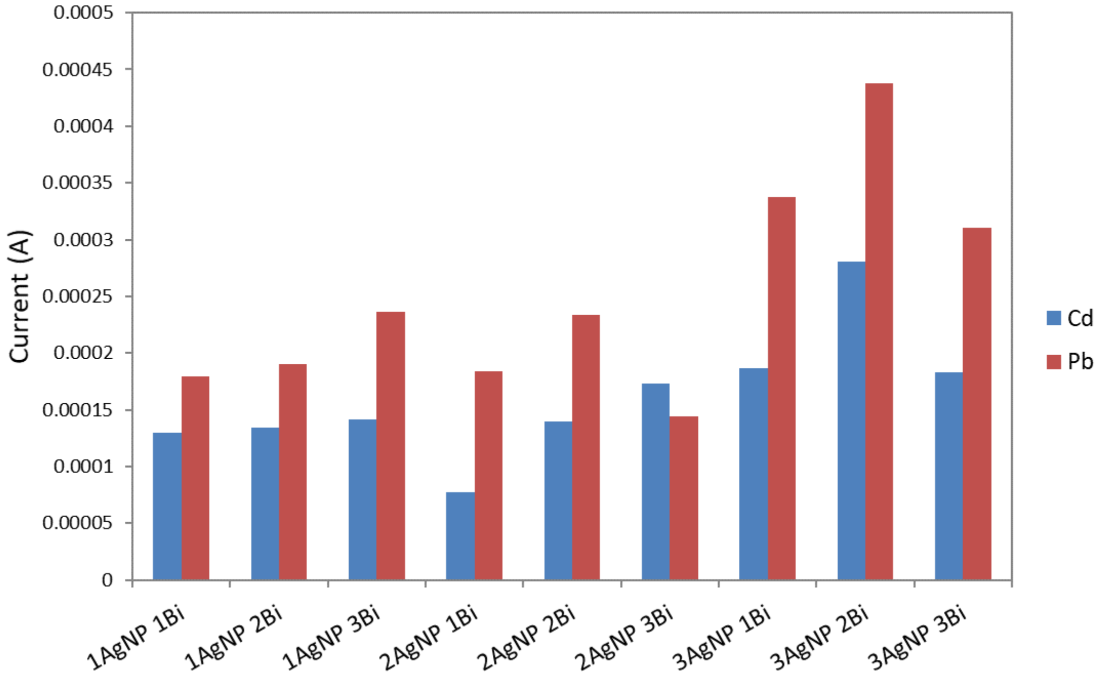


Figure 2. Anodic current peaks for various amounts of AgNPs and Bi for the simultaneous detection of Cd^{2+} and Pb^{2+}.

In general, the anodic peak current increased as the amounts of AgNP and Bi were increased. This can be attributed to the increase in the electrical conductivity and the rate of electron transfer of the electrode as the amounts of AgNP and Bi were increased [34,36,]. Also, the nanoparticles increased the surface area of the electrode [19]. However, increasing the AgNP content higher than 2mg did not further enhance the current signal. Thus, 2mg was chosen as the optimized amount of AgNP. Among the electrodes fabricated, it was the electrode with 3 mg AgNP and 2 mg Bi that exhibited the highest anodic current peak. Thus, it was the electrode used for the acquisition of the optimum measurements.

3.2 Characterization of the Modified Electrode

The morphological characterization of the modified electrode was performed with field emission scanning electron microscopy (FESEM-EDX). The FESEM-EDX analysis exhibited the morphological characteristics of both AgNPs and Bi respectively. The FESEM image shown in Fig. 3 (a) revealed the presence of both AgNPs and Bi on the electrode surface. In the EDX point analysis of the AgNPs/Bi/Nafion® modified electrode, the purity of the AgNPs, Bi and Nafion® were verified as shown in Fig. 3 (b) and (c). Spectrum 1 showed 71.9% of Ag and spectrum 3 showed 68.9% Bi. The Nafion® component of the modified electrode is responsible for the remaining elements such as fluorine (F), oxygen (O) and sulfur (S). The routine cleaning of the electrode can be attributed to the presence of aluminum (Al) in the EDX point analysis as alumina slurry was utilized in the process. The presence of the other elements is due to the inherent impurities of the PGE.

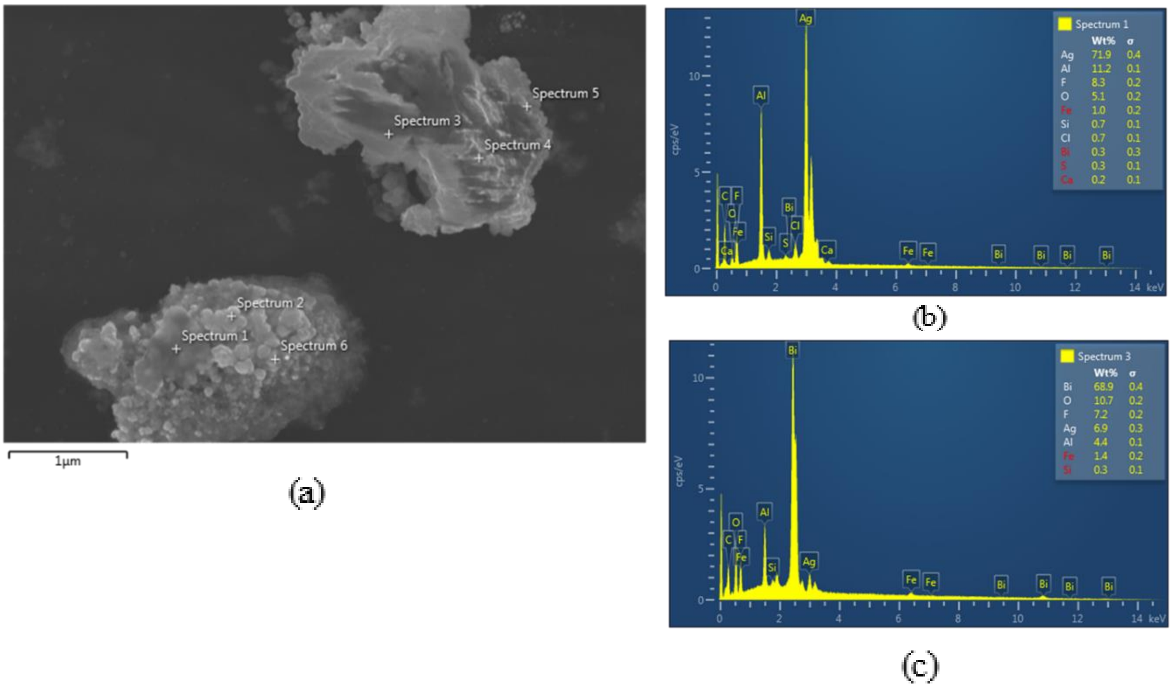


Figure 3. (a) FESEM with (b) & (c) EDX point analysis of modified electrode surface.

3.2 Optimization of ASV Parameters

3.2.1 Accumulation Time

The accumulation time was varied from 15 s to 3 min, with an interval of 15 s while the deposition time and rest period were kept constant at 15 s, and the scan rate at 100 mV/s. Figure 4 shows the voltammograms and the comparison of the peak currents at varying accumulation time for the detection of Cd^{2+} and Pb^{2+}. As shown in the figure, 2 min yielded the highest detection of both Cd^{2+} and Pb^{2+}, and as the time increased further from 2 min, the level of detection decreased, until eventually no Cd^{2+} nor Pb^{2+} were detected at all. Thus, 2 min was chosen as the optimum time for the succeeding ASV runs.

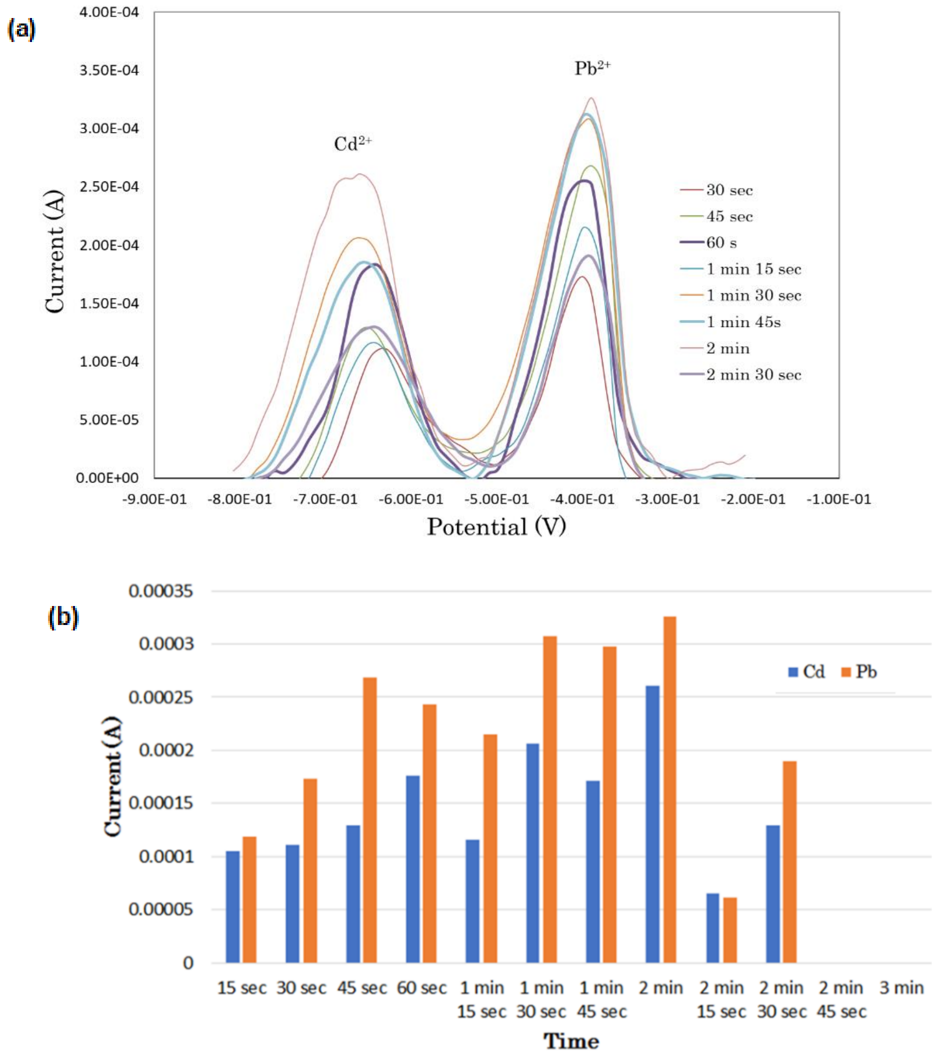


Figure 4. (a) Voltammograms for the accumulation time optimization. (b) Comparison of the peak currents of Cd^{2+} and Pb^{2+} at varying accumulation time.

3.2.2 Deposition Time

The deposition time was varied from 5 s to 45 s with 5 s interval while the accumulation time was kept constant at 2 min, rest period at 15 s and the scan rate at 100 mV/s. Figure 5 shows the voltammograms and the comparison of the current peaks for this parameter. As can be observed from the figure, the anodic peak current increased as the deposition time increased. However, after 15 seconds the current peak has noticeably decreased. Therefore, the optimum value for the deposition time was 15 s.

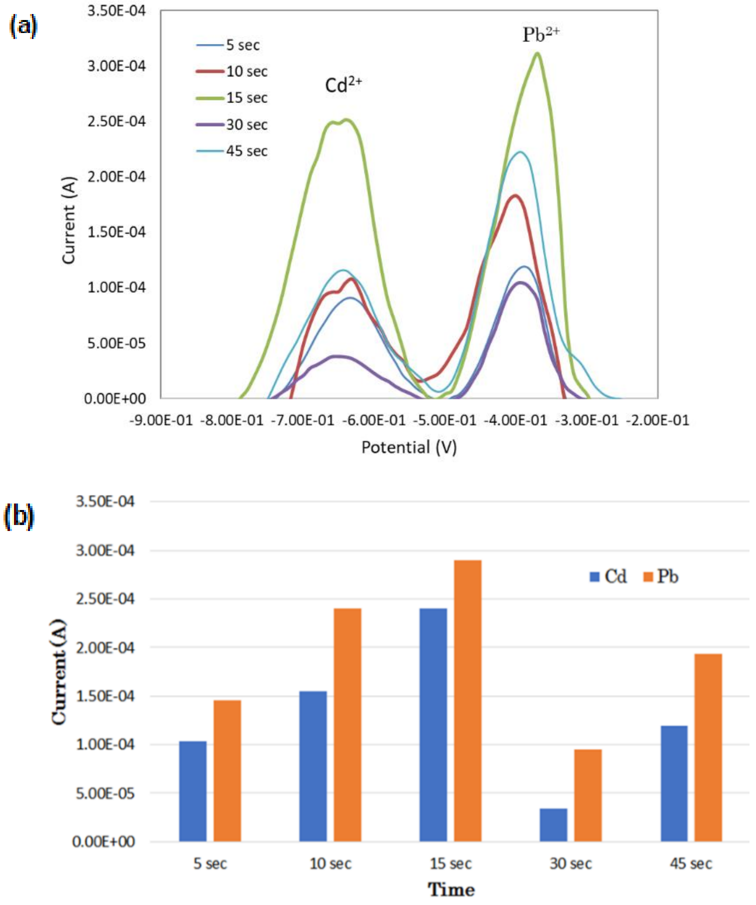


Figure 5. (a) Voltammograms for the deposition time optimization. (b) Comparison of the peak currents of Cd^{2+} and Pb^{2+} at varying deposition time.

3.3 Calibration Curves

The calibration curves of the optimized electrode were obtained by varying the concentrations of Cd^{2+} and Pb^{2+} from 100 ppb to 1000 ppb. Figure 6 shows the ASV curves for the increasing concentrations of Cd^{2+} and Pb^{2+} while Figs. 7 and 8 show the calibration plots. It can be seen from the plots that there is a strong line correlation between the heavy metal concentration and the reduction current which indicates that more heavy metals accumulate on the electrode surface as the heavy metal concentration was increased. This result was also observed in previous studies [27-35].

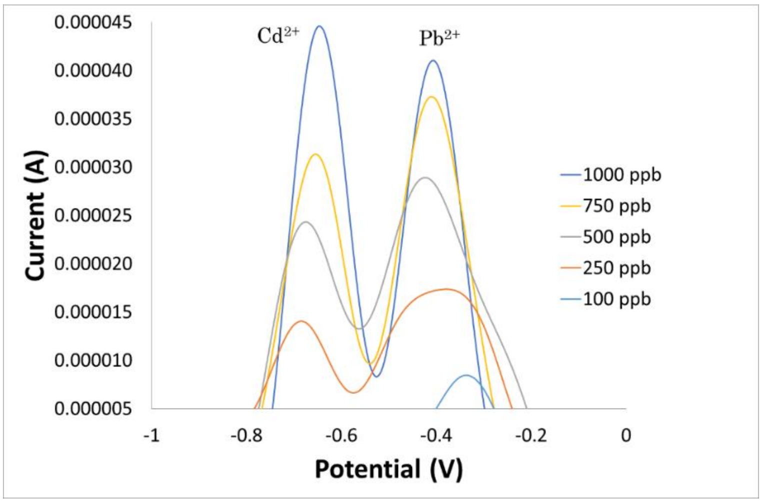


Figure 6. Voltammograms of Cd^{2+} and Pb^{2+}, with concentrations each at 100 ppb, 250 ppb, 500 ppb, 750 ppb, and 1000 ppb.

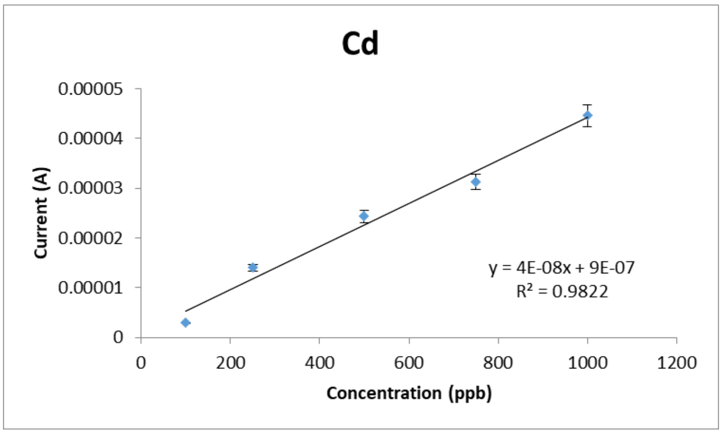


Figure 7. Calibration plot of peak current versus Cd^{2+} concentration.

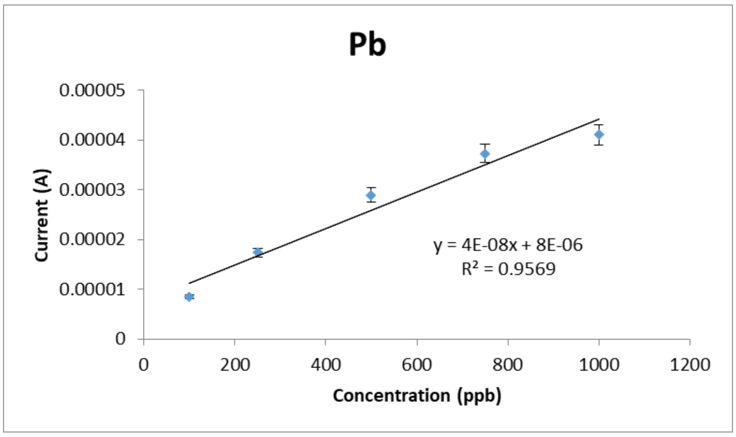


Figure 8. Calibration plot of peak current versus Pb^{2+} concentration in ppb

3.4 Limit of Detection and Limit of Quantification

Both the limit of detection (LOD) and limit of quantification (LOQ) were determined using the calibration curves. The LOD is 0.19 ppb for Cd^{2+} and 0.30 ppb for Pb^{2+}. The LOQ of the electrode for Cd^{2+} is 568 ppb and 894 ppb for Pb^{2+}. Table 1 shows the comparison of the LOD of the AgNP/Bi/Nafion modified PGE with other modified electrodes in previous works. It can be seen from the table that the modified PGE in this study has a lower LOD than most of the electrodes reported previously.

Table 1. Performance comparison of the modified PGE with previous works.

Electrode	Modifier	Method	LOD	Reference
Glassy carbon	$[Ru(bpy)_3]^{2+}$/graphene/Nafion	DPV	Cd - 49 ppb Pb - 48 ppb	[33]
Indium Tin Oxide	$[Ru(NH_3)_6]^{3+}$/Nafion	ASV	Cd & Pb - 500 ppb	[27]
Graphene paste	AgNP	ASV	Cd - 17 ppb Pb - 12 ppb	[34]
Pencil graphite	Electrochemically reduced graphene oxide	SWASV	Cd – 0.09 ppb Pb – 0.12 ppb	[37]
Pencil graphite	AgNP/Bi/Nafion	ASV	Cd – 0.19 ppb Pb – 0.30 ppb	This work

3.5 Real Sample Analysis of Wastewater

To demonstrate the utility of the fabricated electrode in sensing applications, wastewater filtrate was tested using ASV in order to detect its heavy metal content. Figure 8 shows the voltammogram obtained from the ASV analysis of the sample. The voltammograms obtained from the ASV reveal the presence of Cd^{2+} and Pb^{2+} as well as Cu^{2+} and Mn^{2+} in the wastewater sample. The concentrations of Cd^{2+} and Pb^{2+} present in the sample were determined by substituting the values of the resulting anodic current peaks as the y-values in the calibration curve equations. The calculated concentrations are 57.5 ppb for Cd^{2+} and 597.5 ppb for Pb^{2+}. The concentrations of Cu^{2+} and Mn^{2+} were not determined since the electrode was calibrated for Cd^{2+} and Pb^{2+} only. Table 2 shows the ASV and AAS results of the real sample analysis. As can be seen from the table, the concentration detected via ASV for Cd^{2+} is closer to the value detected by AAS than that for Pb^{2+}. This may be attributed to the non-homogeneity of the assay when the measurements were taken [34].

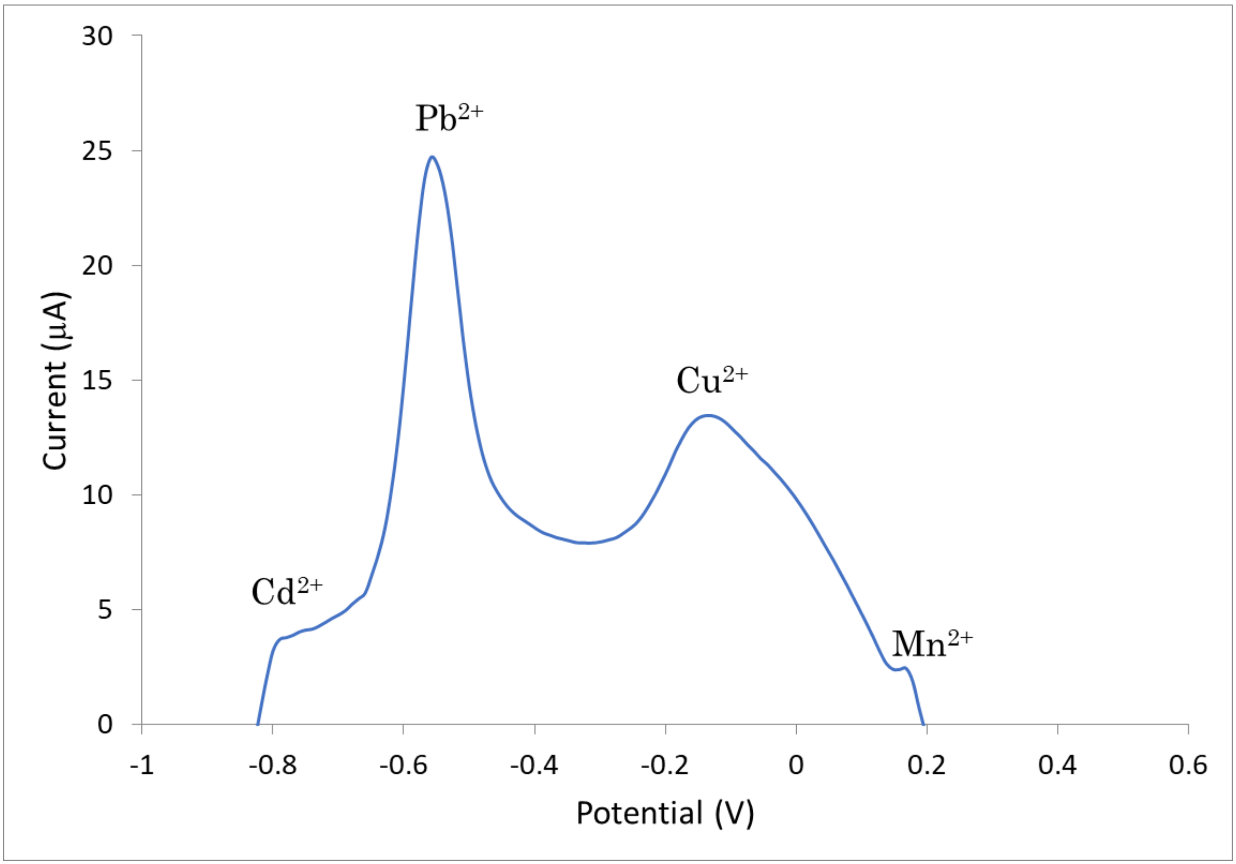


Figure 9. Voltammogram obtained from the analysis of wastewater filtrate.

Table 2. Comparison of ASV and AAS determination of Cd^{2+}and Pb^{2+} in real wastewater sample.

Heavy Metal	ASV (ppb)	AAS (ppb)	%Difference
Cadmium	57.5	40.9	33.7%
Lead	597.5	72.8	156.5%

4. CONCLUSIONS

Pencil graphite electrodes modified with AgNPs, Bi, and Nafion® using the drop coating method were successfully fabricated in this study. They were found to be effective in detecting trace heavy metals. Among the nine concentration ratios modified for the substrate, 3 mg AgNP and 2 mg Bi produced the highest anodic current peaks, and were therefore chosen to be the electrode in detecting Cd^{2+} and Pb^{2+}. The optimum parameters for accumulation time and deposition time were 2 minutes and

15 seconds, respectively. The Pearson coefficients in the calibration plot of Cd^{2+} and Pb^{2+} are 0.9822 and 0.9569, respectively. The ASV runs for the wastewater sample reveal the presence of Cd^{2+} and Pb^{2+}, as well as Cu^{2+} and Mn^{2+}.

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