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Effect of Binary Nanoparticles on Signals Enhancement of Electrochemical Sensors

Woli, T. O[1, 2], Azeez, M. A[1, 3] Ibrahim L. A[1], Olatinwo, F. T[1], Muhammed, K. O[1] and Orilonise, A[1]

[1]Department of Mechanical Engineering, Federal Polytechnic Offa, P.M.B. 420, Offa, Kwara State.
[2]Faculty of Mechanical Engineering, Universiti of Teknologi Malaysia, 81310 Skudai, Johor Bahru.
[3]School of Materials Engineering, university Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia
Corresponding E-mail: taiyewoli@gmail.com

Abstract: *A novel approach has been employed to create a highly responsive system capable of detecting Pb (II), Cd (II), and Cu (II) ions in aqueous solutions. This system utilizes a modified indium tin oxide (ITO) electrode coated with Nafion, graphene, and Mn3O4. The detection method employed is Square Wave Anodic Stripping Voltammetry. The electrode modified with Nafion/Graphene/Mn3O4NPs/ITO at a concentration of 5mg/mL exhibits a high sensitivity for the detection of Pb (II), Cd (II), and Cu (II) ions. The sensitivity values are 55.25 µA/cm2 for Pb (II), 66.125 µA/cm2 for Cd (II), and 80.375 µA/cm2 for Cu (II). The corresponding limits of detection (LOD) for Pb (II), Cd (II), and Cu (II) ions are 346.46 µg/L, 241.15 µg/L, and 253.23 µg/L, respectively. These measurements were obtained within the linear range of 20-400 µg/L for the detection of Cd (II), Pb (II), and Cu (II) ions. In addition, the electrode modified with Nafion/Graphene/Mn3O4NPs/ITO was effectively utilized for the analysis of Cd (II), Pb (II), and Cu (II) ions in seawater samples. This analysis resulted in the detection of stripping peaks for Cd (II), Pb (II), and Cu (II) ions, with corresponding sensitivities of 77.667 µA/cm2 for Cd (II), 20.958 µA/cm2 for Pb (II), and 30.125 µA/cm2 for Cu (II). The built-modified electrodes exhibit significant promise in the realm of heavy metal detection.*

Keywords: *Graphene/Mn3O4 nanoparticles, Limit of Detection (LOD), Simultaneous detection; Sensitivity, Lead(ll), Cadmium (ll), Copper (ll)..*

1.0 Introduction

Heavy metals, specifically those in the 4th period of the modern periodic table, possess considerable biological importance when present in small quantities. The bodily functions of certain metals, such as selenium for hormone function, nickel for cellular growth, and manganese and vanadium for enzyme functioning, are significant examples of their importance in biological systems. Arsenic plays a crucial role in these functions. Moreover, these essential components must be present in minimal quantities to maintain human well-being, as an excessive accumulation of these substances within the body might lead to adverse health effects. Heavy metals can generally be characterized by their elevated density and biological significance when present in small quantities (Briffa *et al.,* 2020; Duffus, 2002; Mitra et al., 2022; Sonone *et al.,* 2020).

Numerous studies have revealed that excessive buildup of toxic heavy metals can significantly impact several organs, such as the brain, lungs, kidneys, liver, and human brain, as well as exert detrimental effects on the immune system and nervous systems of individuals (Isangedighi & David, 2019; Järup, 2003; Kumar *et al.*, 2018). Certain heavy metals tend to form complexes with biological ligands that possess nitrogen, sulphur, and oxygen. Consequently, even small amounts of specific heavy metal ions, such as Ni^{2+}, Cu^{2+}, Cd^{2+}, and Cr^{2+}, can adversely affect dental health. Similarly, As^{3+}, Pb^{2+}, and Hg2+ ions can affect the central nervous system, while the liver and kidneys may experience detrimental effects due to Cd^{2+}, Cu^{2+}, Pb^{2+}, and Hg^{2+} ions. Hence, developing a sensitive, rapid, and straightforward technique for detecting them is paramount (Sofu *et al.,* 2015).

Numerous analytical methodologies have been utilized to assess heavy metal concentrations in various environmental settings. The presence of heavy metal ions (HMIs) in the environment has been identified through the utilization of different analytical techniques, including atomic fluorescence spectrometry (AFS), atomic absorption spectrometry (AAS), fluorescence spectrophotometry, inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) (Lu *et al.*, 2016).

Despite the advantages associated with spectroscopic techniques, such as their ability to provide detailed information on samples, it is essential to acknowledge that some limitations characterize these methods. These limitations include the high cost of the required instrumentation, the complexity of sample preparation procedures, the need for operators with significant expertise, the lengthy analysis time, and the impracticality of doing on-site measurements.

The utilization of sensors, such as gravimetric, chemical, optical, biosensors, and electrochemical sensors, has gained recognition as a promising approach for the detection and quantification of heavy metal ions due to their advantageous characteristics, including high sensitivity, rapid analytical time, selectivity, mobility, affordability, and simplicity (Ali *et al.,* 2022; Attaallah & Amine, 2022; Yang *et al.*, 2015). The electrochemical methodology is a subject of interest in heavy metal ion detection. The approach above has several advantages: enhanced accuracy, on-site sensing capabilities, simplicity, heightened sensitivity, multiple detection efficacy, and cost-efficiency (Zhang *et al.,* 2016).

The efficacy of bulk electrodes in electrochemical sensors for detecting heavy metals is limited, necessitating modifications to boost sensitivity and reduce the limit of detection (LOD)—the restricted active surface area of the electrode results in diminished sensitivity and selectivity of the electrochemical sensor. According to Lee et al. (2016), using a mercury electrode is highly advantageous in electrochemical sensors because of its remarkable ability to pre-concentrate heavy metals.

Nevertheless, due to the inherent toxicity of mercury, there is a growing demand for alternative electrodes that are free from this hazardous substance. Bismuth is a highly attractive substitute electrode for electrochemical measurements due to its comparable performance to mercury. The features of bismuth are associated with its propensity to create a "fused alloy" with heavy metals and undergo oxidation in the presence of air, rendering it non-sustainable (Bagheri *et al.*, 2015).

The recent development of integrating nanomaterials with electrochemical detecting device platforms has resulted in a highly influential analytical method for detecting heavy metal

ions. Manganese oxide nanoparticles (Mn3O4NPs) possess a high theoretical specific capacitance, excellent chemical stability, environmentally friendly characteristics, and cost-effectiveness. These attributes provide Mn3O4NPs with a remarkable option for identifying and quantifying heavy metal ions (Li *et al.*, 2015).

In the study conducted by Adarakatti *et al.* (2018), utilizing Mn3O4 nanoparticles functionalized with calyx as an electrochemical sensor was explored to detect the presence of Cd^{2+} and Pb^{2+} particles in aqueous medium. The detection method employed was differential pulse anodic stripping voltammetry (DPASV). Their research used Mn3O4/graphitic carbon sensors to detect Cd^{2+}, Pb^{2+}, and Hg^{2+}. The linear range for detection spanned from 20 to 680nm with a corresponding limit of detection values of $0.51x10^{-11}$ m, $0.48\ x10^{-11}$ m, and $9.66\ x10^{-11}$ m, respectively. Therefore, this work primarily investigated the application of Nafion/Graphene/Mn3O4NPs to modify the ITO electrode to detect heavy metal ions in which Nafion is a binding agent and enhances the sensitivity for detecting heavy metal ions.

2.0 Experimental Section

2.1 Materials and Methods

Table 2.1 presents comprehensive information regarding the raw materials and chemicals utilized in the research study, which include hydrogen peroxide, ammonia hydroxide, propanol, ethanol, potassium chloride, potassium ferricyanide, copper II ion solution, lead II ion solution, and cadmium II ion solution.

Table 2.1 Details raw materials and chemicals used for the research work.

Process	Chemical/ reagent	Function	CAS No	Assay (%)	Manufacture details (g/mol)	Supplier
Cleaning of indium tin electrode (ITO)	Hydrogen peroxide (H2O2)	Cleaning	7722-84-1	30.0	Mw = 34.015	Merck
		Cleaning		25.0	Mw = 35.046	Merck

	Ammonia hydroxide (NH4OH)	Modification	1336-21-6	99.9	Mw = 60.095	Merck
	Propanol (C3H8O)		67-63-0			
Fabrication of ITO electrode	Ethanol (C2H5O)	Modification	67-17-5	96.0	Mw = 46.07	Merck
Heavy metal ions detection	Potassium chloride (KCl)	Electrolyte	7447-40-7	99.0	Mw = 74.55	Merck
	Potassium ferricyanide K3[Fe(CN)6]	Electrolyte	13746-66-2	99.0	Mw = 329.24	Merck
	Acetate buffer	Electrolyte			Mw = 3M	Sigmal Adrich
	Cd (II) standard solution				Concentration =100ppm	Sigmal Adrich
	Pb (II) standard solution				Concentration =100ppm	Sigmal Adrich
	Cu (II) standard solution				Concentration =100ppm	Sigmal Adrich

2.2 Modification of Electrode using the drop-casting method

A 50 µL solution containing a concentration of Graphene/Mn3O4NPs was applied onto the surface of a cleaned ITO electrode using the drop-casting method. The electrode was subsequently dried in an oven at 80oC for 30 minutes. Following 30 minutes, the samples were extracted from an even. Later, drop-casting applied an additional 50µL of Graphene/Mn3O4NPs to the models. The samples were then dried for another 30 minutes at a temperature of 180oC. Subsequently, a volume of 20µL of Nafion was utilized as a binding agent to securely adhere the nanoparticles onto the surface of the modified electrode, specifically the Nafion/Graphene/Mn3O4NPs/ITO composite. Subsequently, an investigation was conducted on the electrochemical characteristics of the modified electrode, including Nafion/graphene/Mn3O4NPs/ITO, employing cyclic voltammetry (CV) as the analytical technique. The study used square wave anodic stripping voltammetry (SWASV) to examine the sensitivity and selectivity of modified Nafion/graphene/Mn3O4NPs/ITO electrodes.

2.2 Electrochemical Measurement of the Modified Electrode

This study conducted the electrochemical measurement analysis using a DropSens-stat 400 Bipotentiostat/galvanostat (DropSens, Spain). The reference electrode used in the experiment was

Ag/AgCl, while the counter electrode was made of platinum (Pt). Conversely, the working electrode was a modified glass electrode with indium tin oxide (ITO) coating. The electrodes were afterwards linked to the potentiate, and the output signal was displayed on the computer through a cable connection. This setup facilitated the detection of heavy metal ions.

2.3 Cyclic Voltammetry

The utilization of cyclic voltammetry analysis is vital within this investigation as it enables the examination of the charged electrodes' conductivity and electron transfer rate. The cyclic voltammetry experiment had a potential scan range of 0.01 and a scan rate of 0.05 V/s. A solution containing 5.0 × 10-3 mol/L of potassium ferrocyanide (III) [Fe (CN)6)$^{3-}$] in a 0.1 mol/L potassium chloride solution with a pH of 7.0 was employed as the supporting electrolyte.

2.5 Square Wave Anodic Stripping Voltammetry

The concentration of 20 µg/L, 40 µg/L, 60 µg/L, 80 µg/L, 100 µg/L, 120 µg/L, 200 µg/L, and 400 µg/L was utilized to conduct individual and simultaneous electrochemical sensing for Pb (II), Cd (II), and Cu (II) using SWASV analysis. The initial concentration of Pb (II), Cd (II), and Cu (II) was reduced from 1000 parts per million (ppm) to 1 ppm using a 0.1 molar (M) acetate buffer solution with a pH of 4.5, which served as a supporting electrolyte. In addition, 0.2M acetate buffer solution was employed to dilute 1000 parts per billion (ppb) of Pb (II), Cd (II), and Cu (II) individually, resulting in the production of solutions containing 100 parts per million (ppm) of Pb (II), Cd (II), and Cu (II).

The experiment involved conducting Sequential Wave Adsorptive Stripping Voltammetry (SWASV) with continuous stirring using a magnetic stirrer. The SWASV technique was applied separately and concurrently for the analysis of Pb (II), Cd (II), and Cu (II) to determine their respective sensitivity and selectivity. Following the SWASV study, further investigation involved examining the stripping response of the analyte, specifically Cd (II) at concentrations ranging from 20-400 µg/L, Pb (II) at concentrations ranging from 20-400 µg/L, and Cu (II) at concentrations ranging from 20-400 µg/L. The obtained linear calibration plot was subsequently utilized to ascertain the limit of detection (LOD), linear range, and sensitivity of the modified electrode. Ultimately, the electrode that underwent modifications was employed in a practical setting to detect the presence of Cd (II), Pb (II), and Cu (II) ions in seawater.

3.0 Result and Discussion

3.1 Electrochemical Characterization of Nafion/Graphene/Mn3O4NPs/ITO modified electrode

The electrochemical performance of an electrode modified with a 5mg/mL concentration of Nafion/Graphene/Mn3O4NPs/ITO was examined using the cyclic voltammetry (CV) technique. A comprehensive examination of CV was performed within a potential range spanning from -0.5 to +0.7 volts in a five-millimolar concentration of $[Fe(CN)6]^{3-}$ and a 0.1 molar concentration of KCl solution. Figure 3.1 compares the concentration of 5mg/ml of Mn3O4NPs/ITO modified electrode and the concentration of 5mg/mL of Graphene/Mn3O4NPs/ITO modified electrode.

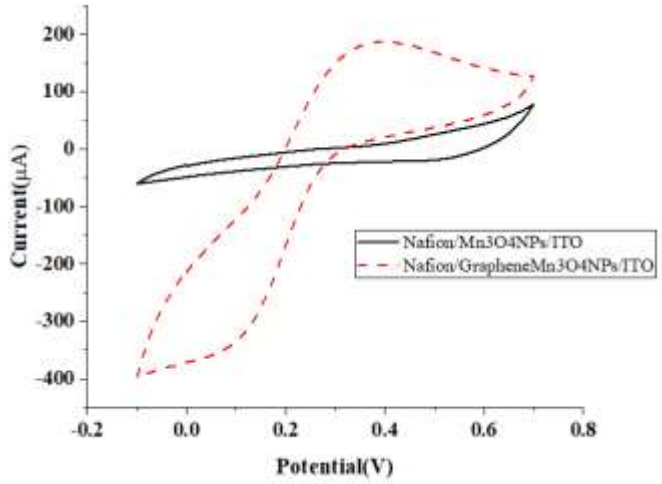

Figure 3.1: Comparing cyclic voltammograms of 5mg/mL Nafion/Mn3O4NPs/ITO modified electrode and graphene/Mn3O4NPs/ITO modified electrode in 5mM $[Fe(CN)6]^{3-}$ and 0.1M KCl solution as a supporting electrolyte.

The findings indicate that the electrochemical performance was improved by changing the electrode with Graphene/Mn3O4/ITO. This enhancement can be attributed to the increased conductivity resulting from the presence of graphene, as pointed out in the work of Zuo et al. (2019). Graphene enhances conductivity and augments the specific active surface area of the underlying electrode, hence facilitating increased electrolyte conductivity and inducing alterations in mass transport associated with nanoparticle structure. The heightened electrochemical activity may also be attributed to manganese oxides' considerably positive surface charge (Adarakatti et al., 2018). Manganese oxide nanoparticles possess exceptional characteristics, distinguishing them from other metal oxide nanomaterials.

These properties include remarkable catalytic activity, electrochemical stability, cost-effectiveness, ease of synthesis, ability to deliver high charge rapidly, and availability in various forms. This is a similar observation in the work conducted by Falcaro et al. (2016). The Nafion/Graphene/Mn3O4NPs/ITO modified electrode was utilized as an electrochemical sensing platform to detect Cd (II), Pb (II), and Cu (II) in seawater samples, owing to its exceptional properties.

3.2 Individual determination of Cd (II), Pb (II) and Cu (II) using 5mg/mL Nafion/Graphene /Mn3O4NPs/ITO Modified Electrode

In this study, a modified electrode consisting of Nafion/Graphene/Mn3O4NPs/ITO with a concentration of 5mg/mL was utilized as the optimal electrode configuration for the detection of heavy metal ions, specifically Cd (II), Pb (II), and Cu (II), using SWASV analysis. The analysis was performed in a 0.1 M acetate buffer solution with a pH of 4.5 while maintaining continuous stirring. The results of individual detection for Cd (II), Pb (II), and Cu (II) throughout a concentration range of 20-400 µg/L utilizing a modified electrode consisting of Nafion/Mn3O4NPs/Graphene/ITO are presented in Figure 3.2(a-c).

Figure 3.3(a-c) shows the linear calibration plot illustrating the individual measurement of Cd (II), Pb (II), and Cu (II) within a concentration range of 20-40 µg/L. This determination was

achieved utilizing an electrode modified with Nafion/Mn3O4NPs/Graphene/ITO. The peak currents of SWASV were acquired after applying baseline correction, followed by the assessment of calibration curves based on these peak currents. Shifting peaks in the stripping elevation of individual heavy metal ions detection were readily apparent, and this phenomenon can be linked to voltage drop, as Hu et al. (2021) discussed.

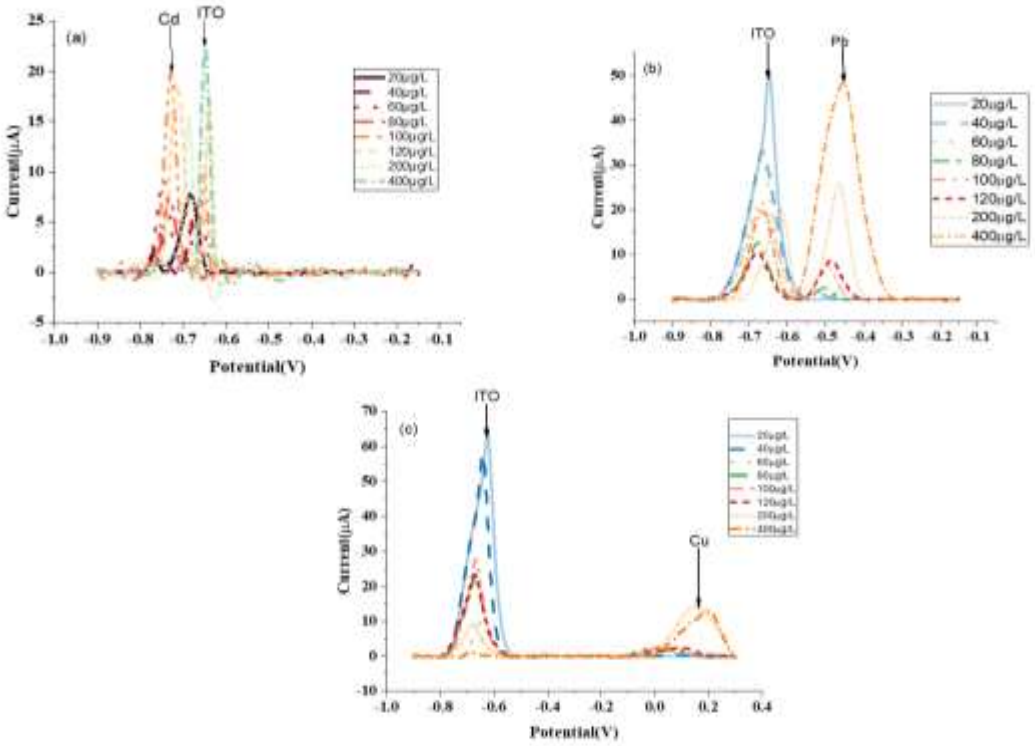

Figure 3.2: SWASV examination of 20-400 µg/L Cd (II), Pb (II), and Cd (II) utilizing 5mg/mL Nafion/Graphene/Mn3O4/ITO modified electrode in 0.1M acetate buffer solution (pH 4.5).

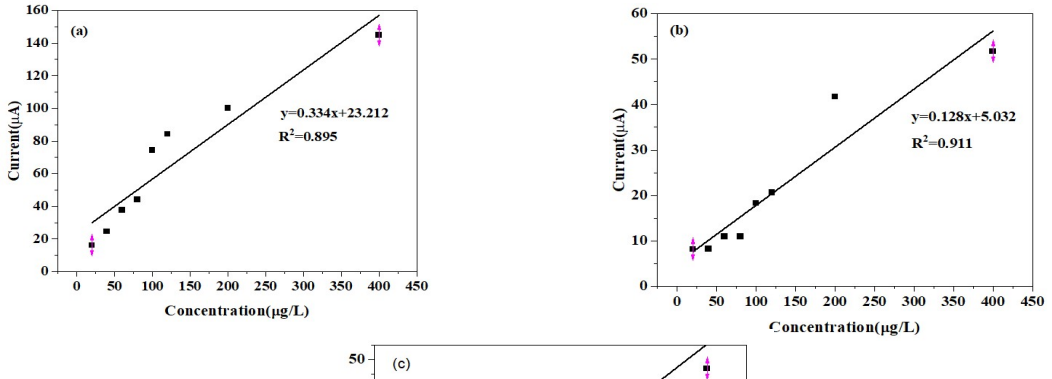

Figure 3.3: Linear calibration plots for (a) 20-400 µg/L of Cd (II), (b) 20-400 µg/L of Pb (II) and (c) 20-400 µg/L of Cu (II) using 5mg/mL Nafion/Graphene/ Mn3O4/ITO modified electrode in 0.1M of acetate buffer solution (pH 4.5).

3.3 Simultaneous determination of Cd (II), Pb (II) and Cu (II) using 5mg/mL Nafion/Graphene /Mn3O4NPs/ITO modified electrode.

The results depicted in Figure 3.4 illustrate the stripping peak obtained from the concurrent detection of Cd (II), Pb (II), and Cu (II) within the concentration range of 20µg/L to 400µg/L. This detection was achieved utilizing an electrode modified with Nafion/Graphene/Mn3O4NPs/ITO. Furthermore, the linear calibration curve plots for the simultaneous detection of heavy metal ions in a 0.1 M acetate buffer solution at pH 4.5, under continuous stirring, are depicted in Figure 3.5(a-c). The potential peaks for Cd (II), Pb (II), and Cu (II) are -0.77 V, -0.53 V, and 0.055 V, respectively. The increase in peak current was seen to be directly proportional to the concentration of the analyte. This phenomenon can be attributed to the augmentation of adsorption sites on the surface of the modified electrode. Table 3.1 presents a summary of the linear equations, correlation coefficients, and limit of detection (LOD = 3σ/S) about the detection of Cd (II), Pb (II), and Cu (II) ions in a 0.1M acetate buffer solution (pH 4.5). The table provides information on both individual and simultaneous detection methods.

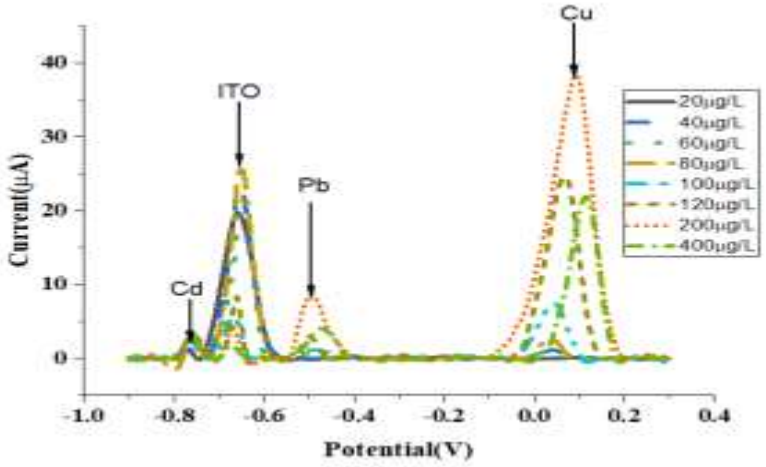

Figure 3.4: SWASV analysis for simultaneous detection for 20 µg/L-400 µg/L of Cd (II), 20 µg/L-400 µg/L of Pb (II), and 20 µg/L-400 µg/L of Cu (II) using Nafion/Graphene/Mn3O4/ ITO modified electrode with deposition potential -1V, deposition time 180s, potential scan range -0.9 to +0.3V

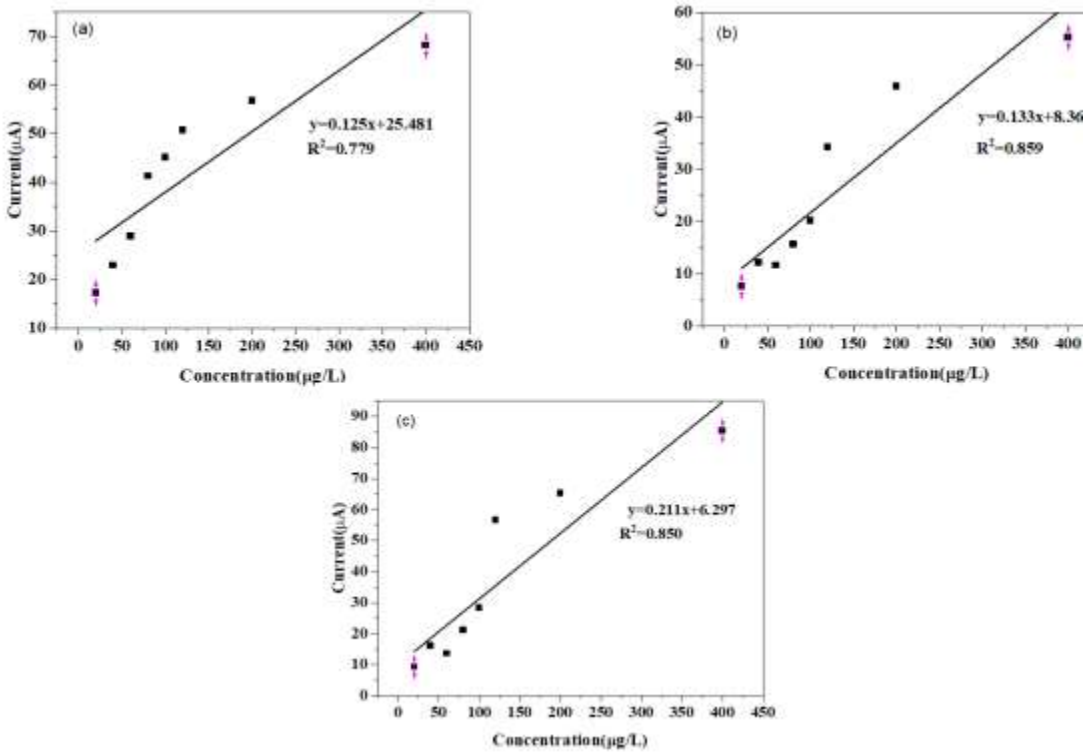

Figure 3.5: Linear calibration plots for (a) 20µg/L-400µg/L of Cd (II), (b) 20 µg/L-400 µg/L of Pb (II), and (c) 20 µg/L-400 µg/L of Cu (II) detection in the same electrolyte within 0.1M of acetate buffer solution (pH 4.5) under constant stirring

Table 3.1: Comparison of individual and simultaneous analysis of Cd (II), Pb (II) and Cu (II) using Nafion/Graphene/Mn3O4/ITO modified electrode.

Analysis	Target heavy metal ions	Deposition time(s)	Linear range(µg/L)	Sensitivity (µA)	Linear equation	Correlation coefficient(R^2)	LOD (µg/L)
Individual	Cd (II)	180	20-400	145.0	Y=0.334x+23.212	0.895	204.080
	Pb (II)	180	20-400	59.708	Y=0.128x+5.032	0.911	185.344
	Cu (II)	180	20-400	48.458	Y=0.105x+10.563	0.906	191.943
Simultaneous	Cd (II)	180	20-400	66.125	Y=0.125+25.481	0.779	346.464
	Pb (II)		20-400	55.25	Y=0.133+8.369	0.859	241.150
	Cu (II)		20-400	80.375	Y=0.211x+6.297	0.850	253.237

Upon analyzing the data presented in the table, a comparison was made between the individual detection of heavy metal ions and the simultaneous detection of heavy metal ions. The findings indicate that simultaneous detection's sensitivity was inferior compared to individual detection. This disparity in sensitivity may be attributed to the presence of intermetallic compounds, which have a detrimental effect on the detection sensitivity. Additionally, the competitive nature of deposition and the interaction of ions during the deposition process may contribute to this discrepancy. This observation holds significance as heavy metal ions are known to be present in environmental water, as reported by other researchers (Hu et al., 2021). Hence, the obtained outcome suggests that the developed Nafion/Graphene/Mn3O4NPs/ITO modified electrode holds the potential for detecting heavy metal ions.

3.5 Seawater Analysis

The main objective of developing this electrochemical platform, which involves the modification of an electrode with Nafion/Graphene/Mn3O4NPs/ITO, was to examine the levels of Cd (II), Pb (II), and Cu (II) in seawater. Figure 3.6 depicts the stripping peak observed during the simultaneous detection of Cd (II), Pb (II), and Cu (II) ions at concentrations of 20 µg/L, 40 µg/L, 60 µg/L, and 80 µg/L. This detection was conducted using an electrode modified with Nafion/Graphene/Mn3O4NPs/ITO. Figures 3.7 (a-c) depict the calibration plots corresponding to the addition of 20 µg/L, 40 µg/L, 60 µg/L, and 80 µg/L of Cd (II), Pb (II), and Cu (II), respectively. The peak currents of SWASV were acquired after applying baseline correction, followed by the evaluation of calibration curves based on these peak currents. The results presented in Table 3.2 demonstrate the utilization of a modified electrode composed of Nafion/Graphene/Mn3O4NPs/ITO to detect heavy metal ions in seawater. The concentrations of 20 µg/L, 40 µg/L, 60 µg/L, and 80 µg/L were employed for the detection of Cd (II), Pb (II), and Cu (II) utilizing the SWASV analytical technique.

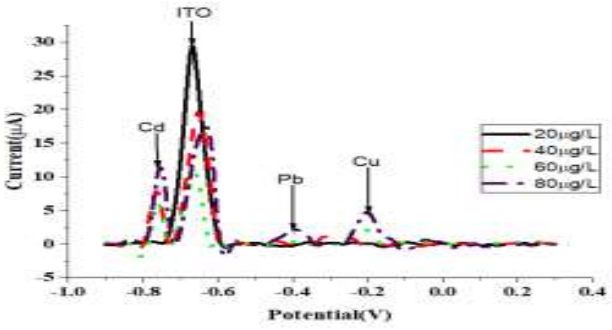

Figure 3.6: (a) Stripping peaks of simultaneous detection for 20µg/L, 40 µg/L, 60 µg/L and 80 µg/L of Cd (II), Pb (II) and Cu (II) in seawater using Nafion/Mn3O4NPs/Graphene/ITO modified electrodes.

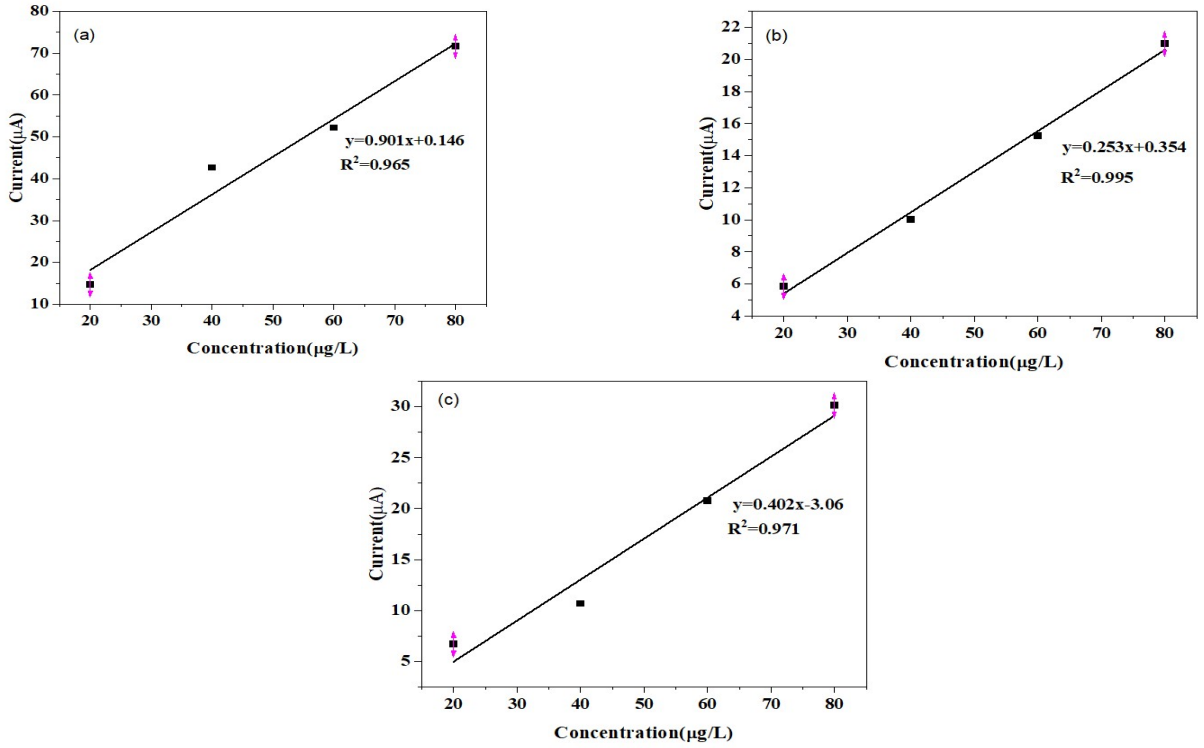

Figure 3.7: Linear calibration plots for (a) 20 µg/L, 40 µg/L, 60 µg/L, and 80 µg/L of Cd (II), (b) 20 µg/L, 40 µg/L, 60 µg/L, and 80 µg/L of Pb (II), and (c) 20 µg/L, 40 µg/L, 60 µg/L, and 80 µg/L of Cu (II) detection in seawater using Nafion/Graphene/Mn3O4NPs/ ITO modified electrodes.

Table 3.2: Determination of trace heavy metal ions in seawater using Nafion/Graphene/Mn3O4NPs/ITO modified electrodes.

Sample	Heavy metal analyte	Concentration added (µg/L)				Correlation coefficient(R^2)	Sensitivity (µA)	Limit of =3δ/S detection(µgL^{-1})	Regression linear equation
Seawater	Cd (II)	20	40	60	80	0.965	76.667	43.947	Y=0.903x+0.146
	Pb (II)	20	40	60	80	0.995	20.958	16.316	Y=0.253x+0.354

	Cu (II)	20	40	60	80	0.971	30.125	39.896	Y=0.402x-3.063

These findings indicated that the novel 5mg/mL Nafion/Graphene/ Mn3O4NPs/ITO modified electrode has a high degree of accuracy and precision and could be applied with confidence to the simultaneous detection of Cd (II), Pb (II), and Cu (II) in seawater samples.

4.0 Conclusion

The CV study examined the electrochemical performance of the Nafion/Graphene/Mn3O4NPs composite. Additionally, SWASV analysis was carried out to evaluate the sensitivity and selectivity of the Nafion/Graphene/Mn3O4NPs/ITO modified electrode. The electrode changed with an optimized concentration of 5mg/mL of Nafion/Graphene/Mn3O4NPs/ITO was subsequently made and investigated for the concurrent quantification of trace amounts of Pb (II), Cd (II), and Cu (II). The modified electrode exhibited a favourable linear range, exceptional sensitivity, and a low detection limit. The modified electrode consisting of Nafion/Graphene/Mn3O4NPs/ITO shows promising capabilities for the detection of low concentrations of Pb (II), Cd (II), and Cu (II) in seawater analysis, indicating its potential for application in environmental research.

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