

A mercury free 2, 4, 6-Trimercaptotriazine-Gold nanoparticles modified electrode for anodic stripping voltammetric determination of Pb (II)

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ABSTRACT

A simple and sensitive mercury free modified electrode using gold nanoparticles and metal chelating 2, 4, 6 -Trimercaptotriazine (GNPs-TMT) was fabricated for anodic stripping voltammetric determination of Pb (II). The modified electrode was prepared by drop casting the gold nanoparticles over paraffin impregnated graphite electrode followed by incorporation of TMT over the gold nanoparticles. Various analytical parameters such as pH, pre-concentration time, nature of background electrolyte were studied and optimized. The GNPs-TMT modified electrode showed a linear range from 3.2 µg/L to 112 µg/L for the determination of Pb (II) by means of differential pulse anodic stripping voltammetry (DPASV). With the optimized and improved experimental conditions, a detection limit of 1.06µg/L was obtained.

Keywords: DPASV, Lead, gold nanoparticles, 2, 4, 6 -Trimercaptotriazine

1. INTRODUCTION

Heavy metals are hazardous, non-biodegradable environmental pollutants and are found to have a major negative impact on human health and environment. Among all the heavy metal, lead is of great concern, because even at very low concentration, lead causes adverse health issues to mankind [1, 2]. Some of the major health issues caused by lead are damage of central nervous system, disorders in kidney, liver, and reproductive system. Children are most affected by the exposure of lead even at low concentration and may affect the deficit hyperactivity disorder (ADHD), lower IQ and higher risk of childhood aggression [3]. Lead poisoning is caused by drinking water contaminated with lead by the solder in the pipe joints and lead pipes, accidental exposure of lead based paints, ingestion of soil and air contaminated with lead [4]. Due to its toxic effects, there is a need to develop an analytical method which accurately quantifies the lead ions.

Some of the earlier methods used for determination of Pb (II) are flame atomic absorption spectroscopy [5], flow injection analysis [6], atomic fluorescence spectroscopy [7], solid phase extraction [8], UV-Visible spectroscopy [9] and inductive coupled plasma- mass spectrometry [10]. Even though the above-mentioned methods have been used for determination of Pb (II), they possess some of the demerits such as complicated sample preparation, expensive instrument, difficulty in handling and inappropriate for online monitoring [11]. In contrast, the electroanalytical methods have some special features which are highly sensitive for the determination of various metal ions in a polluted sample. Stripping voltammetry has been recognized as one of the most sensitive methods for trace analysis of lead (II) and it has a wide range of measurement, low detection limit, multi-ion analysis and used for real-time analysis [12]. The stripping voltammetric method was found to be highly remarkable and sensitive because of the preconcentration step. During preconcentration step, all the metal ions are accumulated as at the surface of the working electrode or deposited completely by reduction of metal ions to metal [13].

Normally mercury-based electrodes such as hanging mercury electrode [14] and mercury film electrode [15] have been used for the determination of metal ions by ASV because mercury will form an amalgam with most of the reduced metal ions. But due to the serious toxicity of mercury, an alternative modified electrode was used for the determination of Pb (II). Some of the alternative chemically modified electrodes used for the anodic stripping voltammetric determination of Pb (II) are bismuth film electrode [16], antimony film electrode [17], tellurium film electrode [18], and 1-(2-pyridylazo)-2-naphthol modified screen-printed carbon electrode [19]. These electrodes also have some of the disadvantages such as instability and non-economical. To replace these drawbacks a modified electrode with high stability, low cost with nontoxic materials have been fabricated by using gold nanoparticles and 2, 4, 6 - Trimercaptotriazine a metal chelating ligand.

In this work, a mercury-free electrode is reported which was prepared by incorporation of TMT and gold nanoparticles over PIGE for determination of Pb (II). The electrochemical behavior of GNPs-TMT modified was studied and various operating parameters that influence the performance of the modified

electrode were optimized. The results obtained by the modified electrode for determination of Pb (II) by ASV were found to be good with very low detection limit.

2. MATERIALS AND METHODS

2.1. MATERIALS

Auric chloride, graphite rod 3mm, and 2, 4, 6 -Trimercaptotriazine (TMT) were purchased from Aldrich chemicals. All the chemicals and reagent used for the experiments were of analytical grade and they were used without any further purification. Double distilled water was used for all the solution preparation. All the electrochemical experiments were done by using CHI 660B electrochemical workstation. The electrochemical cell set up consists of a conventional three-electrode system where GNPs-TMT modified electrode is used as working electrode, a platinum wire as a counter electrode and saturated calomel electrode as a reference electrode. The pH of the solution was measured with Elico pH meter (model LI 120).

2.2. EXPERIMENTAL METHODS

2.1.1. Fabrication of GNPs-TMT modified electrode

The procedure for preparation of GNPs-TMT modified electrode was already reported [20]. In short, the gold nanoparticles were synthesized reported method [21] and the resulted GNPs were drop cast over the PIGE which was the base material for the working electrode. The resulted GNPs-PIGE was dipped into a solution of TMT ligand solution for 10 mins. After completion of 10 the electrode was washed with distilled water and dried at room temperature. The obtained GNPs-TMT electrode was further used for the determination of Pb (II).

2.1.2. PROCEDURE FOR STRIPPING ANALYSIS

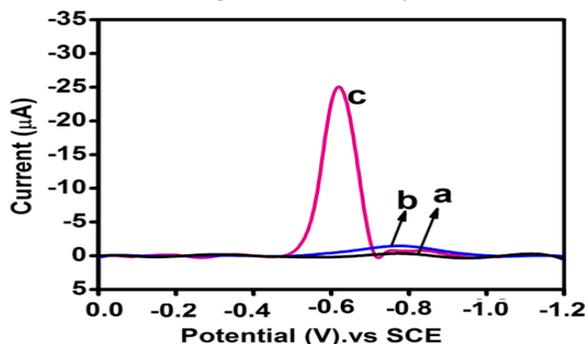
The GNPs-TMT modified electrode was kept in a stirred solution of 0.1M acetate buffer solution (pH 5) containing known amount of Pb (II) for a period of 240 sec. The above procedure was considered to be the preconcentration step where the Pb (II) ions are complexed with the TMT ligand present at the electrode surface. The complexed Pb (II) ions were reduced by applying a reduction potential of -1.2V for 60 sec. This step is the reduction step where the Pb (II) ions are converted to metallic form Pb (0). The metallic Pb (0) is stripped out anodically by scanning differential pulse voltammetry from -1.2 V to 0 V and the corresponding anodic current of Pb (II) was measured. The surface of the GNPs-TMT modified electrode was regenerated by dipping in 0.1M EDTA solution for 2 min and washed with distilled water. This ensures the electrode surface to be free from metal ions and used for further stripping analysis of Pb (II).

3. RESULTS AND DISCUSSION

3.1. Determination of Pb (II) by GNPs-TMT modified electrode using DPASV

Using GNPs-TMTs modified electrode Pb (II) ions were determined by DPASV. The Pb (II) ions were preconcentrated for 240 sec followed by reduction of the Pb (II) ions to Pb (0) by applying reduction potential at -1.2V. The reduced Pb (0) was stripped anodically in the potential range of -1.2V to 0V. **Fig 3.1** presents the comparative stripping voltammetric response of Pb (II) for **(a)** bare PIGE, **(b)** GNPs modified electrode **(c)** GNPs-TMTs modified electrode in ABS (pH 5) containing 32 μ g/L Pb (II) ions. For the same concentration of Pb (II) ions the bare PIGE, GNPs, and GNPs-TMTs modified electrode showed different stripping response. When compared with GNPs-TMTs modified electrode, bare and GNPs modified electrode showed very less current response for Pb (II). The higher current response of GNPs-TMTs modified electrode is due to its strong metal chelating nature of TMT over the electrode surface and this forms very effective complex with Pb (II).

Fig.3.1 DPASV responses of (a) Bare PIGE electrode, (b) GNPs modified electrode and (c) TMT/GNPs modified electrode in 32 μ g/L Pb (II) ions at a scan rate of 50mV/s in acetate buffer (pH 5) as background electrolyte



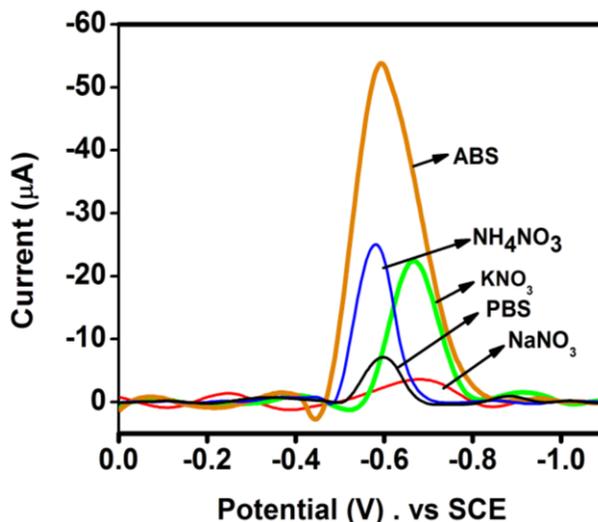
3.2. Optimization of various experimental parameters

In order to improve the sensitivity of the GNPs-TMT modified electrode towards the determination of Pb (II) various experimental parameters such as the effect of preconcentration time, nature of supporting electrolyte and pH of the electrolyte medium were optimized.

3.2.1. Electrolyte study for determination of Pb (II) at GNPs-TMT modified electrode

Depending upon the nature of supporting electrolyte the complexation of Pb (II) with GNPs-TMT modified electrode may differ. Hence different electrolyte medium such as acetate buffer (ABS), NH_4NO_3 , KNO_3 , NaNO_3 and phosphate buffer (PBS) have been used to study to the complexing ability of Pb (II) with GNPs-TMT modified electrode. The anodic stripping responses of Pb (II) at different electrolyte medium are shown in Fig.3.2. Since the higher current response was obtained for acetate buffer (ABS), 0.1M ABS was selected as the best pre-concentration media for Pb (II) at GNPs-TMT modified electrode.

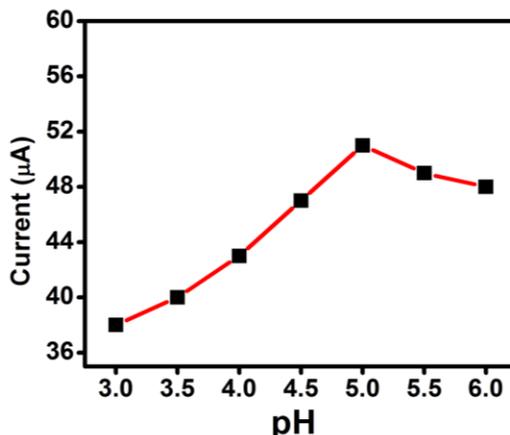
Fig.3.2. DPASV of TMT/GNPs modified electrode for $150\mu\text{g/L}$ Pb(II) ions in different electrolyte medium (0.1 M) (a) acetate buffer (ABS) (b) NH_4NO_3 (c) KNO_3 (d) NaNO_3 (e) Phosphate buffer (PBS)



3.2.2. Effect of pH on stripping of Pb (II) at GNPs-TMT modified electrode

The pH plays a very important role in the complex formation of Pb (II) at GNPs-TMT modified electrode. 0.1 M ABS was used to study the pH effect and the results obtained in the pH range of 3 to 6 were shown in Fig.3.3. From the figure, we can clearly state that the pH was found to be increasing with increase in the pH range from 3 to 6 and it starts decreasing after pH 5 this may be to the hydroxylation of metal ions. Therefore pH 5 was chosen and subjected for further stripping measurement of Pb (II) at GNPs-TMT modified electrode.

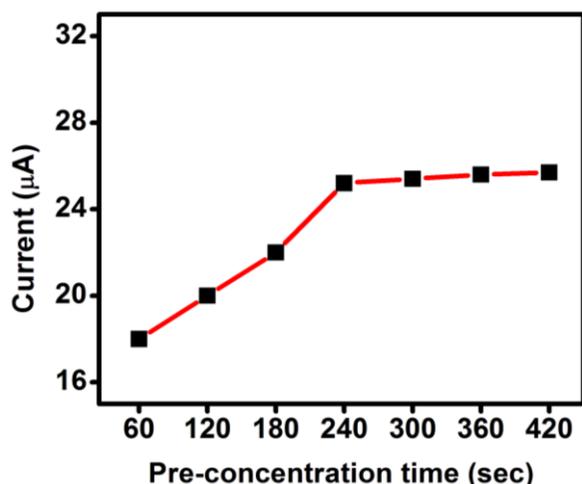
Fig.3.3. Effect of different pHs for preconcentration of Pb (II) ions at TMT/GNPs modified electrode (pH ranges from 3 to 6)



3.2.3. Influence of Pre-concentration time for the determination of Pb (II) at GNPs-TMT modified electrode

Pre-concentration of Pb(II) at GNPs-TMT modified electrode was studied by varying different pre-concentration time from 60 to 420 sec. **Fig.3.4** shows the stripping response of Pb (II) at a various pre-concentration time in 0.1M ABS (pH 5). When the pre-concentration time is increased from 60 sec to 240 sec the current for GNPs-TMT- Pb (II) complex was also increased. After 240sec the current remains almost same which represent that the modified electrode surface is saturated with Pb (II) ions. Hence a minimum time of 240 sec was needed for the maximum complex formation of Pb (II) at GNPs-TMT modified electrode. The complexed Pb (II) ions are reduced by applying a reduction potential of -1.2V for 60 sec.

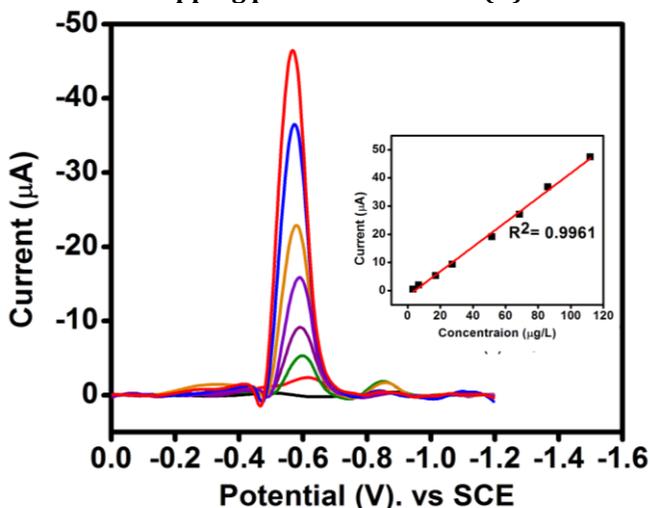
Fig.3.4. Effect of preconcentration time on the stripping current for the determination of Pb (II) ions at TMT/GNPs modified electrode from 60 sec to 420 sec at a scan rate of 50mVs-1



3.3 DPASV studies for the determination of Pb (II) at GNPs-TMT modified electrode

The GNPs-TMT modified electrode was also used to measure the stripping response for different concentration of Pb (II). The stripping current was found to be increasing at -0.6V for successive addition of lead ions in 0.1M ABS (pH 5). **Fig.3.5** shows DPASV response of GNPs-TMT modified electrode for subsequent addition of Pb (II) and the corresponding calibration plot is shown in the inset of **Fig.3.5**. A linear increase in the stripping response was observed for Pb (II) with a linear range of 3.2 µg/L to 112 µg/L and the calculated correlation coefficient (R^2) was 0.9970. The detection limit of GNPs-TMT modified electrode for the determination of Pb (II) was found to be 1.06µg/L.

Fig.3.5. DPASV response of TMT/GNPs modified electrode for detection of Pb (II) with concentration ranges from 3.4µg/L to 112µg/L for Pb (II) (inset of the Figure) calibration curve corresponding to stripping peak current of Pb (II)



The mechanism for the determination of Pb (II) at GNPs-TMT modified electrode involves following steps

1. Preconcentration of Pb (II) 0.1M acetate buffer (pH 5) - 4 mins
GNPs-TMT + Pb (II) \longrightarrow GNPs-TMT - Pb (II) (1)
2. Reduction in Pb (II) 0.1M Acetate buffer (pH 5) at -1.2 V - 60seconds
GNPs-TMT - Pb (II) \longrightarrow GNPs-TMT - Pb (0) (2)
3. Stripping of Pb (0) in the potential range -1.2V to 0 V in 0.1 M Acetate buffer (pH 5).
GNPs-TMT - Pb (0) \longrightarrow GNPs-TMT - Pb (II) (3)
4. Regeneration of GNPs-TMT - Pb (II) electrode surface by dipping in 0.1 M EDTA - 2 mins
GNPs-TMT - Pb (II) \longrightarrow GNPs-TMT + Pb (II)-EDTA (4)

3.4. Regeneration of GNPs-TMT modified electrode

The regeneration of the modified electrode was achieved by dipping the GNPs-TMT- Pb (II) in 0.1M EDTA solution for 2 min. The EDTA helps to remove the complexed Pb (II) ions at the electrode surface via complex formation. Water-soluble Pb (II) - EDTA complex was removed by washing the electrode surface with distilled water. For every stripping analysis, the electrode surface was regenerated with 0.1M EDTA solution. This method of electrode regeneration was found to be the most effective and the stability of the modified electrode remains unaltered.

3.5. Selectivity of GNPs-TMT modified electrode for determination of Pb (II)

Determination of Pb (II) ions in presence of some of the possible interfering metal ions at GNPs-TMT modified electrode was studied using DPASV. Metal ions such as Zn (II), Hg (II), Ca (II), Mg (II) does not affect the stripping response of Pb (II), because the potential for stripping these metal ions was different and the pH for complex formation of each metal ions was also different. When the concentration of Cu (II) was added 20 fold excess of Pb (II), the Cu (II) ions may interfere with the stripping response of Pb (II) which is due to the inter-metallic formation.

4. CONCLUSION

A mercury-free GNPs-TMT modified electrode was successfully prepared and used for the determination of Pb (II). The sensitive determination of Pb (II) was achieved by optimizing various operational parameters such as pH, preconcentration time and supporting electrolyte. Under optimized experimental conditions, the GNPs-TMT modified electrode showed a linear range of Pb (II) determination from 3.2 $\mu\text{g/L}$ to 112 $\mu\text{g/L}$ with a detection limit of 1.06 $\mu\text{g/L}$. An easy method of electrode regeneration for further stripping analysis was employed. The GNPs-TMT modified electrode showed high selectivity, sensitivity, and good reproducibility.

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