Electrochemical determination of Pb(II), Cd(II) and Hg(II) ions using metal oxide nanoparticles modified carbon paste electrodes
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Due to a strong environmental and biological impact, trace metal ions determination has received particular attention in the last few years. Atomic absorption spectrometry [1], X-ray fluorescence spectrometry [2], inductively coupled plasma optical emission spectrometry [3], flow injection combined with inductively coupled plasma mass spectrometry [4], polarography [5], chromatography [6] spectrophotometry and electrochemical methods [7-10] have been used for the determination of metal ions in different samples. Among all the electrochemical techniques, the anodic stripping voltammetry have been employed for the determination of metal ions with chemically modified electrodes.

Electrochemists are always searching for optimal electrode surfaces which can offer significant advances. A common way to achieve this is through electrode modification with the aim of producing electrocatalytic responses. Desirable characteristics for modified electrodes are the reduction in the overpotential of the analyte under investigation, increased stability of the electrode response coupled with increments in peak height facilitating lower detection limits and increased specificity compared to the bare underlying electrode.
Chapter 7 Electrochemical determination of Pb(II), Cd(II) and Hg(II) ions

There is an extensive literature on chemically modified electrodes for the electroanalysis of target analytes which are ultimately utilized to increase selectivity and sensitivity [11-16]. However, common problems of this approach are instability, low sensitivity, high cost and non-reproducible thicknesses which may limit their applications.

This section is focused on the quantitative determination of Cd(II), Pb(II) and Hg(II) ions from aqueous solutions. Further this chapter has been divided into three sub chapters. Chapter-7.1 deals with the detection of Cd(II), Pb(II) and Hg(II) ions using ZnO nanoparticles modified carbon paste electrode. Chapter-7.2 presents the study on the detection of Cd(II), Pb(II) and Hg(II) ions using NiO nanoparticles modified carbon paste electrode whereas Chapter-7.3 outlines the results on the detection of Cd(II), Pb(II) and Hg(II) ions using CuO nanoparticles modified carbon paste electrode.
Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions using ZnO nanoparticles modified carbon paste electrode

Over the past few decades, carbon paste, i.e., a mixture of carbon (graphite) powder and a binder (pasting liquid), has become one of the most popular electrode materials used for the laboratory preparation of various electrodes, sensors, and detectors. Variety of materials are used to modify the carbon paste electrodes for the sensitive determination of the analytes.

Mechanical admixing of modifiers into the carbon paste bulk is the frequent way of modification which is done with substances in solid state and which is especially simple when using soft and easy-to-homogenize carbon pastes [17, 18]. Usually, the content of modifiers in carbon pastes varies between 1-5% (w/w) [19, 20], however, there are chemically modified CPEs with 30-50% of the respective modifier [17, 21] and if some chemically active binders are considered as special modifiers, the resultant content can be yet higher, up to 70% [22, 23].

This chapter presents the results and discussions on the determination of Cd(II), Pb(II) and Hg(II) ions using ZnO nanoparticles modified carbon paste electrode.
7.1 Voltammetric behavior of $K_3[Fe(CN)_6]$

The $[Fe(CN)_6]^{3/4-}$ couple was used as the electrochemical redox probe to investigate the electrochemical properties of ZnO nanoparticles modified carbon paste electrode (ZnO-CPE) and carbon paste electrode (CPE). Figure 7.1.1 shows the cyclic voltammograms obtained at ZnO-CPE and CPE. The peak shape of $[Fe(CN)_6]^{3/4-}$ redox reaction at CPE was broad and the peak to peak potential separation ($\Delta E_p$) is as large as 400 mV (curve a), whereas at ZnO-CPE the separation between redox peaks was decreased to 294 mV (curve b) with a subsequent increase in the peak current. The enhancement in peak current and decrease in peak separation ($\Delta E_p$) indicated the catalytic ability of ZnO-CPE compared to CPE.

![Cyclic voltammograms of 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl at the scan rate of 100 mVs$^{-1}$: (a) CPE and (b) ZnO-CPE.](image)

**Figure 7.1.1:** Cyclic voltammograms of 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl at the scan rate of 100 mVs$^{-1}$: (a) CPE and (b) ZnO-CPE.
7.1.2 Simultaneous determination of Cd(II) and Pb(II) Ions

7.1.2a Differential pulse voltammetric response of Cd(II) and Pb(II) ions

Figure 7.1.2 shows the DPASV response of $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions at CPE and ZnO-CPE respectively. The stripping peak current for Cd(II) and Pb(II) ions at ZnO-CPE (curve b) was larger than those obtained at CPE (curve a). This may be due to the larger surface area and catalytic behavior of ZnO nanoparticles present in the carbon paste electrode.

![Figure 7.1.2: DPASVs of $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions in 0.1 M KCl at pH 7.0: (a) CPE and (b) ZnO-CPE.](image)

In order to identify the optimum operating conditions for the high sensitivity of the electrode, the effect of various operating parameters such as preconcentration potential, preconcentration time and pH were studied.
7.1.2b Effect of preconcentration potential

Influence of preconcentration potential is always important factor on the sensitivity and detection limit of the electrode. Optimal preconcentration potential for $1 \times 10^{-6}$ M Cd(II) and Pb(II) ions was determined in the range -0.8 V to -1.4 V. For the preconcentration potentials lower than -0.9 V, no Cd(II) peak was observed. Increase in preconcentration potential from -0.9 V to -1.4 V, resulted in increased peak intensity for Cd(II) and Pb(II) ions. At deposition potential greater than -1.2 V the peak shapes were distorted and resulted in hydrogen evolution. Hence, for further experiments, preconcentration potential was applied at -1.2 V.

7.1.2c Effect of preconcentration time

![Graph showing effect of preconcentration time on stripping current.](image)

**Figure 7.1.3:** Effect of preconcentration time on stripping current.

The effect of preconcentration time on the stripping current of $1 \times 10^{-6}$ M Cd(II) and Pb(II) ions is as shown in Figure 7.1.3. The peak current increased linearly with increase in the preconcentration time from 60 to 600 s because of the increased rate of accumulation of Cd(II) and Pb(II) ions on surface of the electrode. For a preconcentration time greater than 600 s, stripping peak current was approximately
same and the plot tends to deviate from linearity because of brisk saturation. Hence, 300 s of preconcentration time has been selected for further studies.

### 7.1.2d Effect of pH

The effect of pH on peak current of $1 \times 10^{-6}$ M Cd(II) and Pb(II) ions at ZnO-CPE is as depicted in Figure 7.1.4. It can be seen from the Figure, that the peak current increases with increase in pH of the solution, this trend may be attributed to the fact that with increase in pH, the surface charge of ZnO becomes less positive. This is a favorable condition for the deposition of the metal cations on surface of the electrode. Further increase in pH above 7.0 may results in the formation of insoluble metal hydroxides; hence pH 7.0 was selected for the further studies.

![Figure 7.1.4: Effect of pH on peak intensity of $1 \times 10^{-6}$ M Cd(II) and Pb(II) ions.](image)

### 7.1.2e Calibration curve, detection limit and reproducibility of the electrode

Figure 7.1.5 shows the DPASVs of 1 to $8 \times 10^{-8}$ M Cd(II) and Pb(II) ions at ZnO-CPE under the optimized conditions. The calibration curves constructed for the Cd(II) and Pb(II) ions were linear in the studied concentration range with the correlation coefficients 0.9953 and 0.9923 respectively (Figure 7.1.6).
Figure 7.1.5: DPASVs of 1 to $8 \times 10^{-8}$ M Cd(II) and Pb(II) ions at ZnO-CPE in 0.1 M KCl at pH 7.0.

Figure 7.1.6: Calibration plots of Cd(II) and Pb(II) ions on ZnO-CPE.

The sensitivity of the electrode calculated from the slope of calibration curve was $0.35 \times 10^{-8}$ and $0.27 \times 10^{-8}$ A/nM for Cd(II) and Pb(II) ions respectively. The detection limit for Cd(II) and Pb(II) ions determined experimentally was found to be 6.5 nM and 8.5 nM respectively. The relative standard deviations calculated from six identical measurements at the same electrode were 4.25% and 6.31% for Cd(II) and Pb(II) ions respectively. For the five different set of electrodes, the calculated RSD was found to be more than 6% for both the metal ions.
Chapter 7.1 Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

The stripping peak current of $10 \times 10^{-8}$ M Cd(II) and Pb(II) ions was measured in presence of equimolar solutions of Triton X-100, sodium dodecyl sulfate and cetyltrimethylammonium bromide. All the three surfactants resulted in negligible decrease in stripping current, which indicated that ZnO-CPE had more tolerance to the presence of surfactants.

7.1.3 Determination of Hg(II) ions from aqueous solutions

7.1.3a Differential pulse anodic stripping voltammetric response of Hg(II) ions

Figure 7.1.7 shows DPASV response of 2 to $10 \times 10^{-8}$ M Hg(II) ions in 0.1 M KNO$_3$ at CPE and ZnO-CPE. The stripping peak current of Hg(II) at 0.18 V was greatly enhanced at ZnO-CPE (curve a-h) compared to CPE (dotted line). The increase in peak current at ZnO-CPE is probably due to the enhanced specific surface area of electrode. It was found that the peak current of Hg(II) ions increased with increase in Hg(II) ions concentration.

![Figure 7.1.7: DPASVs of 2 to $10 \times 10^{-8}$ M Hg(II) ions in 0.1 M KNO$_3$ at pH 7.0: CPE (dotted line) and ZnO-CPE (solid lines- a to h).](image)

163
7.1.3b Effect of preconcentration Time

The amount of Hg(II) deposition on the electrode surface has been probed by increasing the deposition time. Figure 7.1.8A shows the effect of preconcentration time on stripping current of $10 \times 10^{-8}$ M Hg(II) ions. It can be seen from the Figure that the stripping current increases with increase in deposition time up to 600 sec and further increase in the deposition time did not show any influence on the stripping current.

7.1.3c Effect of preconcentration potential

The nominal stripping peak current of Hg(II) ions can be controlled by varying the preconcentration potential. The influence of preconcentration potential on the current response of $10 \times 10^{-8}$ M Hg(II) was studied in the range -0.1 to -0.5 V versus SCE and is shown in Figure 7.1.8B. The stripping peak current increases with increase in preconcentration potential from -0.1 V to -0.3 V. This is due to the complete reduction of Hg(II) ions to their neutral forms however, the peak current remains almost unchanged at more negative preconcentration potentials. Hence, preconcentration potential of -0.3 V has been fixed in the subsequent studies.

![Figure 7.1.8: Effect of preconcentration time (A) and preconcentration potential (B) on the differential pulse anodic stripping current of $10 \times 10^{-8}$ M Hg(II) ions.](image)
7.1.3d Effect of preconcentration solution pH

![Graph showing the effect of pH on the differential pulse stripping current of 10×10^-8 M Hg(II) ions.](image)

**Figure 7.1.9:** Effect of pH on the differential pulse stripping current of 10×10^-8 M Hg(II) ions.

The effect of pH on the stripping peak current of 10×10^-8 M Hg(II) ions at ZnO-CPE is shown in Figure 7.1.9. It was observed that, the peak current increases with increase in pH values. This trend is probably due to the decreased positive charge on the surface of ZnO-CPE.

7.1.3e Calibration curve, detection limit and reproducibility of the electrode

Figure 7.1.10 describes the DPASV curves for variable concentrations (20, 30, 40, 50, 60, 70, 90 and 100 nM) of Hg(II) ions at ZnO-CPE. The respective calibration curve (Figure 7.1.10) was linear with the correlation coefficient 0.9908. The detection limit calculated by making replicate current measurements was found to be 10×10^-9 M. The sensitivity of the electrode calculated from the slope of calibration curve was found to be 0.216 ×10^-8 A/nM.

Precision of the electrodes is usually expressed as the relative standard deviation. The relative standard deviations of 10×10^-8 M Hg(II) was found to be 6.3% for a single electrode with six measurements and 7.8% for five electrodes prepared
with identical procedures. Reproducibility of the electrode surface has also been tested by studying the Hg(II) ions response in two serial interday experiments. The calibration plots of these measurements of Hg(II) ions have been resulted the linear curves with similar slopes.

![Figure 7.1.10: The calibration plot of 2 to 10×10^{-8} M Hg(II) at ZnO-CPE.]

7.1.3f Effect of modifier composition

DPASV signals on six different modified carbon paste electrodes with different percentage of modifier (2.5%, 5%, 7.5%, 10%, 15%, 20%) was examined by taking 10×10^{-8} M Hg(II) solution. The maximum peak current was obtained for 5% of modifier in the carbon paste. Further increase in the concentration of modifier showed a considerable decrease in the peak current. This may be due to the surface coverage of the electrode by modifier and hence a considerable decrease in the effective conducting area available on the electrode surface, which leads to a lesser electron transfer rate between the electrode surface and analyte. Therefore, 5% of modifier was used for the modification of the electrode. Similar results were observed on CuO-CPE and NiO-CPE.
Chapter 7.1  Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

7.1.4 Conclusion

The present study demonstrates the use of ZnO nanoparticles modified CPE for the determination of Cd(II), Pb(II) and Hg(II) by differential pulse anodic stripping voltammetry. Factors that influence the stripping current were optimized to get the good response. Under the optimized conditions the calibration curves were linear with high regression coefficients. The electrode has shown good linearity, good sensitivity and stability towards the detection of Cd(II), Pb(II) and Hg(II) ions, under the studied conditions.
Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions using NiO nanoparticles modified carbon paste electrode

7.2.1 Voltammetric behavior of K₃[Fe(CN)₆]

Figure 7.2.1 shows the cyclic voltammetric response of 5 mM K₃[Fe(CN)₆] in 0.1 M KCl at CPE and nickel oxide modified carbon paste electrode (NiO-CPE). The curve-a shows the electrochemical response of [Fe(CN)₆]³⁻⁻⁻ redox couple at CPE, which exhibited the peak to peak separation (ΔEₚ) nearly equal to 400 mV. A pair of well defined redox couple with remarkably increased peak current was observed on NiO-CPE. It was observed that the anodic peak potential shifted negatively whereas the cathodic peak potential shifted positively on NiO-CPE. As a result of this shift in peak potentials, the ΔEₚ decreased to 180 mV. The increased peak signal and decreased ΔEₚ on NiO-CPE could be due to the increased catalytic activity and specific surface area of the electrode.

Figure 7.2.1: Cyclic voltammograms of 5 mM K₃[Fe(CN)₆] in 0.1 M KCl at pH 7.0 at scan rate 100 mVs⁻¹: (a) CPE and (b) NiO- CPE.
Chapter 7.2  Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

7.2.2  Simultaneous determination of Cd(II) and Pb(II) ions

7.2.2a  Differential pulse voltammetric response of Cd(II) and Pb(II) ions

Differential pulse stripping voltammograms of Cd(II) and Pb(II) ions on CPE and NiO-CPE are depicted in Figure 7.2.2. Very small stripping peaks were obtained for $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions at CPE. Under the identical conditions, larger stripping peak currents at -0.84 V and -0.66 V for NiO modified electrode were observed. Increased peak signals at NiO-CPE can be attributed to the increased rate of mass transport of the analyte as a consequence of increased surface area of the electrode.

![Figure 7.2.2: DPASVs of $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions in 0.1 M KCl: (a) CPE and (b) NiO-CPE.](image)

7.2.2b  Effect of preconcentration potential

Improving the electroanalytical performance of NiO-CPE required the examination of several key operation parameters. The effect of preconcentration potential on the stripping peak currents of $1 \times 10^{-6}$ M Cd(II) and Pb(II) has been studied in the potential range from -0.8 to -1.2 V. The peak current increased with increase in
preconcentration potential. However when the preconcentration potential was kept corresponding to -0.9 V no characteristic signal of Cd(II) was observed. When the predeposition potential shifted from -0.9 to -1.2 V, the stripping peak currents increased considerably, which is due to the fact that Pb(II) and Cd(II) ions can be reduced more efficiently at more negative potentials. Experiments also showed that further increase in the accumulation potential (>1.2 V) could not increase the peak current but cause a relatively higher background current. This can be attributed to the increased hydrogen evolution at higher negative potentials. Therefore, -1.2 V of predeposition potential was kept as optimum.

7.2.2c Effect of preconcentration time

![Graph showing effect of preconcentration time on stripping current intensity of Cd(II) and Pb(II) ions.]

**Figure 7.2.3:** Effect of preconcentration time on stripping current intensity of Cd(II) and Pb(II) ions.

The sensitivity of the proposed method for detection of Pb(II) and Cd (II) ions has been undoubtedly promoted with the increase of accumulation time because of the increased amount of Pb(II) and Cd(II) on the NiO-CPE. However, this tendency would not be prolonged due to the limited active sites available for Pb(II) and Cd (II) accumulation. The response of NiO-CPE towards the detection of $1 \times 10^{-6}$ M Pb(II)
and Cd (II) ions increased rapidly with accumulation time up to 5 min (Figure 7.2.3). Though increase in the accumulation time improves the sensitivity, it also lowers the upper detection limit due to the rapid surface saturation. Therefore, 300 s, was chosen as the preaccumulation time in the subsequent experiments.

7.2.2d Effect of pH

The influence of pH on DPASVs of $1 \times 10^{-6}$ M Cd(II) and Pb(II) was investigated in the pH range 4.0 to 7.0 (Figure 7.2.4). As can be seen from the Figure, peak currents have been increased with increase in pH. This may probably due to the increased surface sites on NiO-CPE with increase in pH of the solution, which intern lead to the increased predeposition of the metal ions. The increase in the number of surface sites on NiO nanoparticles with increase in pH is due to the increased deprotonation of the surface hydroxyl groups.

![Figure 7.2.4: Effect of pH on the peak intensity of $1 \times 10^{-6}$ M Cd(II) and Pb(II) ions.](image)
7.2.2e Calibration curve, detection limit and reproducibility of the electrode

The DPASVs for different concentrations of Cd(II) and Pb(II) ions under optimum conditions at NiO-CPE are shown in Figure 7.2.5. The peak current increased linearly with increasing the concentration in the range 1 to $8 \times 10^{-8}$ M (Figure 7.2.6). In case of Cd(II) ions good linearity has been observed with the slope $0.41 \times 10^{-8}$ A/nM and correlation coefficient 0.9852. For Pb(II) ions, the linearity has been observed with the slope $0.244 \times 10^{-8}$ A/nM and correlation coefficient 0.9847. The detection limit calculated was found to be $2.5 \times 10^{-9}$ M and $5 \times 10^{-9}$ M for Cd(II) and Pb(II) ions respectively.

![Figure 7.2.5: DPASVs of 1 to $8 \times 10^{-8}$ M Cd(II) and Pb(II) ions at NiO-CPE (a-h)](image)

The relative standard deviation for six measurements of $10 \times 10^{-8}$ M Cd(II) and Pb(II) ions at the same electrode were found to be 4.2% and 5.3% respectively. A marginal variation in the peak current (about 6%) was observed for five different modified carbon paste electrodes containing the same amount of NiO nanoparticles.
Thus, the preparation of new calibration plots has been recommended for each of the new electrodes.

![Calibration plots of Cd(II) and Pb(II) ions at NiO-CPE](image)

**Figure 7.1.6**: Calibration plots of Cd(II) and Pb(II) ions at NiO-CPE

The interference of surface active substances (surfactants) on the stripping current of Cd(II) and Pb(II) ions was investigated. These surfactants are expected to adsorb on the surface of the electrode thus hindering the co-deposition and subsequent stripping of Cd(II) and Pb(II) ions from the electrode surface. Triton X-100, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromides (CTAB) were used to investigate the effect of nonionic, cationic and anionic surfactants, respectively. Studies were performed with the solution containing 10×10⁻⁸ M metal ion solution and 10×10⁻⁸ M surfactant. Measurement of peak intensities in the presence and absence of surfactants showed no significant difference in case of anionic and nonionic surfactants whereas the cationic surfactant resulted in the decreased peak intensity nearly (20%).
7.2.3 Determination of Hg(II) ions from aqueous solutions

7.2.3a Differential pulse anodic stripping voltammetric response of Hg(II) ions

Figure 7.2.7 shows the differential pulse voltammetric response of Hg(II) ions at CPE and NiO-CPE. It can be seen from the Figure that the peak signal on CPE was very poor at -0.12 V (as shown in dotted line), whereas a well defined peaks were observed on NiO-CPE at -0.12 V (Curve a-h, solid lines). It was observed that with increase in the concentration of Hg(II) ions, the peak intensity has been increased on NiO-CPE in the concentration range $1 \times 10^{-8}$ M to $8 \times 10^{-8}$ M (curve a-h).

![Figure 7.2.7: DPASVs of 1 to $8 \times 10^{-8}$ M Hg(II) in 0.1 M KNO$_3$ at pH 7: CPE (dotted line) and NiO-CPE (solid lines-a to h)](image)

7.2.3b Effect of the preconcentration potential

Figure 7.2.8A shows the effect of deposition potential (preconcentration potential) on the stripping currents of $10 \times 10^{-8}$ M Hg(II) ions. It was observed that, when the deposition potential increased from -0.1 V to -0.6 V, the stripping peak current was increased. However further increase in the preconcentration potential (> -0.5 V) did
not increase the stripping current. This clearly revealed that preconcentration potential of -0.5 V is sufficient for the complete reduction of Hg(II) ions. Increase in peak current was observed with increase in deposition potential, however above -0.3 V the peak shape was distorted. Therefore, preconcentration potential of -0.3 V has been fixed as optimum in the further studies.

7.2.3c Effect of preconcentration time

The effect of preconcentration time on the stripping currents has been studied from 60 to 900 s and the results are as shown in Figure 7.2.8B. It can be seen that the peak current increased with increase in preconcentration time from 60 s to 900 s. When the deposition time became greater than 600 s, the peak current started to level off, indicating that the amount of metal at the electrode surface tends to saturation. In view of both sensitivity and determination time, preconcentration time of 600 s has been selected as optimum.

**Figure 7.2.8:** Effect of preconcentration potential (A) and preconcentration time (B) on the differential pulse anodic stripping current of Hg(II) ions.
Chapter 7.2  Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

7.2.3d Effect of pH

Figure 7.2.9 shows the DPASV responses of $10 \times 10^{-8}$ M Hg(II) in 0.1 M KNO$_3$ on NiO-CPE with different pH values. It can be seen from Figure that the maximum peak current for Hg(II) ions has been obtained when the pH was 7.0. The peak currents began to increase with increase in pH from 3.0 to 7.0. This is because the surface charge of NiO nanoparticles tends to less positive at higher pH, because of the increased deprotonation from the surface of NiO nanoparticles. Therefore solution pH of 7.0 was kept as optimum.

![Effect of pH on the differential pulse stripping current of Hg(II) ions.](image)

Figure 7.2.9: Effect of pH on the differential pulse stripping current of Hg(II) ions.

7.2.3e Calibration curve, detection limit and reproducibility of the electrode

Under the optimum conditions, the calibration curve of peak currents versus concentrations of Hg(II) has been constructed (Figure 7.2.10). The stripping current was found to increase with increase in the metal ions concentration and resulted in a linear plot with correlation coefficient 0.9778. The sensitivity of the electrode calculated by the slope of calibration curve was found to be $4.2 \times 10^{-8}$ A/nM. The detection limit calculated under the optimized condition was $5 \times 10^{-9}$ M.
Figure 7.2.10: The calibration plot for 1 to $8 \times 10^{-6}$ M of Hg(II) ions on NiO-CPE.

The relative standard deviation calculated for the six different measurements at the same electrode was found to be 5.8%. Five different electrodes were prepared and used for the determination of $10 \times 10^{-8}$ M Hg(II) ions and the RSD calculated was found to be 7%. The same set of experiments was repeated under the optimized conditions on different weeks. Thus obtained calibration curves yielded the same values of slopes. Hence, it can concluded that the same electrode can be used over a period of months for the determination of Hg(II) ions without any significant error. Before each experiment, the electrode must be cleaned electrochemically by applying higher oxidation potentials to ensure the complete removal of reduced Hg.
Chapter 7.2  Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

7.2.4 Conclusion

NiO nanoparticles were used as modifier in the preparation of carbon paste electrode. The determination of Cd(II), Pb(II) and Hg(II) ions using carbon paste electrode modified with NiO nanoparticles has been carried out. The experimental conditions have been optimized and the response characteristics were determined. Under the optimized conditions the calibration curves were linear with correlation coefficient > 0.9. The detection limits were in nano molar range for all the metal ions studied. The proposed electrode has shown good linearity, sensitivity and stability.
Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions using CuO nanoparticles modified carbon paste electrode

7.3.1 Cyclic voltammetric behavior of $K_3[Fe(CN)_6]$

The cyclic voltammetric response of $K_3Fe(CN)_6$ at copper oxide nanoparticles modified carbon paste electrode (CuO-CPE) and CPE is shown in Figure 7.3.1. The voltammograms for $[Fe(CN)_6]^{3-/-}$ redox couple in the absence of CuO nanoparticles exhibited low signal (Curve a) with $\Delta E_p$ nearly equal to 400 mV. However, an improved voltammetric response on CuO-CPE for $[Fe(CN)_6]^{3-/4-}$ redox couple is observed with the enlargement of anodic and cathodic peak currents (Curve b) and decreased $\Delta E_p$ of 214 mV. This increased peak currents and decreased value of peak separation indicated the faster electron transfer on CuO-CPE compared to that of CPE.

![Cyclic voltammograms](image)

**Figure 7.3.1:** Cyclic voltammograms of 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl at pH 7.0 and at scan rate 100 mVs$^{-1}$: (a) CPE and (b) CuO-CPE.
Chapter 7.3  Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

7.3.2  Simultaneous determination of Cd(II) and Pb(II) ions

7.3.2a  Differential pulse voltammetric response of Cd(II) and Pb(II) ions

Differential pulse anodic stripping voltammograms obtained using CPE and CuO-CPE after 300 s of accumulation time in a solution containing $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions are shown in Figure 7.3.2. From the Figure it is evident that, the stripping signals of Cd(II) and Pb(II) ions at CuO-CPE are remarkably larger when compared to that of CPE. The increased peak intensity indicated the good catalytic activity of CuO nanoparticles.

![Figure 7.3.2: DPASVs of $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions in 0.1 M KCl at pH 7.0: (a) CPE and (b) CuO-CPE.](image)

7.3.2b  Effect of pH

The influence of solution pH of on the stripping currents of $1 \times 10^{-6}$ Cd(II) and Pb(II) ions has been investigated in the pH range 4.0-7.0 (Figure 7.3.3). The peak currents of both the metal ions increased with increase in solution pH. This is due to the increased
dissociation of the surface hydroxyl groups, which results in less positively charged surface. In the subsequent experiments the pH of the solution was kept at 7.0.

**Figure 7.3.3:** Effect of solution pH on the peak intensity of Cd(II) and Pb(II) ions.

### 7.3.2c Effect of Preconcentration Time

The parameter of major importance is the time duration allowed for the accumulation of Cd(II) and Pb(II) ions from the preconcentration solution at the electrode surface. The dependence peak current on the preconcentration time of $1 \times 10^{-6}$ M Cd(II) and Pb(II) ions is shown in Figure 7.3.4. The peak currents increased with increase in preconcentration time, indicating an enhancement of Cd(II) and Pb(II) ions deposition on the electrode surface. Normally, the increase in peak current response continues until a maximum signal level, presumably corresponding to either saturation or an equilibrium surface coverage, is attained. The results obtained indicated that a steady-state accumulation has been attained at the electrode surface within the exposure time of 600 s. The stripping current increased with increase in preconcentration time.
however the well defined peaks were observed below 600 s of preconcentration time. Hence, preconcentration time of 300 s was selected in the further studies.

![Graph](image)

**Figure 7.3.4:** Effect of preconcentration time on stripping current intensity of $1 \times 10^{-6}$ M Cd(II) and Pb(II) ions.

### 7.3.2d Effect of preconcentration potential

The effect of preconcentration potential on the anodic peak current of Cd(II) and Pb(II) ions has been investigated by varying the initial potential from -0.8 V to -1.5 V. The anodic peak corresponding to Cd(II) ions began to appear at an applied potential of -1.0 V and at -1.2 V, well separated peaks with the highest peak current were obtained. Further increase in reduction potential from -1.2 to -1.5 V led to a steady-state current and subsequent hydrogen evolution. Hence a potential of -1.2 V was employed as a predeposition potential in the subsequent experiments.
Chapter 7.3 Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

7.3.2e Calibration curve, detection limit and reproducibility of the electrode

The DPASVs at different concentrations of Cd(II) and Pb(II) ions are shown in Figure 7.3.5. Under the previously optimized conditions, an analytical curve was constructed for the solutions of 2 to $10 \times 10^{-8}$ M Cd(II) and Pb(II) ions. It was observed that peak currents have linearly increased with increase in the analyte concentration (Figure 7.3.6). The slope and correlation coefficient values calculated from the calibration plot of Pb(II) ions were $0.31 \times 10^{-8}$ A/nM and 0.9926 respectively. In case of Cd(II) ions the slope and correlation coefficients were $0.14 \times 10^{-8}$ A/nM and 0.958 respectively. These data clearly indicated that the CuO-CPE is more sensitive towards the determination of Pb(II) ions when compare to that of Cd(II) ions. The values of lower detection limit calculated for the Pb(II) and Cd(II) ions on CuO-CPE were 6.5 nM and 9 nM respectively.

![Figure 7.3.5: DPASVs of 2 to $10 \times 10^{-8}$ M of Cd(II) and Pb(II) ions at CuO-CPE](image-url)
The relative standard deviations obtained for six successive determination of $1 \times 10^{-6}$ M Cd(II) and Pb(II) ions, on single electrode were 4.8% and 5.6% respectively. The RSD values for 5 different electrodes prepared under identical conditions were $\approx 6\%$ for both the metal ions studied.

![Calibration plots of Cd(II) and Pb(II) ions at CuO-CPE.](image)

**Figure 7.3.6:** Calibration plots of Cd(II) and Pb(II) ions at CuO-CPE.

The surface active compounds are usually a source of strong interference in the voltammetric measurements. During the measurements with the solutions contaminated with surfactants, adsorption takes place on the working electrode. Therefore, continuous renovation of the electrode surface is necessary. The effect of surfactants on the stripping current responses of $10 \times 10^{-8}$ M Cd(II) and Pb(II) ions has been determined in presence of Triton X-100, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB). The current responses remained unaffected in presence of $10 \times 10^{-8}$ M of Triton X-100 and SDS, whereas the peaks were distorted in presence of CTAB.
7.3.3 Determination of Hg(II) ions from aqueous solutions

7.3.3a Differential pulse anodic stripping voltammetric response of Hg(II) ions

The DPASVs of 2 to $10 \times 10^{-8}$ M Hg(II) in 0.1 M KNO$_3$ are as depicted in Figure 7.3.7. From the Figure it can be seen that relatively very poor stripping current was observed on CPE (dashed line), whereas on CuO-CPE clearly distinguishable well developed peak has been observed (curve a). The reason for the increased current response on CuO-CPE is attributed to the increased specific surface area because of the presence of CuO nanoparticles. The stripping peak current of Hg(II) ions has been increased with increase in the concentration of the Hg(II) ions.

![Differential pulse voltammograms of 2-10×10⁻⁸ M Hg(II) in 0.1 M KNO₃; at CPE (dotted line) and CuO-CPE (solid lines-a to h)](image)

**Figure 7.3.7:** Differential pulse voltammograms of 2-10×10⁻⁸ M Hg(II) in 0.1 M KNO₃; at CPE (dotted line) and CuO-CPE (solid lines-a to h)

7.3.3b Effect of the preconcentration potential

The influence of preconcentration potential on the peak current of $10 \times 10^{-8}$ M Hg(II) ions has been studied in the range -0.1 V to -0.6 V and is shown in Figure 7.3.8A. The magnitude of stripping current was found to increase with deposition potential up to -
0.3 V, and above this potential the analytical signal was independent of deposition potential. Hence, -0.3 V was selected as optimum for the further studies.

7.3.3c Effect of preconcentration time

Figure 7.3.8B shows the effect of preconcentration time on the peak intensity of $10\times10^{-8}$ M Hg(II) ions in presence of 0.1 M KNO$_3$. As can be seen from the Figure, the preconcentration time of 600 s is required to get a well defined peak with high intensity. At higher preconcentration time the peak signal get distorted.

![Figure 7.3.8: Effect of preconcentration potential (A) and preconcentration time (B) on the differential pulse anodic stripping current of $10\times10^{-8}$ M Hg(II) ions.](image)

7.3.3d Effect of pH

The effect of pH on $10\times10^{-8}$ M Hg(II) ions has been studied in the pH range between 3.0 to 7.0. From the Figure 7.3.9 it can be seen that the increase in solution pH has resulted in the increased peak intensity. Similar results were obtained for ZnO-CPE and NiO-CPE. The surface charge on CuO nanoparticles tends to be less positive at higher pH values. The same results were obtained on the other two metal oxide nanoparticles modified electrodes. The decreased positive charge on the electrode
surface results in the accumulation of more cations on the surface and hence the higher peak currents.

![Figure 7.3.9: Effect of pH on the stripping current of $10 \times 10^{-8}$ M Hg(II) ions.](image)

**Figure 7.3.9:** Effect of pH on the stripping current of $10 \times 10^{-8}$ M Hg(II) ions.

### 7.3.3e Calibration curve, detection limit and reproducibility of the electrode

Under the optimized conditions the calibration curve obtained for different concentration of Hg(II) ions (20-100 nM) was linear with the correlation coefficient of 0.9883. The sensitivity of the electrode obtained from slope of the calibration curve was found to be $1.13 \times 10^{-8}$ A/nM. Figure 7.3.10 shows the calibration curve for the determination of Hg(II) at CuO-CPE. It can be seen from the figure that the peak current increases with increase in the concentration of the analyte. The detection limit calculated was found to be $8 \times 10^{-9}$ M at CuO-CPE.

The relative standard deviation (RSD) obtained for the six replicate measurements on the same electrode was 4.7%. The RSD calculated for five different electrodes prepared under identical conditions was 5.8%. The calculated slopes of the
calibration curves constructed by means of the data on different weeks was found to be remain same (<3% error), indicating the good stability of the electrode.

Figure 7.3.10: The calibration plot of 2 to $10 \times 10^{-8}$ M Hg(II) ions on CuO-CPE.

### 7.3.4 Conclusion

The CuO nanoparticles modified CPE is proposed for the determination of Cd(II), Pb(II) and Hg(II) ions using differential pulse anodic stripping voltammetry. Under the optimized conditions, the electrode has shown good linearity with a good correlation coefficient. The detection limit calculated for Hg(II) ions was poor compared to that of Cd(II) and Pb(II) ions. The modified electrode has got the advantage of being stable for more than 30 days and hence same electrode can be used for the analytical estimations over a period of time, without any error.
Chapter 7  Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

References:

Chapter 7  Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions


