Poly(1,5-Diaminonaphthalene)-Modified Screen-Printed Device for Electrochemical Lead Ion Sensing

Mai T. T. Nguyen,1 Huy L. Nguyen,1,2 and Dung T. Nguyen2

1School of Chemical Engineering, Hanoi University of Science and Technology, 1 Dai Co Viet Road, Hanoi, Vietnam
2Institute for Tropical Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Hanoi, Vietnam

Correspondence should be addressed to Huy L. Nguyen; huy.nguyenle@hust.edu.vn and Dung T. Nguyen; ndung@itt.vast.vn

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Poly(1,5-diaminonaphthalene) has been electropolymerized on the screen-printed device with a three-electrode configuration. The modified electrodes have been developed as the new electrode for electrochemical determination of trace levels of lead ions (Pb2+). The poly(1,5-diaminonaphthalene) film prevents the deposition of Pb2+ into the surface defects of the bare carbon screen-printed electrode and possesses sensitivity to heavy metal ions thanks to amine and secondary amino groups on the polymer chain. The square wave anodic stripping voltammetry was applied to detect Pb2+ ions, showing a sharp stripping peak with the linear range from 0.5 μg·L⁻¹ to 5.0 μg·L⁻¹ (R² = 0.9929). The limit of detection was found to be 0.30 μg·L⁻¹. The sensors were applied to the analysis of Pb2+ in the tap water sample matrix with satisfactory results.

1. Introduction

At present, lead is one of the most critical toxic pollutants for biological systems. Lead is not biodegradable and accumulated in the food chain, so this metal remains a significant health concern. Exposure to even a low level of lead ions (Pb²⁺) may cause severe damage to the brain and kidneys [1]. According to the stipulation of the European Union, the maximum allowable concentrations in food have been set to be from 0.02 to 1 mg·L⁻¹ [2], and as for the World Health Organization (WHO), it has been set as 10 μg·L⁻¹ for drinking water [3]. Due to these reasons, the rapid detection of Pb²⁺ at lower concentration levels is an important issue. A series of methods have been used for the detection of Pb²⁺, such as Atomic Absorption Spectroscopy (AAS) [4], Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) [5], and X-Ray Fluorescence (XRF) spectrometry [6]. Using these methods, we can detect high accuracy and high sensitivity, but some disadvantages include bulky equipment size, expensive cost, a requirement of trained professionals, and large-scale analysis for indoor use. Besides, the electrochemistry method with the anodic stripping voltammetry (ASV) technique is also a powerful tool for detecting trace amounts of Pb²⁺. The advantages of the electroanalytical method are its rapid detection, small size, easy operation, and high sensitivity. The working electrodes based on the hanging drop mercury electrodes (HDME), dropping mercury electrodes (DME), and mercury film electrodes (MFE) have been widely reported during the past several decades [7]. However, mercury is toxic and unsuitable for portable devices. To date, there is a tendency to use the alternative of mercury electrodes (mercury-free) such as inorganic materials like bismuth [8], functionalized mesoporous silica [9], boron-doped diamond [10], and boron-doped diamond [14]. The polymer electrodes based on the conductive polymer film have been investigated toward metal ion detection with different approaches.

The conducting polymer’s interesting features are its superior electrical conductivity, high specific surface area, good adhesion, and enhanced signal responses for target metal ions [15]. A large number of reports have shown that people used polymer composite electrodes for detection of Pb²⁺ such as polyaniline/carbon nanotubes [16], poly(vinylsulfonate)-doped polyaniline [17], p-phenylenediamine [18], poly(3,4-
ethylenedioxythiophene) [19], polypyrrole/carbon nanofibers [20], PEDOT/black TiO$_2$ [21], and polydiaminonaphthalene [22, 23]. Among these conducting polymers, poly(1,5-diaminonaphthalene) (p(1,5-DAN)) has shown the capacity of collecting some metal ions because it possesses chelating properties and/or reduction properties owing to the electron-donating groups (amine and secondary amino groups) on the polymer chain [24]. Thus, p(1,5-DAN) could increase the stripping responses and the reproducibility for sensing.

Most of the work about polymer electrodes is based on the glassy carbon electrodes and carbon paste electrodes, which is not suitable for on-site applications. A screen-printed electrode emerged as a promising solution for this problem. The coupling of a screen-printed electrode with anodic stripping voltammetry (ASV) is more favorable in the heavy metal analysis due to the following: prepared in large quantities, rapid, inexpensive, flexible, and miniaturization. This study is aimed at preparing for a "lab-made" screen-printed device with a three-electrode configuration (consisting of the silver chloride pseudoreference electrode, carbon as a working electrode, and counter electrode) modified by p(1,5-DAN) for square wave anodic stripping voltammetry (SWASV) analysis of lead ions.

2. Materials and Methods

2.1. Reagents and Apparatus. 1,5-Diaminonaphthalene monomer, LiClO$_4$, and HClO$_4$ were obtained from Sigma-Aldrich. Lead solutions were prepared from a standard stock solution (1,000 mg\cdot L$^{-1}$, atomic absorption standard solution, Scharlau Chemie). Sodium acetate buffer (0.1 M, pH 4.5), prepared by mixing an appropriate amount of CH$_3$COOH and CH$_3$COONa, was used as a supporting electrolyte. All other reagents of analytical grade and deionized water were used throughout the experiments.

The bare screen-printed devices with a three-electrode configuration (SPES) were fabricated on a polypropylene sheet substrate with a DEK Albany 247 printing machine (DEK, Weymouth, UK). These "lab-made" SPESs have dimensions about 1 cm × 4 cm with a classical three-electrode system.
including a silver chloride-based screen-printed pseudoreference electrode, carbon working electrode, and carbon counter electrode. The SPE fabrication process was described in our previous publication [25]. The working carbon electrode diameter was 1.6 mm in a geometric area of 0.02 cm² with the thickness of coated layers of about 10 μm. The ratio counter electrode/working electrode surface area was 4/1, and the silver chloride pseudoreference electrode with $E_{ref} \approx +0.3$ V and standard hydrogen electrode (SHE) are shown in Figure 1.

All electrochemical experiments were performed with an Autolab PGSTAT30 electrochemical analyzer (EcoChemie, the Netherlands) under the control of GPES version 4.9 data acquisition software. The electrochemical setup measurements were performed with the reaction solution’s droplet (15−50 μL) at room temperature (~25 °C) and nondeaerated solutions. The morphology was observed by field emission scanning electron microscopy (FE-SEM; Hitachi S-4800).

2.2. SPEs Modified by p(1,5-DAN). The p(1,5-DAN) film was electrochemically synthesized on SPEs in an aqueous solution consisting of the 1,5-diaminonaphthalene monomer with a concentration of 1.0 mM and 0.1 M LiClO₄ in a 1 M HClO₄ using cyclic voltammetry. The polymerization was performed in 20 cycles within the potential range from -0.02 V to +0.95 V with a sweep rate of 50 mV·s⁻¹. Afterward, the produced electrodes p(1,5-DAN)/SPEs were washed with deionized water.

2.3. Procedure for the SWASV Analysis. Square wave anodic stripping voltammetry is a frequently used anodic stripping voltammetry method because it can greatly reduce the background noise coming from the charging current during the potential scan [26]. The detection of Pb²⁺ was performed for various concentrations of Pb²⁺ in 0.1 M acetate buffer (pH 4.5) using square wave voltammetry under the following conditions: frequency of 50 Hz, amplitude of 50 mV, and step potential of 5 mV. The stripping voltammetric measurement procedure consisted of two steps: an accumulation step and a stripping step. Firstly, lead ions were deposited on the surface electrode at the negative potential for 180-480 s.

Then, the square wave anodic stripping voltammograms (SWASV) are recorded by applying a positive-going scan from -1.2 to -0.5 V.

3. Results and Discussion

3.1. Electropolymerization of p(1,5-DAN) on the SPEs. Figure 2 displays the cyclic voltammograms between -0.02 and +0.95 V at a scan rate of 50 mV·s⁻¹ taken during the electrochemical polymerization onto SPEs. In the first scan, the anodic peak at around +0.61 V corresponds to the 1,5-diaminonaphthalene monomer oxidation to the radical cation than the dication. In subsequent cycles, this peak seems to disappear, but at lower potentials, two anodic peaks are obtained at +0.27 V and +0.35 V and one cathodic peak at +0.28 V. The characteristic peaks characterized show electroactivity of p(1,5-DAN) in acid medium, and the current continuously increased during scans reflecting the growth of the conductive polymer film on the SPEs [23, 27–29].
To confirm the successful polymerization of 1,5-diaminonaphthalene on SPEs, the electrodes were obtained by scanning the cyclic voltammograms in acetate buffer solution (pH 4.5) in the absence of the monomer. The cyclic voltammetry was performed between -1.5 V and +0.25 V at a scan rate of 50 mV·s⁻¹.

As shown in Figure 3, the cyclic voltammogram of p(1,5-DAN)/SPEs (curve (b)) has shown two typical redox couples \((I_1/I_1')\) and \((I_2/I_2')\) corresponding to doping and undoping of protons and anions in the p(1,5-DAN) film [28] clearly seen when compared with CVs of bare SPEs (curve (a)) under the same conditions. This result confirmed the successful polymerization of 1,5-DAN on screen-printed devices.

The working potential window’s width is important for determining heavy metal ions with the anodic stripping voltammetry technique. As shown in Figure 3 (curve (b)), the voltammogram was almost straight from -1.5 V to -0.4 V (not affected by oxidation peaks of the polymer) and did not show an apparent influence of hydrogen evolution currents until -1.5 V. And the anodic peak for Pb²⁺ ion stripping is inside this potential range. That proves that the p(1,5-DAN)/SPEs are suitable for electrochemical determination of Pb²⁺ in acetate buffer electrolyte solution. The wide range of potential is promising for anodic stripping voltammetry of heavy metals such as Zn²⁺, Cd²⁺, and Cu²⁺.

3.2. Morphological Characteristics. The scanning electron microscope (SEM) morphologies of the bare SPEs and p(1,5-DAN)/SPEs were characterized by scanning electron microscopy, as shown in Figure 4. The bare carbon electrode was displayed with many dispersing small particles (Figure 4(a)). The small particles can be assigned as the carbon particles dispersed in a conductive screen printable ink. After electropolymerization, the morphology of the electrode changed significantly. The fabricated p(1,5-DAN) has a porous structure with a large active area and is homogeneously distributed throughout the electrode surface. The most widely accepted p(1,5-DAN) polymerization mechanism is the radical-mediated one, as reported in previous work [28–31]. In the initiation step, radical cations were generated from monomer oxidation by electrons on the anode. In the next steps, the radicals were then coupled to form oligomers and so on. However, the carbon screen-printed electrode has lower electron conductivity than the other electrodes (such as Au, Pt, and glassy carbon), which is attributed to the polymeric binder in the carbon ink [32]. The decrease in the electron transfer rate for screen-printed electrodes helps the formation of p(1,5-DAN)-like nanowires at the low current density [33]. This film is suitable for the deposition of heavy metal ions in the preconcentration step.

3.3. The Application of p(1,5-DAN)/SPEs for Pb²⁺ Sensors. Figure 5 shows the SWASV of 4.5 µg·L⁻¹ Pb²⁺ detection in acetate buffer (pH 4.5) on p(1,5-DAN)/SPEs.

![Figure 6: Effect of deposition potential (a) and deposition time (b) of 4.5 µg·L⁻¹ Pb²⁺ detection in acetate buffer (pH 4.5) on p(1,5-DAN)/SPEs.](image)

![Figure 7: The SWASV response for the increasing concentration of Pb²⁺ in 0.5–5.0 µg·L⁻¹ and the corresponding calibration plots (inset) of p(1,5-DAN)/SPEs. Electrolyte: acetate buffer (pH 4.5); deposition potential: -1.2 V; deposition time: 360 s.](image)
buffer (pH 4.5) at bare SPEs (curve (a)) and p(1,5-DAN)/SPEs (curve (b)). The current response on bare SPEs is very poor, with a dwarf peak. Under identical conditions, the p(1,5-DAN)-modified SPEs present significantly increased signals at -0.75 V.

The enhancement effects on the p(1,5-DAN)/SPEs are remarkably high in contrast to those on the bare SPEs. This result showed that p(1,5-DAN) was able to preconcentrate lead and was related to the amino and imine groups in the polymer chain. Besides, Wang et al. suggested that the conducting polymer has effectively prevented the adsorption of heavy metal ions on the microporous glassy carbon electrode [34]. So, almost all target ions are deposited on the electrode’s surface, and the stripping voltammetry process is perfect.

### 3.4. Optimization of Conditions for Pb²⁺ Detection

In order to get the best of SWASV of the p(1,5-DAN)/SPEs toward Pb²⁺, some of the key parameters were selected for optimized experiments. The effect of deposition potential and deposition time of Pb²⁺ detection in 0.1 M acetate buffer solution (pH 4.5) was investigated and is shown in Figure 6.

As shown in Figure 6(a), the stripping peak current of 4.5 μg·L⁻¹ Pb²⁺ after 360 s of deposition increased when the deposition potential decreased. The peak current quickly increased as the deposition potential decreased to -1.2 V. The deposition potential decreased from -1.2 and -1.5 V, and the peak current increased but slower. However, to avoid possible interference with other metals and damage to the working electrode, the potential at -1.2 V is chosen for continuous studies.

The effect of the deposition time for 45 μg·L⁻¹ Pb²⁺ detections on p(1,5-DAN)/SPEs was studied in the range from 180 to 480 s (Figure 6(b)). Under a fixed deposition potential at -1.2 V, the peak current increased steadily with increasing deposition time. A 360 s deposition time was selected as a compromise between high signal and reasonable assay time.

#### 3.5. Calibration Plot

The square wave peak current (Iₚ) for Pb²⁺ detection in 0.1 M acetate buffer solution (pH 4.5) in the concentration range from 0.5 μg·L⁻¹ to 5.0 μg·L⁻¹ is shown in Figure 7. The peak current increases with an increase in the concentration of Pb²⁺ ions. The calibration curve (Figure 7, inset) was derived from the peak currents of SWASV curves that exhibit excellent linear dependence on the concentration of Pb²⁺ with a linearity regression equation \( I_p = 0.506 \times C (\mu g \cdot L^{-1}) - 0.078 \) (R² = 0.9929). The limit of detection (LOD) was calculated by using the formula LOD = 3 × standard deviation of response/slope of the calibration curve [35]. The LOD obtained for the sensor was found to be 0.30 μg·L⁻¹.

In order to test the repeatability of sensors, the p(1,5-DAN)/SPEs were used for five measurements of 4.5 μg·L⁻¹ Pb²⁺ in acetate buffer solution. The relative standard deviation (% RSD, n = 5) of 3.1% was found. This result suggests that the poly(1,5-diaminonaphthalene)-modified screen-printed device exhibited good reproducibility and stability toward the Pb²⁺ ion sensing.

The analytical performance of p(1,5-DAN)/SPEs for Pb²⁺ was compared with other reported conducting polymers based on the literature, and results are summarized in Table 1. As can be seen, almost all conducting polymers are usually combined with inorganic nanomaterials for sensor sensitivity enhancement. Comparisons showed that the poly(1,5-diaminonaphthalene)-modified screen-printed device is a potential sensor for electroanalysis of Pb²⁺ with a low LOD value.

#### 3.6. Interferences of Other Metallic Ions

The interferences of some metallic ions on the detection of Pb²⁺ was investigated.

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### Table 1: Summary of publications relevant to the electrochemical detection of Pb²⁺ using conducting polymers.

| Electrode                        | Active layer                                                                 | LOD (μg·L⁻¹) | Linear range (μg·L⁻¹) | Ref. |
|----------------------------------|------------------------------------------------------------------------------|--------------|-----------------------|------|
| Glassy carbon                    | Poly(3,4-ethylenedioxythiophene)/black TiO₂ composites                       | 0.15         | 8.28-256.93           | [21] |
| Sputtered planar platinum        | Poly(1,5-diaminonaphthalene)/graphene                                       | 0.02         | 0.2-700               | [23] |
| Glassy carbon                    | Polyaniline                                                                 | 20.72        | 0-414.4               | [34] |
| Glassy carbon                    | Overoxidized polyppyrole doped with 2(2-pyridylazo) chromotropic acid anion | 10           | 0-200                 | [36] |
| Planar platinum                  | Interpenetrated multiwalled carbon nanotubes/poly(1,5-diaminonaphthalene)   | 2.1          | 4-150                 | [37] |
| Glassy carbon                    | Poly(1,2-diaminoanthraquinone)                                              | 0.58         | 0-120                 | [38] |
| Glassy carbon                    | Imidazole-functionalized polyaniline                                        | 20           | 2.07-2.07 × 10⁵       | [39] |
| Carbon paste                     |                                                                               | 2            | 0.21-2.07 × 10⁵       |      |
| Glassy carbon                    | Silver nanoparticles deposited on poly(1,8-diaminonaphthalene)              | 0.031        | 207.2-2486            | [40] |
| Glassy carbon                    | Polypyrrole-reduced graphene oxide nanocomposite hydrogels                  | 0.062        | 0.1-93.2              | [41] |
| Magnetic glassy carbon           | Core-shell ferroferric oxide@polyaniline                                    | 0.006        | 0.02-2.072            | [42] |
| Glassy carbon                    | Polyaniline-alanine-reduced graphene oxide                                   | 0.009        | 0.016-20.72           | [43] |
| SPE                              | Graphene-polyaniline                                                        | 0.1          | 1-300                 | [44] |
| SPE                              | Graphene/polyaniline/polystyrene                                            | 3.3          | 10-500                | [45] |
| SPE                              | Poly(1,5-diaminonaphthalene)                                                | 0.30         | 0.5-5.0               | This work |
under the optimal experimental conditions discussed above. Table 2 suggests that some metallic ions, such as Zn2+, Mn2+, Fe3+, and Al3+ (each 100-fold excess) and Cu2+ (4-fold excess), did not influence the SWASV peak currents of 5.0 μg L−1 Pb2+ (the ratios for a ±5% peak current change). For the concentration of Hg2+ (>8 μg L−1), the anodic stripping peak currents of Pb2+ increase due to mercury ions that can be reduced and form a mercury film at the electrode surface.

3.7. Analysis of Lead Ions in Tap Water. The p(1,5-DAN)/SPEs were employed for the detection of Pb2+ in the tap water sample matrix. The 2 mL tap water sample was mixed well into a buffer solution (pH 4.5) by sodium acetate and acetic acid, then dropped onto the p(1,5-DAN)/SPEs using a micropipette. The various concentrations of Pb2+ were spiked in the sample matrix. The SWASV was recorded under the optimum conditions. As can be seen in Table 3, the recoveries of Pb2+ were obtained with the concentration found divided by the assigned concentration of Pb2+ in the sample matrix. It is shown that the p(1,5-DAN)/SPEs are promising for the determination of Pb2+ in the real sample.

4. Conclusions

This work describes the use of the integrated screen-printed electrodes for the voltammetric determination of Pb2+ based on the poly(1,5-diaminonaphthalene) conductive polymer. The advantages of screen-printed electrodes, such as mass production, reproducibility, and ease of the preparation process, combined with a conductive polymer p(1,5-DAN), presented the excellent effect as a very inexpensive portable heavy metal ion analyzer. The modified screen-printed electrodes were used for the sensitive determination of Pb2+ by anodic stripping voltammetry.

Data Availability

The data used to support the findings of this study are included in the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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