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Electroanalytical Determination of Cadmium and Lead using Edge Plane Pyrolytic Graphite/Polyaniline Electrode

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Abstract:

In this work edge plane pyrolytic graphite electrode substrate electropolymerized with polyaniline thin film via multipulse cyclic voltammetry to form edge plane pyrolytic graphite/polyaniline (PG/PANI) electrode was successfully used for simultaneous determination of Cd²⁺ and Pb²⁺ ions. Anodic-stripping square wave voltammetric (AS-SWV) technique was used for this sensor development. The results reported indicate that modifying the edge plane pyrolytic graphite electrode with polyaniline increases the detection signals for Cd²⁺ and Pb²⁺ by 1.6 and 2.5 times respectively. Among the variables optimized were: deposition time (60 sec), deposition potential (0.05 V), amplitude (0.02 V) and frequency (35 Hz) for Cd²⁺ and deposition time (60 sec), deposition potential (0.05 V), amplitude (0.02 V) and frequency (25 Hz) for Pb²⁺. The limits of detection, limits of quantitation and linear ranges were found to be 0.11ppm, 0.37ppm and 0.10ppm – 0.50ppm for Pb²⁺ and 0.908ppm, 3.03ppm and 1.0ppm – 5.0ppm for Cd²⁺ respectively. This proposed electroanalytical method uses non-mercury based electrodes. Its also simple and cheaper compared to other alternatives such as carbon nanotube electrode arrays.

Keywords: Edge plane pyrolytic graphite, polyaniline, cadmium, lead and anodic-stripping Square wave voltammetry

1. Introduction

Heavy metals are metals with elemental densities above 5 g/cm³ [1]. As many other metals can be found on the Earth's shell, the human body contains a small amount of these substances. They get into the organisms via food, drinking water and air. Low concentrations of heavy metals like selenium and zinc in biological systems are called essential elements because they are involved in metabolic activities. When concentrations of heavy metals in our ecosystem exceed certain amount, they become toxic. The sources of heavy metal poisoning include metals contained in water pipes, drinking polluted water or air emissions from factories. Bioaccumulation of heavy metals in biological organisms is faster than its decomposition. Therefore, determination of heavy metals in our environment is of great concern [2].

Electroanalytical techniques are designed to provide high sensitivity, low cost and field deployability, wide scope of applicability to a range of substances and simultaneous determination of chemical species [3]. The remarkable sensitivity of stripping techniques is attributed to their unique built-in pre-concentration (electro-deposition) step, making it the widely used heavy metals analytical method. The general performance of the stripping techniques is that they are highly affected by the condition of the working electrode material. Amid each electrode surface modification strategies each new surface is expected to yield reproducible results because all individual compounds are assumed to be homogeneously dispersed or electrodeposited in the bulk of the composite [4].

Polyaniline (PANI) belongs to a group of conducting polymers characterized by alternating single and double bonds [5]. They differ from other polymers in that they can be changed to intrinsic conductors through doping. Their increased conductivity is attributed to their ability to undergo reduction or oxidation when they interact with charge transfer species or dopants. Polyaniline has attracted much attention due to its unique properties such as ease of synthesis, biocompatibility, chemical and electrical stability, good redox properties and moderate electrical conductivity [6]. Interaction between the conjugated systems of PANI with charge transfer species leads to introduction of charge transfer carriers within the polymer backbone converting it from insulator to a conductor [7] Polyaniline has been shown to possess excellent electro-mediation properties. It is environmentally stable, highly conductive, has a facile synthetic process, and provides an excellent hydrophobic environment for analyte housing [6].

In this work, we explore the possibility of simultaneous determination of lead and cadmium in prepared standard solutions using edge plane pyrolytic graphite electrode modified with polyaniline. It's important to mention that the edge plane pyrolytic graphite/polyaniline electrode system has not been utilized before for the simultaneous determination of Cd (II) and Pb (II) ions in aqueous solutions.

2. Experimental

2.1. Chemicals and Reagents

Potassium chloride, Cadmium Bromide, Lead Nitrate, alumina, hydrochloric acid and Polyvinyl sulfonate (PVS) solution were obtained from Aldrich Chemical Co. All these chemicals were analytical reagent grade and were used as received. The rest were reagent grade. Double distilled water (DDW) and deionized water were supplied by the Chemistry department.

2.2. Apparatus and Procedure for Voltammetry

The Autolab Princeton applied research (PAR) analyzer, a three electrode potentiostat, was used for all the electrochemical experiments and all potentials were referred to saturated calomel electrode (SCE). Platinum wire was employed as the counter electrode and edge plane pyrolytic graphite electrode was used as working electrode. All the electrolytic solutions were de-aerated for at least 25 minutes by passing pure nitrogen gas through them before carrying out the experiment. All experiments (cyclic voltammetry and anodic stripping square wave voltammetry) were done at room temperature.

2.3. Electropolymerization of Polyaniline on Pyrolytic Graphite Electrode

The edge plane pyrolytic graphite electrodes were polished on slurry of 0.5 μm alumina and rinsed with distilled water. Then the electrodes were dipped in an electrochemical cell containing 93mL pure aniline, 3.9mL 1M HCl and 1.00mL PVS solution. Polyaniline films were grown electrochemically on the electrode surface by multiple cyclic Voltammetry scanning at 100 mV/s from -500mV to 1100mV and back for 30 cycles at room temperature [8]. The modified electrodes were rinsed well with distilled water before used.

2.4. Preparation of Lead and Cadmium Solutions

0.1 M KCl was used as the electrolyte for all voltammetric experiments. 1.0M Cadmium bromide and 1.0M lead nitrate were prepared as stock solutions, from whence dilutions were done to required concentrations. For calibration purposes, the following concentrations were used: 100mM, 10mM, 1mM, 0.1mM, 0.01mM and 0.0mM for cadmium (II) and 100mM, 10mM, 1mM, 0.1mM, 0.01mM and 0.0mM for lead (II).

3. Results and Discussions

Anodic stripping square wave voltammetry (AS-SWV) is a well known and widely used electroanalytical technique because of its high sensitivity resulting from the pre-concentration step. Figure 1 and 1B shows stripping voltammetric signals for cadmium (II) and lead (II) on bare and polyaniline modified edge plane pyrolytic graphite electrodes.

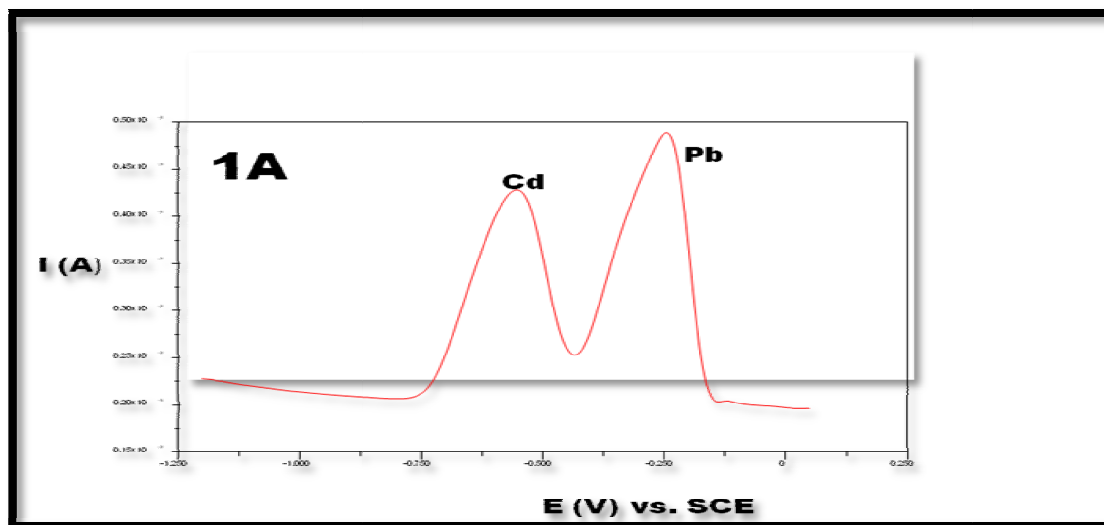


Figure 1: Anodic Stripping-Square Wave Voltammogram of 10 Ppm Mixture of Cadmium (II) and Lead (II) Solution Obtained at Frequency of 30 Hz Using Non-Modified Edge Plane Pyrolytic Graphite Working Electrode

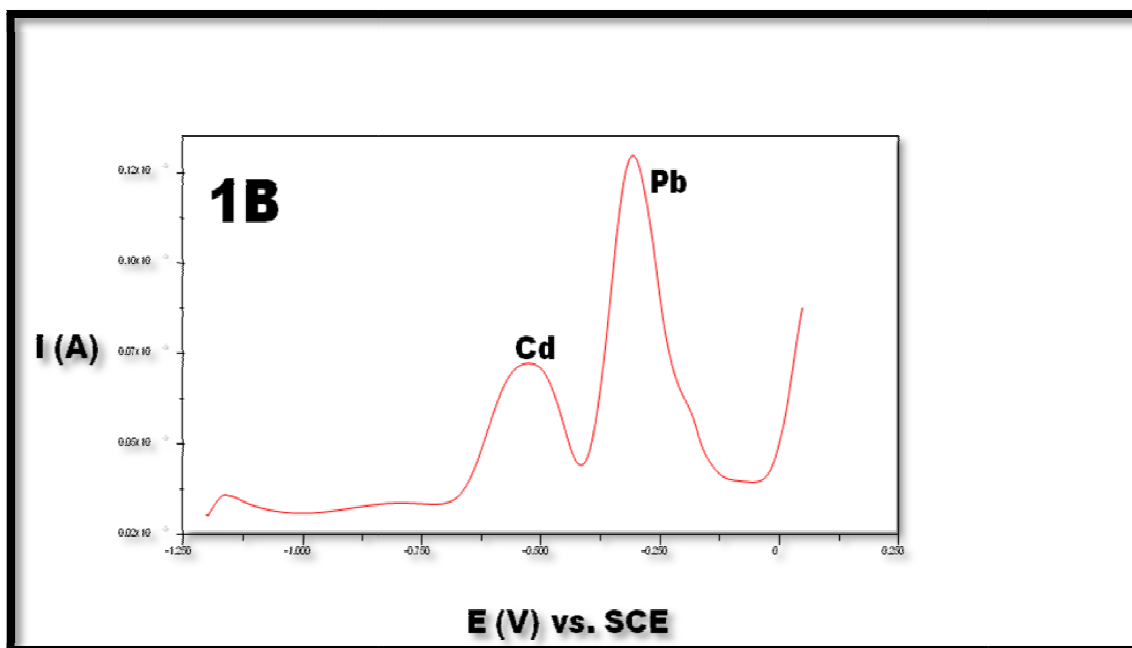


Figure 2: Anodic Stripping-Square Wave Voltammogram of 0.15 Ppm Mixture Lead (II) and Cadmium (II) Solution Obtained at Deposition Potential 0.15 Volts Using Modified Edge Plane Pyrolytic Graphite Working Electrode

Anodic stripping square-wave voltammetry was then used for the simultaneous determination of cadmium (II) and lead (II) on both bare and modified working electrodes. The potential was scanned from -1.250V to $+1.250\text{V}$. Figure 1 shows the AS-SWV on bare working electrode and Figure 2 shows the AS-SWV on PANI modified working electrode. As can be seen, on bare working electrode, well defined stripping peaks are observed for cadmium (II) and lead (II) at potentials of ca. -0.530V and ca. -0.255V (versus SCE) respectively. While on PANI modified working electrode, well defined stripping peaks are observed for cadmium (II) and lead (II) at potentials of ca. -0.520V and ca. -0.260V (versus SCE) respectively. In both cases the oxidative currents for both Cd (II) and Pb (II) are much higher on PANI modified working electrode compared to bare working electrode. This is attributed to the change of the surface chemistry of the working electrode. Polyaniline is known to be a conductive polymer [8]. A thin film of this polymer on the electrode surface increases the conductivity of the electrode surface. In addition, the electrodeposition step in the stripping analysis accumulates the target metal ions on the electrode surface. These combined explains why the much-enhanced stripping currents on the modified electrode compared to bare electrode.

3.1. Optimization of Parameters

In method development, it's important to know the best conditions which provide the highest signals. In this regard the following parameters were optimized for the simultaneous determination of cadmium (II) and lead (II) for both pyrolytic graphite/polyaniline and bare pyrolytic graphite electrodes. The conditions investigated include deposition time, frequency, amplitude and deposition potential (table 1).

NO.	SWV Variables	Modified		Unmodified	
		Cadmium	Lead	Cadmium	Lead
1.	Deposition time (sec)	60	60	240	120
2.	Frequency (Hz)	35	25	45	45
3.	Amplitude (V)	0.02	0.02	0.08	0.08
4.	Deposition potential (V)	0.05	0.05	0.05	0.05

Table 1: Summary of the Square Wave Voltammetric Optimal Conditions for the Proposed Sensor

The effect of deposition potential was investigated for both cadmium (II) and lead (II) by following the stripping signals by varying potential over the range of -1.0 to $+1.0\text{V}$ which reached a maximum at 0.05V . Beyond 0.05V , the signals diminished. Therefore, the optimal deposition potential was 0.05V for the simultaneous determination of both cadmium (II) and lead (II).

The deposition time for the determination of cadmium (II) and lead (II) was also explored. This was done by following how the anodic stripping signals varies with various deposition times from 0 to 300 seconds. It was observed that the anodic stripping voltammetric currents increased with increasing deposition time from 0 to 60 seconds. After 60 seconds the signal

remained the same. This indicated that the electrode surface was fully saturated at 60 seconds of cadmium (II) and lead (II) deposition. Therefore 60 seconds of deposition time was ultimately used for further experiments as a compromise between relatively short analysis time and high sensitivity. Further, we investigated the frequency and amplitude for maximum stripping analysis. We found that both cadmium (II) and lead (II) had a maximum signal at 0.02V amplitude. Cadmium (II) and lead (II) had a maximum signal at 35Hz and 25Hz frequency respectively. During simultaneous analysis, we used 30Hz as the optimal frequency (table 1).

3.2. Calibration Data

The applicability of the proposed AS-SWV procedure as an analytical method for the determination of cadmium (II) and lead (II) was examined by measuring the stripping voltammetric peak current as a function of cadmium (II) and lead (II) concentrations for at least three times under the optimized operational parameters in 0.1M KCl solution. The stripping voltammograms from additions of cadmium (II) were studied over the range of 0.0 to 20ppm while for lead (II) from 0.0 to 20ppm.

No.	Analyte	LOD	LOQ	LCR
1.	Pb ²⁺	0.11ppm	0.37ppm	0.1ppm – 0.5ppm
2.	Cd ²⁺	0.91ppm	3.30ppm	1.0ppm – 5.0ppm

Table 2: The Values of the LOD, LOQ and LCR of Lead and Cadmium Detection on PG/PANI Electrode
LCR = Linear Concentration Range, LOD = Limit of Detection and LOQ = Limit of Quantitation

Now, both cadmium (II) and lead (II) were added simultaneously. Two well defined and highly resolved stripping voltammetric peaks at potentials of -0.55V for cadmium and -0.300V for lead were observed (figure 2). Plots of varying concentrations versus stripping voltammetric currents produced one linear range for cadmium (II) and one linear range for lead (II). The calibration range for cadmium (II) was observed to range from 1.0 to 5.0ppm while that for lead (II) from 0.1 to 0.5ppm (table 2). From the calibration curves for cadmium (II) and lead (II), the detection limits of 0.91ppm and 0.11ppm were obtained respectively. While their limits of quantitation were found to be 3.3ppm and 0.37ppm respectively (table 2).

No.	Electrode	Modifier	Method	LOD of CD/ μ g/L	LOD of PB/ μ g/L	Ref.
1.	Gold	-	FSCV	0.07	0.06	9
2.	GCE	Heparin	DPASV	-	0.062	10
3.	CPE	Zr-Ph silica	DPASV	-	0.0725	11
4.	Gold	-	SWSV	-	0.08	12
5.	CPE	BHAMS	DPASV	-	0.081	13
6.	BDD	-	SonoSV	0.112	-	14
7.	GCE	Hg film	DPASV	0.0001	-	15
8.	GCD	Hg film	ASV	0.00056	0.0016	16
9.	Carbon fiber-Pt	Hg film	ASV	0.0013	NA	17

Table 3: Comparison of the Various Methods for Determination of Cadmium (II) and Lead (II)

Table 3 provides comparisons of different electrodes which have been used before for the determination of cadmium (II) and lead (II). It's evident from table 3 that the detection limits for mercury-based electrodes are much more sensitive than non-mercury-based electrodes for both cadmium (II) and lead (II) detection. However, the high toxicity of mercury electrodes renders them unfavorable electrode materials. It's interesting to note that the detection limits using the proposed edge plane pyrolytic electrode/polyaniline electrode is in the same order of magnitude as the lowest detection limits for non-mercury electrode. This proposed electroanalytical method uses non-mercury-based electrodes. Its also simple and cheaper compared to other alternatives such as carbon nanotube electrode arrays.

4. Conclusion

Anodic stripping-square wave voltammetric sensor based on edge plane pyrolytic graphite/PANI electrode has been developed for the simultaneous determination of Pb²⁺ and Cd²⁺ standard samples. The deposition time, deposition potential, amplitude and frequency were found to have very strong influence on the voltammetric signal. With the AS-SW voltammetry, the following optimal conditions were established: deposition time (60 sec), deposition potential (0.05 V), amplitude (0.02 V) and frequency (35 Hz) for Cd²⁺ and deposition time (60 sec), deposition potential (0.05 V), amplitude (0.02 V) and frequency (25 Hz) for Pb²⁺. The limits of detection, limits of quantitation and linear ranges were found to be 0.11ppm, 0.37ppm and 0.1ppm – 0.5ppm for Pb²⁺ and 0.908ppm, 3.03ppm and 1.0ppm – 5.0ppm for Cd²⁺ respectively. Generally, this proposed sensor holds significant potential for real sample analysis.

5. Acknowledgement

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