Simultaneous Determination of Cd(II) and Pb(II) at a glassy carbon electrode immobilized with ceria nanoparticles by Anodic Stripping Voltammetry

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ABSTRACT

Unique and fascinating features of cerium oxide nanoparticles are gained significant research interest in recent years as they can lead to crucial technological advancements in fabrication of sensing devices. In the present paper, crystalline cerium oxide nanoparticles have been successfully prepared using a facile one step nitrate-sucrose decomposition method. The prepared cerium oxide nanoparticles were drop casted on the glassy carbon electrode (GCE) and then it was investigated for the trace analysis of toxic cadmium and lead present in water samples. The cerium oxide modified GCE was characterized using electrochemical impedance and cyclic voltammetry. The differential pulse anodic stripping voltammetry (DPASV) results showed that the detection limits for cadmium and lead was found to be 3.1 and 3.5 μg/L respectively under optimized conditions. The observed high sensitivity and selectivity is due to high surface to volume ratio of cerium oxide nanoparticles.

1. Introduction

The discharge of non-biodegradable lead and cadmium ions into the water system by electroplating, metallurgical processes, and paper mills has been conspicuously increasing due to modernization[1,2]. Hence, the presence of these elements even in low concentration causes serious threat both to the human and aquatic systems. Therefore, the world health organization (WHO) has recommended threshold limit values for the lead and cadmium 10 μg/L and 3 μg/L respectively in drinking water[3]. Several analytical protocols such as inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectrometry, inductively coupled plasma atomic emission spectrometry and atomic absorption spectroscopy[4-7] have been successfully demonstrated for the accurate detection of cadmium and lead present in various environmental samples. However, the development of simple and cost effective protocol for the detection of lead and cadmium is still a matter of challenge. Contrary, electrochemical techniques gained considerable interest owing to their high sensitivity/selectivity, repeatability, and two or more metal ions were analyzed simultaneously[8]. The sensitivity and selectivity of the target metal ions is mainly determined by the electrode modifier in case of electrochemical techniques and therefore the identification/selection of potential electrode modifier plays an important role in fabricating efficient and reliable sensing devices, which can be operated for on-site applications[9]. In this context, enhanced electron-transfer kinetics and strong adsorption capability of lead and cadmium on nano cerium oxide makes more advantageous over other conventional materials.

As a consequence, the present interest of this research lies in the preparation of nano-sized cerium oxide and the exploration of the corresponding size-induced property to develop highly sensitive and selective electrochemical sensor for the detection of trace cadmium and lead. Nano-sized cerium oxide has been prepared by simple and robust one pot sucrose-nitrate decomposition method. Furthermore, the glassy carbon electrode(GCE) has been modified by the prepared nano-sized cerium oxide. The electron transfer kinetics of the cerium oxide modified GCE was studied by using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry. Finally, the performance of the modified...
GCE was evaluated for cadmium and lead in acetate buffer solution using differential pulse anodic stripping voltammetry (DPASV).

2. Experimental

2.1 Materials

Analytical grade potassium hexacyanoferrate(III) (>99%), potassium hexacyanoferrate(II) trihydrate (>99.99%), potassium chloride, sodium acetate, cerium nitrate (>99%), cadmium(II) nitrate (99.999%), lead(II) nitrate and acetic acid (99–100%) were purchased from Sd fine and used without further purification. Acetate buffer solution was prepared using 0.1M sodium acetate and 0.1 M acetic acid prepared in doubly deionized water.

2.2 Preparation of the cerium oxide nanoparticles

The cerium oxide nanoparticles were prepared by using our previously reported method [10]. Briefly, the stoichiometric amount of cerium nitrate was dissolved in minimum quantity of water at room temperature. Sucrose (Oxidized/Fuel ratio of 2) was subsequently added to the cerium nitrate solution and stirred for 5 minutes to ensure homogeneous solution. Finally, the beaker containing homogeneous solution was placed in a preheated muffle furnace maintained at 450 ± 10 °C for 3 minutes. The resultant powder was crushed with mortar and pestle, and used for further studies.

2.3 Fabrication of cerium oxide nanoparticles modified glassy carbon electrode

Firstly, the bare GCE was polished with 1, 0.3 and 0.05 μm alumina powders using soft cloth. The polished bare GCE was subjected to sonication in water for three times for a period of three minutes each. Then the GCE is rinsed with ethanol followed by drying at room temperature. Secondly, the prepared cerium oxide nanoparticles (10 mg) were dispersed in 10 mL of water by sonication for 10 minutes and then the 10 μL of the homogeneous cerium oxide nanoparticles suspension was drop casted on GCE and allowed for drying at room temperature. The resulted cerium oxide film has good adhesion and has not peel off. The schematic representation of the GCE modification was illustrated in Scheme 1.

2.4 Instrumentation

X-ray powder diffraction (PAnalyticalX’pert PRO X-ray diffractometer) was used to analyze the phase purity, and crystallinity of the prepared cerium oxidonanoparticles. The specific surface area, pore size and pore diameter of cerium oxidonanoparticles were determined by nitrogen adsorption at 77 K on the basis of the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods (Quanctochrome corporation NOVA 1000). Fourier transform infrared (FT-IR) spectra of cerium oxidonanoparticles were monitored by Perkin-Elmer FT-IR spectrometer (Spectrum 1000) using KBr pellets over the range of 400-4000 cm⁻¹. The absorption spectrum of cerium oxidonanoparticles was measured by SL 159 ELICO UV-visible absorption spectroscopy. The morphology, particles size and crystallinity of cerium oxidonanoparticles were analyzed by using FEI Tecnai F-30 transmission electron microscope (TEM).
The electrochemical experiments were performed with biologic SP-150 computer controlled electrochemical workstation utilizing electrochemical techniques such as cyclic voltammetry (CV), electrochemical impedance (EI) and differential pulse anodic stripping voltammetry (DPASV) and a standard three-electrode configuration was used throughout, consisting of a glassy carbon as working electrode, with a Ag/AgCl wire as reference electrode and a platinum wire as counter electrode.

3. Results and Discussion
3.1 Characterization of the prepared cerium oxide nanoparticles

The crystal structure, crystallite size and surface morphology of the as-prepared CeO₂ nanoparticles were characterized by XRD, FTIR and TEM.

The powder XRD pattern of the as-prepared cerium oxide nanoparticles is shown in figure 1, wherein all the diffraction peaks appeared in the XRD pattern are identical to the (111), (200), (220), (311) and (222) planes of pure cubic cerium oxide structure [JCPDS 34-0394]. The crystallite size of the cerium oxide nanoparticles calculated based on Scherrer formula[11] is found to be 9 nm.

![Figure 1. Powder XRD pattern of the as-prepared cerium oxide nanoparticles.](image)

The TEM analysis of the as-prepared cerium oxide nanoparticles has been carried out to confirm the crystallite size obtained from powder XRD pattern. As shown in the figure 2(a and b), the cerium oxide nanoparticles exhibit spherical shape with particle size of 8 nm, which is in good agreement with the powder PXRD result. Further, the as-prepared cerium oxide nanoparticles were further analyzed using SAED pattern where the clear appearance of diffraction rings confirms the polycrystalline nature (figure 2c). The spacing between two fringes is found to be 3.12 Å in HRTEM image (figure 2d) which corresponds to inter planar distance of (111) crystalline plane of cubic phase cerium oxide.
The purity of the as-prepared cerium oxide nanoparticles was further confirmed by FTIR spectrum (figure 3a). The Ce–O stretching band was observed at 540 cm\(^{-1}\) along with two additional vibration modes appeared at 1387 for A\(_{1g}\) of carbon and 1580 cm\(^{-1}\) for E\(_{2g}\) of graphitic carbon. In addition, the bands at 3420, and 1634 cm\(^{-1}\) are also observed for O-H stretching and H\(_2\)O bending frequencies of physisorbed water molecules.

The specific surface area and pore size of the CeO\(_2\) nanoparticles were analyzed using nitrogen adsorption–desorption isotherm data. The specific surface area of the cerium oxide nanoparticles was found to be 18.37 m\(^2\)g\(^{-1}\) and the presence of mesopores has been confirmed by the type IV isotherm as shown in figure 3b. The pore-size distribution curve (figure 3c) exhibit sharp and narrow peak centered at 36 Å, further it confirms the mesoporous nature of the as-prepared cerium oxide nanoparticles.
3.2 Electrochemical Impedance Spectroscopy study of cerium oxide nanoparticles modified

Electrochemical impedance spectroscopic (EIS) study is suitably applied for measuring resistance and capacitance as well as describing the charge transfer in electrode surface and interface. In EIS, semicircle appeared at higher frequency is attributed to a process, which limits electron transfer. The diameter of this semicircle shows resistance (Rct) against the electron transfer. Rct affects the interface-related kinetics of electron transfer of the redox probe. The Faradaic mode in frequency was applied to measure EIS where redox-probe ferrocyanide/ferricyanide was used to follow interfacial changes in resistance of solution-electrode. The electrode composition was modified by CeO$_2$ NPs, which resulted in the Rct changes. The most sensitive and accurate sensing electrode was obtained by measuring the Rct following each electrode composition modification. The results of EIS measurements in 5.0 mmol L$^{-1}$ solution of [Fe(CN)$_6$]$^{3-}$/4- and the Nyquist plots of the bare and modified electrode were plotted between the frequency 0.01 and 100000 Hz are shown in Fig. 4. The Rct of unmodified GCE (3519 $\Omega$) (Fig. 4a) is considerably higher than that of CeO$_2$ NPs modified GCE (1127 $\Omega$) (Fig. 4b), which means that the conductivity of the former GCE is poorer and thus it has lower electron transfer rate. The Rct of the modified GCE is significantly reduced, which indicates that the CeO$_2$ nanoparticles provides necessary conduction pathway across the electrode interface and thereby enhances the electron transfer rate.

![Figure 4](image_url)
3.3 Cyclic Voltammetry

The electrochemical response of the bare and CeO$_2$ NPs modified GCE has been tested using cyclic voltammetry in the absence and presence of 10 mM of Cd(II) and Pb(II) between the potential -1.5 to +0.2 V at a scan rate 50 mV s$^{-1}$ (Figure 5). The cerium oxide nanoparticles modified GCE does not show electrochemical response for the oxidation/reduction of CeO$_2$. However, cerium oxide nanoparticles modified GCE showed a two well resolved oxidation peak at peak potential of -0.70V and -0.40 V for Cd(II) and Pb(II) respectively (Figure 5c)[12]. The bare GCE also showed oxidation peaks (Figure 5(b)) for Cd(II) and Pb(II) but the intensity of the peak current is less as compared to the cerium oxide modified GCE. This result confirms that the CeO$_2$ NPs modified GCE exhibit better electrochemical response and the observed better signal is due to the presence of mesopores and small crystallite size. The presence of mesopores and small crystallite enhances the accumulation of the Cd(II) and Pb(II) and thereby increased the electrochemical response.

![Cyclic voltammograms](image)

**Figure 5.** Cyclic voltammograms of (a) CeO$_2$ NPs modified GCE in absence of Cd(II) and Pb(II), (b) bare electrode in the presence of 10 mM Cd(II) and Pb(II) and (c) CeO$_2$ NPs modified GCE in presence of 10 mM Cd(II) and Pb(II) in a buffer solution of pH 5 containing 0.1 M KCl as supporting electrolyte with scan rate 50 mV/s.

3.4 Optimization of experimental parameters

3.4.1 Effect of pH

It is important to investigate the working pH of the modified electrode for the detection of Cd(II) and Pb(II) ions present in water samples. Figure 6 shows the anodic current obtained for Cd(II) and Pb(II) in DPSV at different PH (pH = 4-6). From the Figure 6, it is observed that the optimum working pH for the modified electrode is 5 and thus the acetate buffer solution of pH 5 was selected for further studies.
Figure 6. Effect of pH on the anodic peak current of Cd(II) and Pb(II) in presence of acetate buffer containing 0.1 M KCl with preconcentration time 300 s and preconcentration potential of -1.0 V.

3.4.2 Effect of Deposition Potential and Deposition Time

The sensitivity and selectivity of the modified electrode greatly influenced by the deposition potential and time. Therefore, the optimization of the deposition potential has been carried out. Figure 7a shows the effect of deposition potential (-1.4 to -0.6 V) on the anodic peak current of Cd(II) and Pb(II) for the modified electrode. As depicted in the figure that the anodic peak current for both Cd(II) and Pb(II) reached maximum at -1.0 V. Optimization of the deposition time has been carried out in the range 1 to 7 minute under applied potential of -1.1 V in an acetate buffer solution of pH 5. One can see from the figure 7b that the anodic peak current for the Cd(II) and Pb(II) increases with increase in deposition time and reached a maximum at 5 minutes. The increase in anodic peak current with increase in time is due to the increase in accumulation of Cd(II) and Pb(II) on the modified electrode surface. Further increase in time (i.e. after 5 min) leads to the constant anodic peak current due to the saturation of the electrode surface[13]. Thus, deposition potential of -1.0 V and deposition time of 5 min was selected for further studies.

Figure 7. Effect of (a) deposition potential and (b) Pre-concentration time on the anodic peak current of Cd(II) and Pb(II) in an acetate buffer of pH 5.

3.5 Simultaneous detection of cadmium and lead

Simultaneous detection of cadmium and lead has been carried out under optimized conditions. The stripping
voltammograms for Cd(II) and Pb(II) at different concentration are shown in Figure 8a. The appearance of well resolved peak indicating that the modified electrode could be used for the simultaneous detection of Cd(II) and Pb(II). The anodic peak current for both Cd(II) and Pb(II) increase with increase in concentrations.

The calibration graph for Cd(II) and Pb(II) has been constructed between the concentration 10 and 400 µg/L and the obtained plot is shown in Figure 8(b-c), where the anodic peak current increases proportionally for both Cd(II) and Pb(II) with increase in concentration. The limit of detection has been calculated based on the anodic peak current values and it is found to be 3.1 and 3.5 µg/L respectively for Cd(II) and Pb(II). The calibration equations obtained for Cd(II) and Pb(II) are given as follows: Cd(II): \[ I_{pa} \, (\mu A) = 0.0627 \, (\mu A/\, \mu g/L) \, C + 2.4415 \, (\mu A), \] with \[ R^2 = 0.989 \] and Pb(II): \[ I_{pa} \, (\mu A) = 0.0759 \, (\mu A/\, \mu g/L) \, C + 10.1521 \, (\mu A), \] with \[ R^2 = 0.986. \]

Figure 8. (a) Differential pulse anodic stripping voltammograms of Cd(II) and Pb(II) as function of concentration (10 and 400 µg/L) using the CeO$_2$ NPs modified GCE. Conditions: deposition potential -1.0 V, deposition time 5 min, potential scan range from -1.0 to 0.3 V; (b) Corresponding calibration plot.

3.6. Reproducibility and stability of the cerium oxide nanoparticles modified GCE

To check the reproducibility of the results, five similarly modified electrodes have been used. All the five electrodes show almost same peak currents in presence of Cd(II) and Pb(II) with relative standard deviation of 3.4 and 4.1%.

In order to test the stability of the modified electrode, the anodic current for both Cd(II) and Pb(II) in acetate buffer solution of pH 5 in the intervals of 1 day, 30 days and 60 days. It is observed that the relative standard deviation for Cd(II) and Pb(II) is found to be 1.5 and 2.1% respectively. Therefore, the cerium oxide nanoparticles modified electrode could be used as potential candidate for the quantification of Cd(II) and Pb(II) ions in real sample matrices.
3.7 Interference Study

To study the selectivity of the proposed method, the effects of various common cations and anions on the simultaneous determination of 50 µg/Leach of Pb(II) and Cd(II) was studied. An error of ±5% was considered tolerable. The developed sensor showed least interference from most of the common cations and anions due to adsorption between the pores of the modifier material and the target analytes i.e. lead and cadmium ions (Table 1).

<table>
<thead>
<tr>
<th>Interferent</th>
<th>Tolerance Limit (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺, Ba⁺⁺, Mg⁺⁺, Cu²⁺, Ni²⁺, Zn⁺⁺</td>
<td>1000</td>
</tr>
<tr>
<td>Cl⁻, F⁻, SO₄²⁻, K⁺, Mn²⁺, Li⁺, Ag⁺, Fe³⁺</td>
<td></td>
</tr>
<tr>
<td>Co³⁺, C₂O₄²⁻, CO₃²⁻</td>
<td>40</td>
</tr>
<tr>
<td>Hg²⁺, Bi³⁺, Sn²⁺, Fe⁺⁺</td>
<td>20</td>
</tr>
<tr>
<td>Cu²⁺, Ni²⁺</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 1. Interference Study

3.8 Analytical Applications

The analytical utility of the proposed sensor has been validated by measuring cadmium and lead levels present in various real sample matrices like lead acid batteries, chrome plating and textile industrial effluent samples. The pretreated industrial effluents of chrome plating industry and textile dyeing industry were collected from the State pollution control board, Karnataka and the lead-acid battery effluents were collected from the battery servicing stations. The recovery study was carried out for all these samples by spiking with known concentrations of Pb(II) and Cd(II) ions (Table 2). The results are shown in Table 2 clearly demonstrate that the recoveries of spiked samples greater than 95% indicating that the proposed method could be applied in the quantitative measurements. The results obtained by the proposed method are in agreement with the results obtained by the atomic absorption spectroscopic (AAS) method. The results obtained by this method are compared with the results reported by other groups which are tabulated in Table 3.
**Table 2. Application Study**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Originally found (µg/L)</th>
<th>Added (µg/L)</th>
<th>Total (µg/L)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battery effluent</td>
<td>22.3</td>
<td>15.0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Waste water*</td>
<td>22.5</td>
<td>13.5</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Waste water*</td>
<td>34.4</td>
<td>12.5</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

* The samples were obtained from different locations from open sewer lines within the city limits.

**Table 3. Comparison of the proposed method with other existing reports**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Linear range (µg/L)</th>
<th>Detection limit (µg/L)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi film/crownether/Nafion/SPCE</td>
<td>0.5-60</td>
<td>0.11</td>
<td>[14]</td>
</tr>
<tr>
<td>TiO₂/ZrO₂ composite/CPE</td>
<td>1-200</td>
<td>0.48</td>
<td>[15]</td>
</tr>
<tr>
<td>ERGNO film/SPCE</td>
<td>1-60</td>
<td>0.80</td>
<td>[16]</td>
</tr>
<tr>
<td>Bi-CNT/SPCE</td>
<td>2-100</td>
<td>1.3</td>
<td>[17]</td>
</tr>
<tr>
<td>CeO₂-NPs modified GCE</td>
<td>10-400</td>
<td>3.1</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Bi film/crownether/Nafion/SPCE = Bismuth film/crown ether/Nafion/screen-printed carbon electrode; TiO₂/ZrO₂ composite/CPE = Titanium dioxide/zirconium oxide composite/carbon paste electrode; ERGNO film/SPCE = electrochemically reduced graphene oxide film/screen-printed electrode; Bi-CNT/SPCE = Bismuth- carbon nanotube screen-printed electrode; CeO₂-NPs modified GCE = Cerium oxide nanoparticles modified glassy carbon electrode.

**4. Conclusions**

In this work, cerium oxide nanoparticles film modified glassy carbon electrode has been fabricated and demonstrated it successful application for the analysis of trace levels of Cd(II) and Pb(II) present in real samples. The fabricated electrode is stable for at least 3 months and is capable repetitive and reproducible measurements. The DPASV
results demonstrated that cerium oxide nanoparticle is a promising new sensor material and suitable for developing portable low cost devices for the analysis of heavy metals present in environmental samples.

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