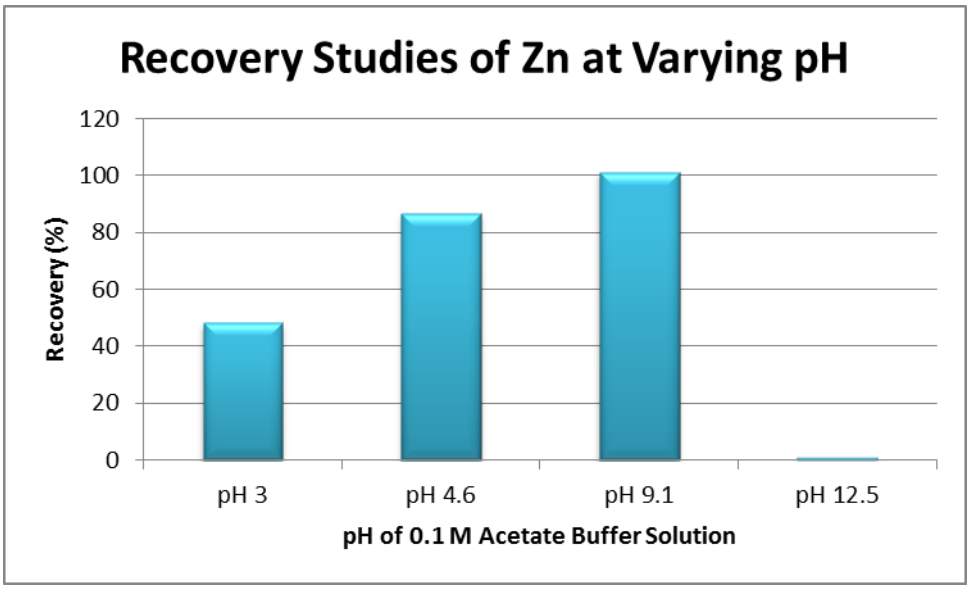

Figure 6.12: Effect of pH on Recovery of Zn^{2+} in 0.1 M acetate buffer solution with deposition time of 12

6.11. Application to T

The NG-PG-BiE d as an electrochemical sensing platform for the analysis of tap water samples. Tap water was collected in our laboratory and analysed for Zn^{2+}, Cd^{2+} and Pb^{2+}, detected by the standard addition method. None of the target metal ions were detected at a pre-concentration time of 120 s for either simultaneous or individual analysis due to their low concentrations. Spiking tap water samples with 20 µg L^{-1} and 30 µg L^{-1} of the target metal ions respectively yielded good recoveries as shown in Table 6.5. Increasing concentrations from 20 to 30 µg L^{-1} as well as performing individual analysis improved the percentage recoveries for all three metal ions. The lower recoveries for Zn^{2+} can be largely attributed to errors arising from the distortion of the zinc oxidation peak current caused by hydrogen gas evolution. The lower recoveries obtained for tap water samples spiked with 20 µg L^{-1} can be attributed

to the fact that errors are generally greater when working closer at the detection limits of the metal ions [139]. As reported for test solutions, good recoveries were achieved at elevated concentrations.

Table 6.5: Recovery percentages for $Zn^{2+,}$ $Cd^{2+,}$ and $Pb^{2+,}$ at the NG-PG-BiE in tap water samples using a deposition time of 120 seconds.

Simultaneous Analysis					
Metal Ion	**Original ($\mu g\ L^{-1}$)**	**Added ($\mu g\ L^{-1}$)**	**Found ($\mu g\ L^{-1}$)**	**RSD (%)**	**Recovery (%)**
Zn^{2+}	ND	20	12.52	2.84	62.59
	ND	30	20.52	3.83	68.42
Cd^{2+}	ND	20	18.03	5.43	90.14
	ND	30	30.73	4.19	102.43
Pb^{2+}	ND	20	18.69	5.36	93.47
	ND	30	29.44	1.46	98.12
Individual Analysis					
Metal Ion	**Original ($\mu g\ L^{-1}$)**	**Added ($\mu g\ L^{-1}$)**	**Found ($\mu g\ L^{-1}$)**	**RSD (%)**	**Recovery (%)**
Zn^{2+}	ND	20	17.84	5.77	89.23
	ND	30	28.60	2.38	95.34
Cd^{2+}	ND	20	17.29	4.85	86.45
	ND	30	29.94	1.22	99.79
Pb^{2+}	ND	20	20.30	1.11	101.51
	ND	30	29.53	2.84	98.43

n = 3, where n is number of repetitive cycles performed

ND, not detected

To meet the United States Environmental Protection Agency's (USEPA) maximum contaminant level (MCL) for zinc (5 mg L^{-1}), cadmium (0.005 mg L^{-1}) and lead (0.015 mg L^{-1}) in drinking water, a longer deposition time of 360 seconds

was used. Typical voltammograms obtained during the simultaneous analysis of heavy metal ions together with their corresponding standard addition curves is shown in Figure 6.13.

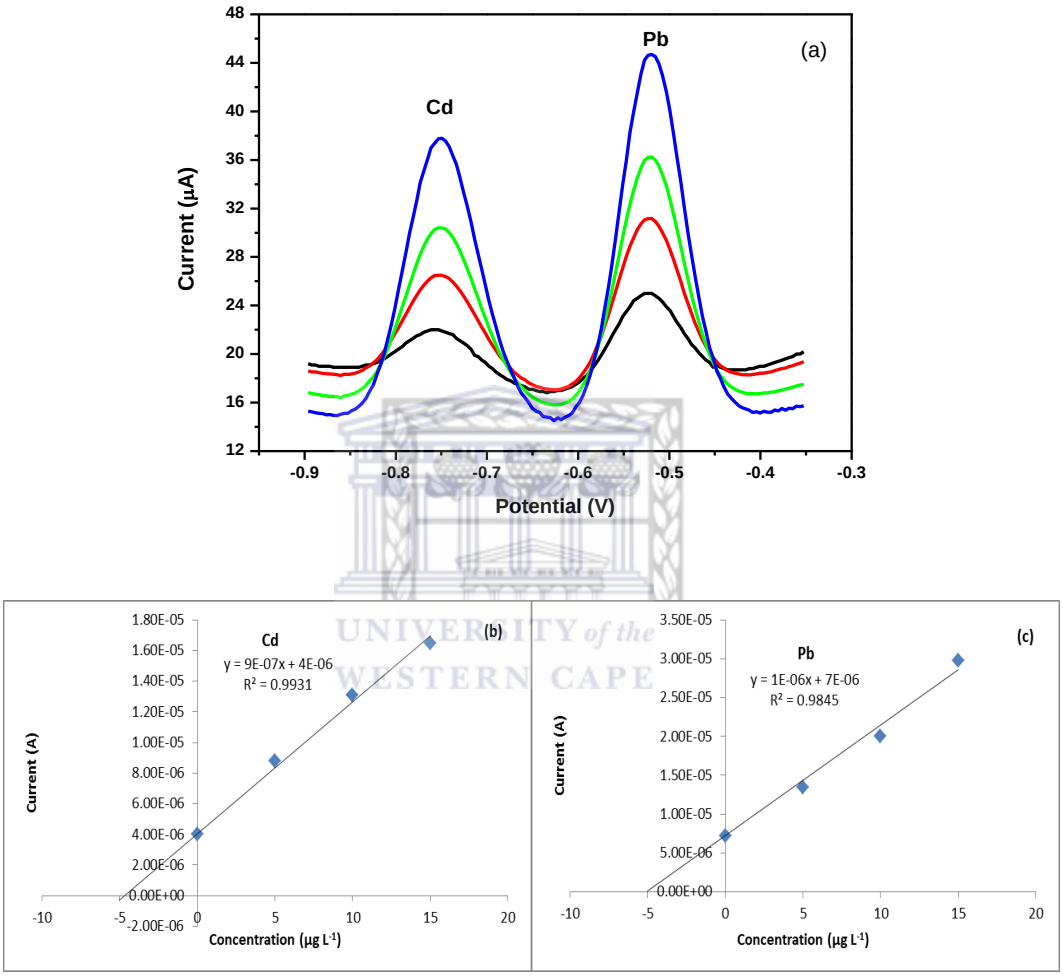

Figure 6.13: Simultaneous analysis of tap water (pH 4.6) spiked with 5 µg L^{-1} of each of metal ion using a deposition time of 360 seconds. Square wave voltammograms (**a**) and corresponding standard addition calibration curves for Cd^{2+} (**b**) and (**c**) Pb^{2+}.

Table 6.6 shows the percentage recovery obtained when using a deposition time of 360 seconds during simultaneous and individual analysis. As expected, the longer pre-concentration time allows for more metal ions to be deposited at the electrode surface resulting in improved sensitivity.

Table 6.6: Recovery for the determination of Zn^{2+}, Cd^{2+} and Pb^{2+} in tap water samples using NG-PG- BiE at pre-concentration time of 360 seconds

Recovery for the determination of Zn^{2+}, Cd^{2+} and Pb^{2+} in tap water samples					
Simultaneous Analysis					
Metal Ion	Original (µg L^{-1})	Added (µg L^{-1})	Found (µg L^{-1})	RSD (%)	Recovery (%)
Zn^{2+}	ND	5	ND	ND	ND
Cd^{2+}	ND	5	4.72	2.11	94.36
Pb^{2+}	ND	5	5.18	1.93	103.52
Individual Analysis					
Metal Ion	Original (µg L^{-1})	Added (µg L^{-1})	Found (µg L^{-1})	RSD (%)	Recovery (%)
Zn^{2+}	ND	5	ND	ND	ND
Cd^{2+}	ND	5	5.08	1.90	101.68
Pb^{2+}	ND	5	4.95	1.87	98.91

n = 3, where n is number of repetitive cycles performed

ND, not detected

Recovery percentages summarised in Table 6.6 show improved recoveries for individual analysis at 102 % and 99 % for Cd^{2+} and Pb^{2+} respectively. The accurate quantitation of heavy metals at concentration below the USEPA

standards proves the effective use of the NG-PG-BiE in conjunction with SWASV for detection of trace amounts of metals in drinking water.

6.12. Conclusions

Modification of pencil graphite electrodes with a Nafion-graphene nanocomposite and *in situ* plated bismuth film resulted in an ultra-sensitive sensing platform (NG-PG-BiE) for the detection of trace amounts of Zn^{2+}, Cd^{2+} and Pb^{2+} by square-wave anodic stripping voltammetry. Improved detection limits at values comparable to other known bismuth-film electrodes and below the USEPA standards, as well as accurate detection of metal ions in drinking water with a 5 % error prove the enhanced sensing capabilities of the binder-graphene platform.

CHAPTER SEVEN:

Conclusions and Future Work

A highly enhanced sensing platform based on the direct electrochemical reduction of colloidal graphene oxide at pencil graphite electrodes was developed for the determination of Zn^{2+}, Cd^{2+} and Pb^{2+} by square-wave anodic stripping voltammetry. The electrodeposited graphene pencil graphite bismuth-film electrode (EG-PG-BiE) showed improved sensitivities and detection limits to bismuth-film electrodes utilised in literature due to the combination of enhanced electron transfer rate, surface-to-volume ratio and improved sensitivity due to the graphene and metal-film. The analytical application of the EG-PG-BiE was assessed by recovery studies and real sample analysis within a 10 % error. The low detection limits obtained showed results well below the USEPA standards of 5 ppm, 5 ppb and 15 ppb for Zn^{2+}, Cd^{2+} and Pb^{2+} respectively.

Modification of pencil graphite electrodes with a Nafion-graphene nanocomposite and *in situ* plated bismuth film resulted in an ultra-sensitive sensing platform (NG-PG-BiE) for the detection of trace amounts of Zn^{2+}, Cd^{2+} and Pb^{2+} by square-wave anodic stripping voltammetry. Improved detection limits at values comparable to other known bismuth-film electrodes and below the USEPA standards, as well as accurate detection of metal ions in drinking water with a 5 % error prove the enhanced sensing capabilities of the binder-graphene platform.

Future work includes the use of bismuth films on various substrate materials to offer green approaches to existing techniques. The results achieved in the study show encouraging proof that the electroanalytical use of bismuth electrodes is possible.

The pencil graphite substrate has proved to offer good comparable results to common electrode substrates. In future, investigating the pencil graphite substrate for a wide range of applications is possible at low costs. The use of pencil graphite as substrate could also be investigated for low cost point-of-care devices due to its ease of use, robustness and low cost.

Minimizing errors in recoveries of Zn^{2+} at BiEs is of vital importance. The investigation of increased pH water samples should also be further interrogated.

Lastly, the use of nanomaterials and functionalised graphene sheets could be further investigated at various metal-films.

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