

Construction and Evaluation of a Carbon Paste Electrode Modified with Polyaniline-co-poly(dithiodianiline) for Enhanced Stripping Voltammetric Determination of Metal Ions

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Abstract: A modified carbon paste electrodes (MCPE) have been prepared in this study as an alternative “mercury-free” electrochemical sensor for the determination of Pb²⁺ and Cd²⁺ metal ions in aqueous solutions. CPE containing a conducting copolymer of polyaniline-co-poly(2,2'-dithiodianiline) (PANI-co-PDTDA) was used as a modified substrate transducer to achieve enhanced selectivity in stripping voltammetric analysis. The experimental conditions optimised included the supporting electrolyte pH, deposition potential (E_d) and time (t_d), set at -0.6 V vs. ref. for Pb²⁺ and -0.8 V for Cd²⁺; both kept for $t_d = 120$ s. The results with the CPE/PANI-co-PDTDA sensor have revealed the linear range within the range of $0.15 - 0.5$ $\mu\text{g/L}$ for Pb²⁺ and the same interval for Cd²⁺. Finally, the electrode of interest, CPE/PANI-co-PDTDA, can be characterised by the LODs of 0.03 and 0.09 $\mu\text{g/L}$ for Pb²⁺ and Cd²⁺ respectively.

Keywords: Carbon paste electrode; PANI-co-PDTDA; Differential pulse anodic stripping voltammetry, Lead and cadmium, Determination.

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Introduction

Environmental problems associated with anthropogenic pollution sources have increased in the last two decades and although more efficient management of these incidents have taken place, the disastrous effects it has on the aquatic ecosystem lingers longer.

Wastewaters arising from human activities are generally discharged into our water resources. Such wastewater can be a combination of liquid or water-carried waste that has been removed from residences, institutions, commercial and industrial establishments, together with surface and stormwater, runoff and groundwater [1]. Although the characteristics of wastewaters may be different, depending on its origin, the impact of effluent discharges and its effect on the environment can be disastrous and negatively impacts on human health. Furthermore, metal-contaminated wastewater from different industrial sources generally contains toxic heavy metals such as Cd, Pb, Cr, Cu, Ni, Hg and Zn that tend to accumulate in the food chain. Some of these heavy metals are highly soluble (depending on the pH of the receiving waters) in the aquatic environment and are absorbed by aquatic organisms. Once these metals enter the food chain, they may accumulate in the food chain and via this route impact on human health. If ingested beyond the permitted concentration levels, these metals can cause mild to serious health disorders such as depression, lethargy, seizures and ataxia, liver damage, Wilson's disease, renal disorder, dermatitis, asthma and human carcinogen disorders [2-9].

Various methods are available for the simultaneous analysis and determination of metal ions, which include inductively coupled plasma-mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), and X-ray fluorescence spectrometry (XRF). These methods are considered reliable, but can be time consuming and require tedious sample pre-treatments, highly qualified technicians and sophisticated instruments [10,11].

An alternative to the spectroscopic methods of metal ion determination is voltammetric techniques. The use of stripping voltammetry for trace metal analysis is been widely published and involves the pre-concentration of metal ions at an electrode surface, followed by quantification of the accumulated species by voltammetry in square wave or differential pulse mode [10,11,13-16].

Another topic of interest in this work is the construction of carbon paste electrodes (CPEs). Further modification of CPEs that are referred to as chemically modified electrodes (CMEs), have received considerable attention for several years, due to its ability to accumulate metal ions on the basis of the interaction of these ions with a functional group on the electrode surface. The ease of preparation and use are some of the popular reasons for the application of these sensors in stripping voltammetric determination of metal ions. The surface of the electrode is easily renewed during operation and these electrodes offer very low backgrounds. The use of these electrodes has also introduced mercury-free electrodes for stripping analysis, making them also environment friendly.

Various modifiers have been used in the construction of CMEs and the selection of modifier is determined by the application of the CMEs. Some of the common modifiers used are organic polymers, ligands, as well as inorganic ion exchangers such as clays depending on the analyte of interest [10].

The use of a conducting polymer (CP) for the modification of carbon paste in the construction of a modified CPE (MCPE) is of interest in this study. Conducting polymers (CPs) offer great advantages in electro-catalytic devices that include: high accessible surface area, low resistance, good stability and desirable film thickness. These polymers can also function as redox mediators, shuttling not only electrons but also protons between electrodes and the electro-active reactants. In this way it compensates for the shortcomings of plain carbon materials used in electrochemical devices [17].

The co-polymer of polyaniline-co-poly(2,2'-dithiodianiline) was used in this study for the construction of the MCPE. Polyaniline (PANI) as a conducting polymer is well-known due to its ease of preparation, well behaved electrochemistry and easy incorporation into biosensors. However, PANI also has some limitations such as low solubility in common organic solvents and restricted processability [18,19]. For this reason, it was decided to synthesise a co-polymer of PANI with poly(2,2'-dithiodianiline) (PDTDA) to improve some of the limitations of PANI. The polymer of poly(2,2'-dithiodianiline) is known for having -S-S- links in the backbone of the polymer that is similar to that of PANI. The disulphide bond is directly connected to the backbone of PANI macromolecule, improving the electrocatalytic activity of PDTDA and also acting as a stable energy storage material [20,21].

In the present work, we describe the use of a co-polymer of polyaniline-co-poly(2,2'-dithiodianiline) or PANI-co-PDTDA that was used to modify carbon paste in the construction of a modified carbon paste electrode. The use of CPEs modified with CPs have shown that this electrode surface can be used for selective pre-concentration and quantitation of Pb^{2+} and Cd^{2+} ions by differential pulse anodic stripping voltammetry (DPASV) in standard solutions.

Experimental

Chemicals, Reagents, Stock and Standard Solutions

The reagents aniline (99%), 2,2'-dithiodianiline (95%), N,N-dimethylformamide (98%), graphite powder (< 20 μm) and mineral oil were purchased from Sigma-Aldrich, Germany. Potassium chloride, sulphuric acid (95%), ethanol (95%) and hydrochloric acid (32%) were

purchased from Merck, South Africa. The diethyl ether (99.8%) and ammonium persulfate (APS) were purchased from Fluka (Germany) and used as received. All other chemicals were of analytical grade, or better, and were used as received. All solutions were always prepared using Milli-Q (Millipore) water [10].

Electrochemical Apparatus and Other Instrumentation

Voltammetry. Electrochemical measurements were conducted with an Epsilon electrochemical analyzer (BASi Instruments, 2701 Kent Ave., West Lafayette, IN 47906, USA) using cyclic voltammetry (CV) and differential pulse stripping voltammetry (DPSV) mode. A conventional three electrode system was employed, consisting of a constructed carbon paste working electrode, a 3 M NaCl-type Ag/AgCl reference electrode, and a platinum wire auxiliary electrode (the last two electrodes supplied by BASi). All electrochemical experiments were carried out in a single compartment electrochemical cell and at room temperature (20 ± 1 °C).

Electron Microscopy. Scanning Electron Microscopy (SEM) measurements were performed in order to analyse the morphology of the normal CPE, compared to that of the polymer modified CPE (MCPE). Microscopy studies were performed using a LEO 1525 Field Emission Scanning Electron Microscope (FESEM) with interchangeable accelerating voltages (maximum of 15.00 kV) for optimal sensitivity [10].

Carbon Paste Electrode

Preparation of Polymer Composite. The chemically synthesised co-polymer of PANI-co-PDTDA was obtained by preparing a solution of 10 M H₂SO₄ and adding approximately 3.4 g of ammonium persulfate (APS) to the solution, while mixing it with a magnetic stirrer on a hot plate. Monomers of aniline (0.2 M) and dithiodianiline (0.02 M) was consecutively added to the above mixture, while the solution was heated to ~70 °C with continuous stirring.

After two hours, the stirring was stopped and the green-coloured solution obtained was filtered, washed with ethanol and water obtaining from the Milli-Q purification system, and followed by drying in a fume hood at room temperature. The dried polymer was then thoroughly milled using a mortar and pestle and transferred to a dry poly-top container for further use [10].

Carbon Paste Electrode (CPE). The carbon paste electrode was freshly prepared by homogenising PANI-co-PDTDA powder with graphite powder and mineral oil using an agate mortar and pestle. The paste mixtures were packed firmly into piston-driven electrode holders made of polytetrafluoroethylene cylindrical tube (i.d. 3.5 mm). The electrical contact for the carbon paste working was established with a copper rod. The tip of the electrode was smoothed on a filter paper, until it had a shiny appearance.

Electroanalytical Measurements and Related Procedures

Voltammetric Techniques

Cyclic Voltammetry (CV). After preparation of the CPE/PANI-co-PDTDA sensor electrode, cyclic voltammetric measurements were performed after the electrode was washed with copious amounts of deionised water. Between measurements the electrode was stored in 5 mL of deionised water at 4 °C. To obtain a typical CV, the potential was scanned between +200 and +1100 mV (vs. Ag/AgCl), scan rate of 40 mV/s and a sensitivity of 1 μ A/V [15].

Differential Pulse Anodic Stripping Voltammetry (DPASV). DPASV measurements involved a pre-concentration step at -0.6 V (Pb^{2+}) and -0.8 V (Cd^{2+}) for 120 s, which was followed by recording the differential pulse anodic stripping voltammogram, through sweeping the potential from -1.0 V to -0.2 V (vs. Ag/AgCl). The experimental parameters used were: differential pulse amplitude, 50 mV; step amplitude, 4 mV; pulse width, 50 ms; pulse period, 200 ms; frequency, 100 Hz [10].

Electron Microscopy. Scanning Electron Microscopy (SEM) measurements were performed at interchangeable accelerating voltages (maximum of 15.00 kV) for optimal sensitivity. Samples were further prepared by mounting each sample on aluminium stubs using conductive glue and then coating it with a thin layer of carbon or gold [10].

Results and Discussion

Electrode Morphology Studies

For each of the carbon paste electrode (CPE) and the polymer modified carbon paste electrode (MCPE), a cross section of the electrode was cut away and prepared for SEM morphology analysis. The morphology of the two different electrodes evaluated in the study was characterised using scanning electron microscopy analysis, with the results shown in Figure 1.

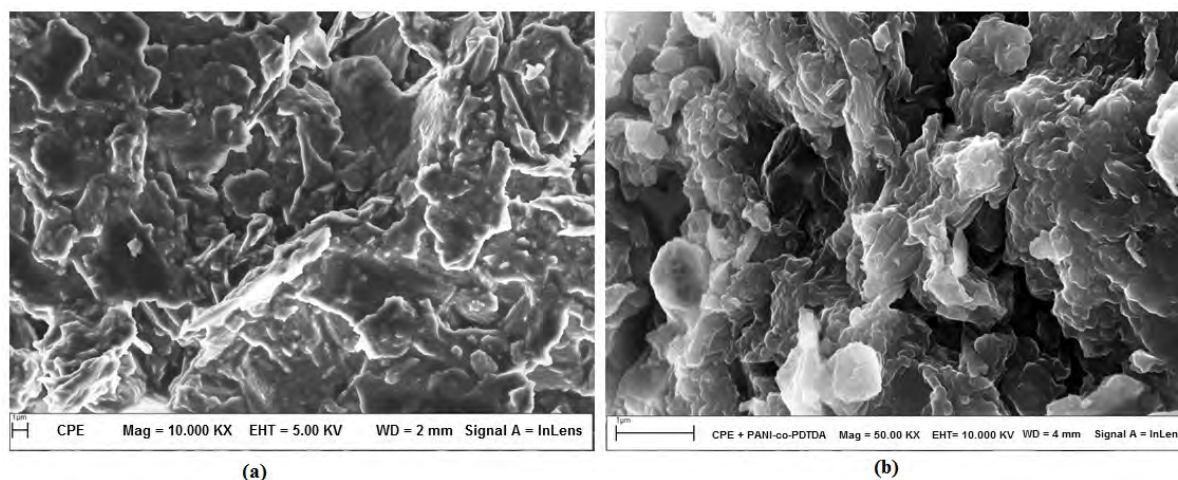


Fig. 1: Scanning electron micrographs of the surface morphology featuring an unmodified CPE in (a) and the modified carbon paste with the copolymer of PANI-co-PDTDA in (b).

Analysis of the SEM results in Fig. 1 indicates that the CPE has a morphology consisting of randomly shaped flakes, characteristic of graphite in the micrometer size range. The PANI-co-PDTDA modified CPE (MCPE) shows a different morphology with short flaky sections observed in some areas, while the rest of the morphology is short spherical stubs similar to the surface a strawberry fruit, resembling valleys and hills. It is noted that the MCPE has increased surface area due to the uniquely shaped morphology.

Optimisation of Stripping Parameters

Several parameters were optimised in the study to facilitate the stripping voltammetry experiments and smooth execution of Pb^{2+} and Cd^{2+} metal ion analysis. The current response signal that is obtained for the DPASV results is dependent on operational parameters, such as the pH of the supporting electrolyte, deposition potential (E_d) and deposition time (t_d).

In this study the effect of pH on the electrode response of the CPE/PANI-co-PDTDA sensor was evaluated using HCl as electrolyte (pH = 2) and phosphate buffer (pH = 6) solutions. The results obtained (not shown here) for the current response maxima have shown that the best results were obtained in HCl medium. It is also known that metals ions such as Pb and Cd of interest in this study are tightly bound to matrices at pH values ranging from 5 to 9, while at low pH values it is easier to strip from solution [15,22,23].

In Fig. 2 the results obtained for the optimisation of the deposition potential (E_d) and deposition time (t_d) is displayed.

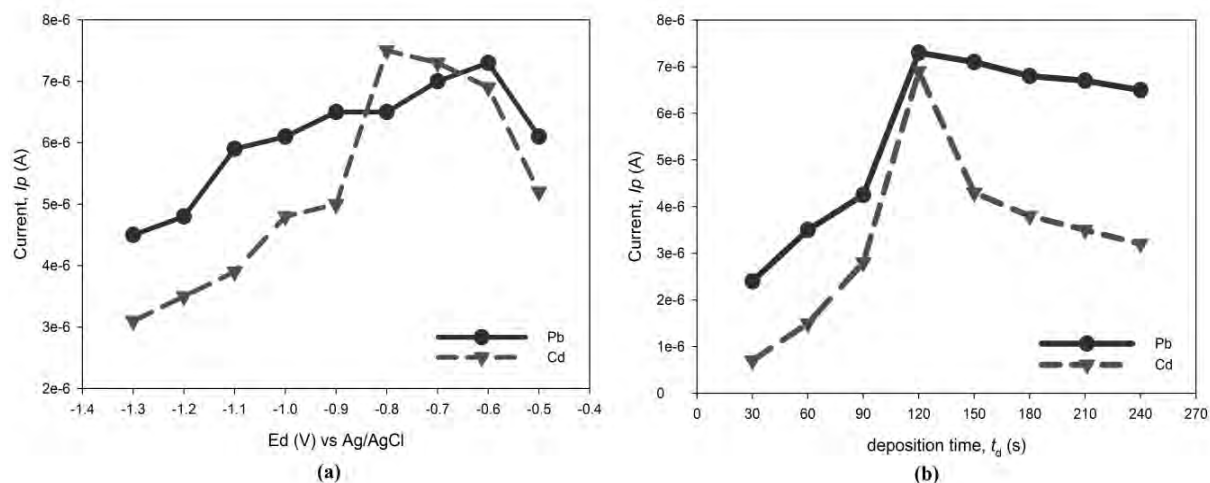


Fig. 2: Results obtained for the optimisation of the DPASV peak currents on the deposition potential in (a) and the deposition time in (b) for the CPE/PANI-co-PDTDA sensor in a solution containing 0.01 M HCl solution ($n = 3$).

Analysis of the results shown in Fig. 2 (a) have shown that the optimisation results for deposition potentials have shown that for Pb a steady increase in the peak current responses was observed up to a E_d value of -0.6 V (vs Ag/AgCl), followed by a decrease in response. The negative value obtained for the deposition potential, indicated that during deposition the lead ions (Pb^{2+}) are reduced to its metallic form, Pb^0 . An almost similar trend in peak current response was obtained for Cd, but the highest peak current response was obtained -0.8 V followed by a gradual decrease in peak current. The negative E_d value for Cd also conforms to the metal ion reduced to metal cadmium, Cd^0 .

The results obtained for the precision of the deposition time, see Fig. 2 (b), have shown that the peak current responses for Pb analysis increased for times from 30 to 120 s, reaching a maximum and then decreased gradually as the deposition time was increased to 240 s. An almost similar trend was observed for Cd analysis, with a maximum peak current response observed at 120 s. It was further observed that the peak current responses for Cd analysis, was lower than for the Pb analysis.

A summary of the optimised DPASV experimental conditions for the stripping voltammetric analysis of Pb^{2+} and Cd^{2+} metal ions are shown in Table I; see overleaf.

Table I. Summary of optimum conditions for Pb^{2+} and Cd^{2+} metal ion determination in standard samples using the CPE/PANI-co-PDTDA sensor constructed in this study.

Stripping step	Determinant	Pb^{2+}	Cd^{2+}
Reduction	pH	2	
	Reduction potential	-0.6 V	-0.8 V
	Deposition time	120	
	Supporting electrolyte	0.1 M HCl	
Measurement	Supporting electrolyte	0.1 M HCl	
	Technique	Differential pulse	
	Potential window	-0.2 to -1.0	

Stripping Voltammetry Measurements

Fig. 3 presents the differential pulse anodic stripping voltammograms obtained for the CPE/PANI-co-PDTDA sensor at acidic pH values.

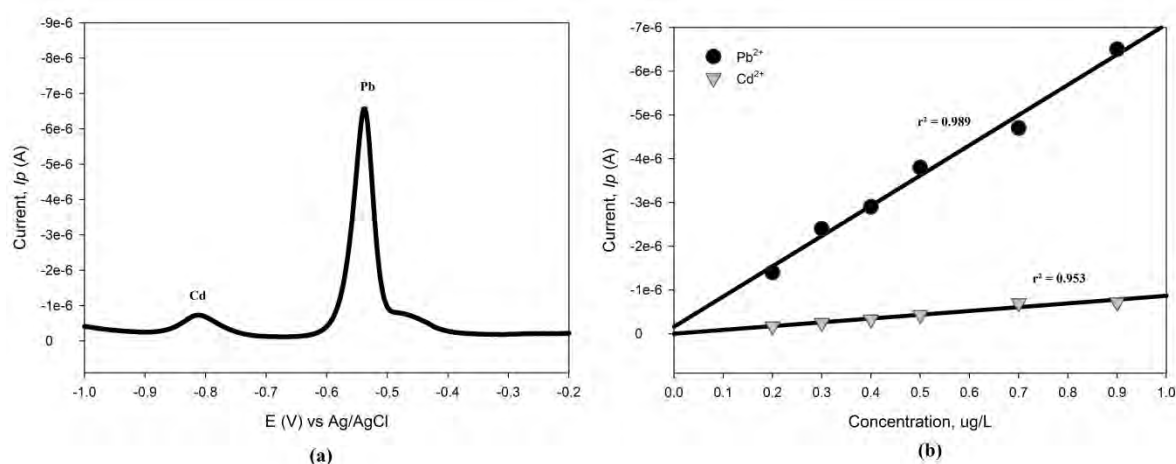


Fig. 3: Results obtained for the differential pulse anodic stripping voltammograms of Pb^{2+} and Cd^{2+} in (a) and the calibration plots obtained for increasing concentrations under the experimental conditions shown in Table I.

Analysis of the results in Fig. 3 (a) have shown that a sharp and strong stripping peak was obtained for Pb^{2+} at approximately -0.55 V (vs Ag/AgCl), while a smaller stripping peak for Cd^{2+} was obtained at -0.82 V. It was also observed that the simultaneous analysis of both metal ions is preferable towards Pb under the same stripping experimental conditions.

The calibration plots in Fig. 3 (b) have shown that a good linear response was obtained for increasing concentrations of Pb^{2+} and Cd^{2+} metal ions. The linear range for both Pb^{2+} and Cd^{2+} analysis was the same and obtained in the range between 0.15 – 5.0 $\mu\text{g/L}$.

These results were also used in determining the electro-analytical parameters and features for the stripping voltammetric application of the CPE/PANI-co-PDTDA sensor, which are discussed in the next section.

Interferences were also studied in the evaluation of the CPE/PANI-co-PDTDA sensor and the presence of other anions (e.g. CO_3^{2-} and PO_4^{3-}) did not significantly interfere with the Pb^{2+} and Cd^{2+} analysis.

Analytical Parameters

In this study we have reported the electrochemical analytical parameters for the stripping voltammetric determination of Pb^{2+} and Cd^{2+} metal ions, in acidic media. The anodic peak currents were collected in the concentration range, 0.1 – 1.0 $\mu\text{g/L}$, with the stripping peak potential for Pb^{2+} at -0.6 V (vs Ag/AgCl) and for Cd^{2+} at -0.8 V (vs Ag/AgCl). The linear range for Pb^{2+} analysis was within the range of 0.15 – 0.5 $\mu\text{g/L}$, while for Cd^{2+} analysis it was within the same range of 0.15 – 0.5 $\mu\text{g/L}$.

The limit of detection (LOD) for each of the metal ions was evaluated as the concentration that gave a response equivalent to three times the SD of the blank ($n = 10$). The limit of quantification (LOQ) for each metal ion was evaluated as the concentration that gives a response equivalent to ten times the SD of the blank. Furthermore, the precision of the procedure was expressed by the relative standard deviation for three measurements of each metal ion. A summary of these parameters are listed in Table II [15,23].

Table II: Summary of the results obtained for the analytical performance of the CPE/PANI-co-PDTDA sensor for the stripping voltammetric determination of Pb^{2+} and Cd^{2+} under optimised conditions.

Metal ion	Linearity range ($\mu\text{g/L}$)	r^2	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)
Pb^{2+}	0.1 – 0.5	0.989	0.03	0.11
Cd^{2+}	0.1 – 0.5	0.953	0.09	0.29

Further analysis of the results in Table II has shown that favourable detection limits were obtained for both metal ion determination, while comparable LOQ values are also shown.

In the next step, the results obtained with the application of the CPE/PANI-co-PDTDA sensor were compared to results obtained in other studies.

Comparison of results with that obtained in other or similar studies have shown favourable similarities, as shown in Table III.

Table III. Comparison of the results obtained for the application of the CPE/PANI-co-PDTDA sensor to other studies with Pb^{2+} and Cd^{2+} standard solutions.

Electrode	Modifier	Method	Linear range	LOD	Ref
CPE	Diacetyldioxime	DPASV	0.04 – 15 μ M	Pb(II) – 1×10^{-8} M Cd(II) – 4×10^{-8} M	14
CPE	Cyclodextrins	DPASV	N/A	Pb(II) – 6×10^{-7} M Cd(II) – 2×10^{-6} M	24
CPE	Bismuth-graphene	DPASV	0.1 – 50 μ g/L	Pb(II) – 0.04 μ g/L Cd(II) – 0.07 μ g/L	23
CPE	PANI-co-PDTDA	DPASV	0.01 – 0.5 μ g/L	Pb(II) – 0.03 μ g/L Cd(II) – 0.09 μ g/L	This work

Comparison of the results in Table III has shown that the LODs obtained in this study compares favourably with results from other studies and it was found that the LODs of the CPE/PANI-co-PDTDA sensor is within the range of other sensors reported.

Conclusions

This study has shown the development of a simple and effective modified carbon paste electrode (MCPE), consisting of the copolymer of PANI-co-PDTDA that was incorporated into carbon paste. The optimised experimental conditions for the application of the MCPE to the stripping voltammetric analysis of Pb^{2+} and Cd^{2+} were identified and described. Differential pulse anodic stripping voltammetric measurements were performed for the analysis of Pb^{2+} and Cd^{2+} ions in standard solutions.

The results obtained have shown that the linear range for Pb^{2+} analysis was within the range of 0.15 – 0.5 μ g/L, while for Cd^{2+} analysis it was within the same range of

0.15 – 0.5 µg/L. The CPE/PANI-co-PDTDA showed LODs of 0.03 and 0.09 µg/L for Pb²⁺ and Cd²⁺ respectively, which compares favourably to results obtained for other sensors for the analysis of the same metal ions.

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