Electrochemical determination of Pb(II), Cd(II) and Hg(II) ions using Barium and Strontium hydrogen phosphate modified carbon paste electrodes
Electrochemical determination of Pb(II), Cd(II) and Hg(II) ions using Barium and Strontium hydrogen phosphate modified carbon paste electrodes

The toxic effects of heavy metals such as mercury, lead and cadmium are well known [1-3]. Accurate determination of these inorganic ions is an important mission in industrial process and environmental protection. The sensitivity and selectivity in the determination of such inorganic ions by electrochemical techniques is strongly dependent on the properties of the electrode material.

The chemically modified electrodes are very interesting tools for the analysis of many substances at trace level, using very sensitive electroanalytical techniques. Chemically modified carbon paste electrodes have been widely used, because of their low background current, easy fabrication and good performance. These characteristics resulted in many practical applications, especially in trace metal analysis [4-11]. An important advantage of using CMCPE is its improved selectivity and detection limit of the voltammetric determination by preconcentrating the analyte on the electrode surface. In this regard a good lot of materials have been attempted to modify electrodes for the accurate determination of inorganic species [12].

Phosphates can be defined as salts of phosphorus oxoacids and in particular salts of phosphoric (V) acid. Phosphates are among the most important classes of inorganic compounds. For example, apatite, a complex mineral form of calcium phosphate, Ca₅(PO₄)₃ is the main compound found on the enamel of teeth [13-15]
Phosphates have a lot of practical uses, for example, fertilizers based on ammonium phosphates. Nowadays, alkali and alkaline earth metal phosphates are gaining significant interest due to their wide variety of applications as heterogeneous catalysts, low thermal expansion materials, ion exchangers and usefulness as biocompatible coatings [16].

The present chapter gives a detailed investigation on the determination of Cd(II), Pb(II) and Hg(II) ions from wastewater using metal hydrogen phosphate modified carbon paste electrodes. Herein two metal hydrogen phosphates were used as modifiers namely, barium hydrogen phosphates (BaHPO₄) and strontium hydrogen phosphate (SrHPO₄).

This section is divided into two sub-chapters. Chapter 8.1 deals with the determination of heavy metal ions using barium hydrogen phosphate modified carbon paste electrode (BHP-CPE). Chapter 8.2 gives the results on the determination of heavy metal ions using strontium hydrogen phosphate modified carbon paste electrode (SHP-CPE).
Electrochemical determination of Pb(II), Cd(II) and Hg(II) ions using BHP modified carbon paste electrode

8.1.1 Characterization of Barium hydrogen phosphate (BHP)

8.1.1a XRD and SEM Analysis

A typical XRD pattern of synthesized barium hydrogen phosphate (BHP) is given in Figure 8.1.1. The major diffraction peaks at 19.9°, 24.2°, 25.1°, 29.1°, 30.2°, 35.5° and 38.9° were assigned to the diffraction from (230), (031), (400), (430), (060), (431) and (261) planes respectively, according to the data base in JCPDS card (No-17-0929). This revealed that the particles were of pure BHP with an orthorhombic structure and space group Pn2₁a. In the SEM images of BHP (Figure 8.1.2) flake like structures were observed.

Figure 8.1.1: Powder XRD pattern of synthesized barium hydrogen phosphate.
Figure 8.1.2: SEM images of barium hydrogen phosphate (BHP) at different magnifications: (A) X 1000 and (B) X 750.

8.1.1b FTIR studies of BHP

The infrared (FT-IR) spectrum of BHP shows the presence of large number of oxygen containing functional groups (Figure 8.1.3). Hydroxyl group (–OH) belonging to the phosphate group in the crystalline compound exhibited stretching band centered at 3440 cm⁻¹. The broad band at 2670 cm⁻¹ is an intermolecular phonon band corresponding to an ionic vibration of Ba–O contacts in an ionic crystal. The peaks at 1721 and 1637 cm⁻¹ reveals thermal vibrations of H⁺ ions in an intermolecular phonon vibration associated with HPO₄²⁻ contacts. The P=O stretching vibrations leads to a distinct peak at 1270 cm⁻¹. The P=O deformation vibration was found at 890 cm⁻¹. At 590 and 530 cm⁻¹ P–O–H wagging and rocking vibrational bands are found [17, 18]. These observations also confirmed that the synthesized compound was pure BHP and is in agreement with literature reports.
8.1.2 Electrochemical behavior of $\text{K}_3[\text{Fe(CN)}_6]$ 

$[\text{Fe(CN)}_6]^{3-/4-}$ couple was used as the electrochemical redox probe to investigate the electrochemical properties of CPE/BHP-CPE (Figure 8.1.4A). The peak shapes for $[\text{Fe(CN)}_6]^{3-/4-}$ redox reaction at CPE are slightly broad and the peak potential separation ($\Delta E_p$) is as large as 400 mV (curve a). A pair of well-defined redox peaks with remarkably increased current responses is obtained at BHP-CPE (curve b). The anodic peak potential ($E_{pa}$) shift negatively while the cathodic peak potential ($E_{pc}$) shift positively. As a result, the $\Delta E_p$ diminishes to about 160 mV, suggesting the faster electron transfer kinetics and more reversible behavior of $[\text{Fe(CN)}_6]^{3-/4-}$ couple on BHP-CPE. These results revealed that BHP-CPE catalyzed the redox reaction of $[\text{Fe(CN)}_6]^{3-/4-}$ more efficiently compared to that of CPE.
Figure 8.1.4: Cyclic voltammograms (A) and Nyquist plots (B) for 5 mM K$_3$[Fe(CN)$_6$] in 0.1 M KCl, at CPE (a) BHP- CPE (b) ((A) scan rate 100 mVs$^{-1}$; (B) frequency range:10 kHz -1Hz. Inset shows the equivalent circuit).

Electrochemical impedance spectroscopy (EIS) was performed to observe the impedance change at the electrode surface in the frequency range of 1Hz to 10 kHz. Figure 8.1.4B shows Nyquist plots for 5mM Fe[(CN)$_6$]$^{3/-4-}$ in 0.1 M KCl solution. The electron-transfer resistance (R$_{ct}$) at the electrode surface is equal to the semicircle diameter, which can be used to describe the interface properties of the electrode. The curve ‘a’ shows a semicircle domain, which offers resistance to electron transfer and the value of charge transfer resistance, determined from the Randle’s circuit was found to be 8.5 kΩ at CPE. On BHP-CPE, the semicircle part on the impedance spectrum decreased obviously with R$_{ct}$ 1.6 kΩ (curve b). The decrease in the charge transfer resistance may be ascribed to the catalytic behavior of BHP, which provides a host matrix to accommodate the charged species and hence increased rate of mass transfer. This implied that the lesser electron-transfer resistance to the redox couple dissolved in the electrolyte solution. These Nyquist plots obtained were in good agreement with the CV behavior (Figure 8.1.4A).
8.1.3 Simultaneous determination of Pb(II) and Cd(II) ions

8.1.3a Differential pulse voltammetric response of Cd(II) and Pb(II) ions

Figure 8.1.5 shows the differential pulse voltammetric (DPV) response of Cd(II) and Pb(II) ions at CPE and BHP-CPE. The DPV signal on CPE is very poor at -0.9 V and -0.7 V for Cd(II) and Pb(II) ions respectively. On BHP-CPE, the stripping peaks for Cd(II) and Pb(II) ions increased considerably (curve b). This increment in the peak current after the modification with BHP is due to its inherent structural properties i.e., the layered structure of the BHP, which can act as a host matrix to accommodate the metal ions, and lead to an increased rate of mass transport across the electrode surface. This phenomenon has directed in the increment of peak currents.

**Figure 8.1.5**: Differential pulse voltammograms of $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions in 0.1 M KCl at CPE (a) and BHP-CPE (b). (Preconcentration time: 5 min; Preconcentration potential: -1.1 V).
8.1.3b Effect of preconcentration potential

Preconcentration potential has been contributed to the sensitivity of the electrode. It was observed that below -0.8 V of preconcentration potential only one peak corresponding to Pb(II) ions appeared. After increasing the deposition (preconcentration) potential to -1.1 V, two well defined oxidation peaks corresponding to Cd(II) and Pb(II) ions were observed. Further increase in the reduction potential to -1.2 V enhanced the peak currents and hence, -1.2 V was selected as the optimum deposition potential for the simultaneous determination of Cd(II) and Pb(II) ions on BHP-CPE.

8.1.3c Effect of preconcentration time

The sensitivity of electrodes was improved by tuning the accumulation time (preconcentration time or deposition time). By the experiments it was observed that the stripping current of $1 \times 10^{-6}$ M Pb(II) and Cd (II) ions increases linearly with increasing the preconcentration time up to 300 s, due to the increased rate of deposition on the electrode. However the plot tends to deviate from linearity with a diminished slope value after 300 s because of brisk saturation, which often lowers the upper detection limit. However, for practical purpose 300 s of preconcentration time was chosen.

8.1.3d Effect of pH

The pH of the analyte solution affects the sensitivity of detection. The voltammetric studies have been carried out at different pH (3.0-10.0) in 0.1 M KCl solution containing $1 \times 10^{-3}$ M Cd(II) and Pb(II) ions. Anodic peak current decreases with decrease in pH of the analyte solution from 7.0 to 3.0. The reason for this trend could be attributed to the higher solubility of BHP in acidic solutions. The maximum peak
Chapter 8.1 Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

current observed at pH 7.0 and further increase in pH resulted in the precipitation of Cd(II) and Pb(II) ions, and hence low intense peaks were observed at pH greater than 7.0. Hence, the optimum pH was selected as 7.0 for all electrochemical studies.

Figure 8.1.6: Effect of preconcentration time (A) and pH (B) on peak currents of Cd(II) and Pb(II) ions.

8.1.3e Calibration plot, detection limit and reproducibility of the electrode

Figure 8.1.7 describes the DPASVs for the variable concentrations of Cd(II) and Pb(II) ions on BHP-CPE. The calibration plots shows linear range between $1 \times 10^{-8}$ M to $8 \times 10^{-8}$ M with correlation co-efficients 0.987 and 0.986 for Cd(II) and Pb(II) ions respectively on BHP-CPE (Figure 8.1.8). From the slopes, it was found that the sensitivity of the electrode towards the detection of Cd(II) ions is more than that of Pb(II) ions. The sensitivity of BHP-CPE towards determination of Cd(II) and Pb(II) ions was $1 \times 10^{-8}$ A/nM and $0.55 \times 10^{-8}$ A/nM respectively. Under the optimized experimental conditions, the lower detection limit (LOD) at BHP-CPE for Cd(II) and Pb(II) ions was found to be $1.5 \times 10^{-9}$ M and $3 \times 10^{-9}$ M respectively.
Chapter 8.1 Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

Figure 8.1.7: DPASVs of $1$ to $8 \times 10^{-8}$ M Cd(II) and Pb(II) ions in 0.1 M KCl at BHP-CPE (Preconcentration time: 5 min; Preconcentration potential: -1.1 V).

Figure 8.1.8: Calibration plots for Cd(II) (A) and Pb(II) ions (B) at BHP-CPE.

Precision of the BHP-CPE electrodes, expressed as the relative standard deviation for eight determinations made on different days on a standard solution of $5 \times 10^{-6}$ M Cd(II) and Pb(II) ions. Relative standard deviation (RSD) of stripping current on BHP-CPE was 3.6% and 4.0% for Cd(II) and Pb(II) ions respectively. The reproducibility of the stripping current was below 10 % RSD for 6 different BHP-CPE electrodes prepared and analyzed by the same method.
8.1.3f Interference studies

The electrochemical estimation of Cd(II) and Pb(II) ions can be affected by the presence of various other heavy metals. In the present work, different metal ions were selected and their effect on the stripping current of Cd(II) and Pb(II) ions was investigated. Tests were made by analyzing a standard solution of $1 \times 10^{-6}$ M of Cd(II) and Pb(II) ions to which aliquots of interfering ions were added under the optimal experimental conditions. Experiments showed that the presence of $1 \times 10^{-3}$ M of Na$^+$, Ca$^+$, Mg$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, Al$^{3+}$, NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ ions and $1 \times 10^{-4}$ M Sn$^{4+}$ and Co$^{2+}$ ions in the solution had no influence on the signal of Cd(II) and Pb(II) ions. A shoulder around -0.74V was appeared on the stripping response of Pb(II) and Cd(II) ions in presence of $1 \times 10^{-5}$ M Ni$^{2+}$ ions, but does not interfere with the measurement of Cd(II) and Pb(II) ions. In presence of $1 \times 10^{-5}$ M Zn$^{2+}$ ions, the peak current for Pb(II) ions disappeared and decrease in peak intensity of Cd(II) ions was observed.

The addition of $1 \times 10^{-6}$ M Cu$^{2+}$ ions also decreased the peak intensity to about 50% of the original. A 10-fold excess of Cu$^{2+}$ ions ($1 \times 10^{-5}$) was found to completely suppress the peak current of Cd(II) ions. This may be accounted to the formation of inter-metallic compound between copper and cadmium deposited on the electrode surface.

The presence of $1 \times 10^{-6}$ M Hg$^{2+}$ ions increased the peak signals and shifted the peak potential. Such kind of amplification in the peak current is due to the in-situ formation of mercury film on BHP-CPE which could enhance the peak intensities. Similar results were observed in case of $1 \times 10^{-5}$ M Bi$^{3+}$ ions, and this could be attributed to the in-situ formation of bismuth film.
Under the employed concentration of interfering metal ions, no precipitation was observed. In this work, the effect of surfactants such as Triton-X, sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) on the electrochemical response of Pb(II) and Cd(II) ions at BHP-CPE was studied. The results showed that Triton-X \((1 \times 10^{-5} \text{ M})\) and SDS \((1 \times 10^{-5} \text{ M})\) had no influence on the current response whereas, the surfactant CTAB \((1 \times 10^{-5} \text{ M})\) had slightly decreased the peak current. This may be attributed to the adsorption of cationic surfactant (CTAB) onto the electrode surface and hence decreases the peak current.

### 8.1.4 Determination of Hg(II) ions from aqueous solutions

#### 8.1.4a Differential pulse stripping voltammetric studies of Hg(II) ions

![Figure 8.1.9](image)

**Figure 8.1.9:** Differential pulse voltammograms of 1 to \(8 \times 10^{-8} \text{ M}\) Hg(II) ions in 0.1M KNO₃, at CPE (dotted line) and BHP-CPE (a-h). (Preconcentration time: 5 minutes; preconcentration potential: -0.2 V).
The potentiality of BHP-CPE for the determination of Hg(II) by using DPASV is as discussed here. As can be seen from Figure 8.1.9, no peak current was observed at CPE (dotted line) whereas, after modification with BHP peak current was enhanced and a well defined peak at 0.15 V (versus SCE) is observed. This increment in the peak current may be due to the inherent structural properties of BHP which might have increased the rate of mass transport across the electrode surface. In Figure 8.1.9 curves a-h shows the DPASVs for different concentration of Hg(II) ions on BHP-CPE.

To determine the optimum conditions for most sensitive analysis, the effect of solution pH, preconcentration potential, preconcentration time, supporting electrolyte and composition of the electrode material have been studied.

8.1.4b Effect of pH

The influence of solution pH on the stripping current of $10 \times 10^{-8}$ M Hg(II) ions was examined. Figure 8.1.10A illustrated an increase in the peak current when the pH increased from 3.0 to 7.0. The stripping current began to increase with increase in pH because of the higher stability of BHP at pH 7.0. The maximum peak current has been observed at pH 7.0 and the same pH was used in subsequent studies.

8.1.4c Effect of preconcentration potential

The effect of accumulation potential on the peak current of $10 \times 10^{-8}$ M Hg(II) ions was examined in the potential range of -0.1 to -0.5 V versus SCE (Figure 8.1.10B). When the deposition potential was set at -0.2 V, well defined peak with the highest peak current was observed. Based on this reason the optimum value of preconcentration was kept at -0.2 V.
8.1.4d Effect of preconcentration time

The dependence of stripping current on the accumulation time has been investigated. From the Figure 8.1.11 it can be seen that, the peak current was found to increase linearly with increase in accumulation time up to 360 s, after 360 s there was a deviation from the linearity, which could be accounted for the surface saturation of the electrode. Longer deposition times (>900 s) did not give rise to any significant increase in the signal intensity, probably due to the incomplete removal of Hg deposited on the electrode. After the preconcentration time of 300 s the peak shape became distorted and broadened, therefore for all practical purpose 300 s of preconcentration time was fixed as optimum.
8.1.4e Effect of supporting electrolyte

The effect of supporting electrolytes has been studied in presence of KCl and KNO₃. Good results were obtained in presence of 0.1 M KNO₃ compared to that of KCl thus KNO₃ was used as supporting electrolyte. The decreased peak current in presence of KCl may be attributed to the following reason. In presence of large excess of Cl⁻ ions (> 0.1 M), the Hg(II) ions in the solution exist as HgCl₄⁻ complex ions, which affects the kinetics of migration of Hg(II) ions towards the electrode during the accumulation (preconcentration) and hence resulted in the lesser mass transfer rate across the electrode surface.

8.1.4f Calibration plot, detection limit and reproducibility of the electrode

The differential pulse anodic stripping voltammograms for different concentrations of Hg(II) ions under the optimized conditions are shown in Figure 8.1.8. The peak current increased linearly with increase in the concentration of Hg(II) ions in the
range 1 to $8 \times 10^{-8}$ M with the correlation coefficient of 0.9967. The sensitivity of the electrode calculated from the slope of calibration curve (Figure 8.1.12) was found to be $5.3 \times 10^{-8}$ A/nM. The detection limit calculated was $8 \times 10^{-10}$ M under the optimized conditions. The slopes of different calibration curves constructed on different days at same electrode were found to be constant and hence a single electrode can be used for the multiple measurements without any analytical error. For five successive determinations using the same electrode, the relative standard deviation was found to be 5.3%. A marginal variation in the peak current ($> 5\%$) was observed for the different set of electrodes. Hence, generation of calibration curve for each of the newly prepared electrodes has been suggested.

![Figure 8.1.12: The calibration plot of 1 to $8 \times 10^{-8}$ M Hg(II) ions on BHP-CPE.](image)

**8.1.4g Interference studies**

Possible interference by other metal ions on the anodic stripping current of Hg(II) was investigated by the addition of other metal ions into the solution containing $1 \times 10^{-6}$ M Hg(II) under the optimized conditions. Experiments showed that the presence of
Chapter 8.1 Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

$1 \times 10^{-3} \text{ M Na}^{+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Al}^{3+}, \text{Cr}^{3+}, \text{NH}_4^+, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{NO}_3^-, \text{SO}_4^{2-}$ ions and $1 \times 10^{-4} \text{ M Zn}^{2+}, \text{Sn}^{4+}, \text{Ni}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}, \text{Co}^{2+}$ ions in the solution had no influence on the signal of Hg(II) ions peak intensity. The presence of $1 \times 10^{-4} \text{ M Cu}^{2+}$ ions and $1 \times 10^{-3} \text{ M Cl}^-$ ions decreased the original peak intensity of Hg(II) ions to about 30%.

The presence of EDTA, thiourea, 1-10 phenothroline and SCN$^-$ (> $1 \times 10^{-5} \text{ M}$) suppressed the peak current of Hg(II) ions. The suppression in the peak current in presence of chelating agents is attributed to the formation of complexes. Generally strong chelates form stable complexes with the Hg(II) ions which hinders the release of free Hg(II) ions at the electrode surface. Hence, the bound fraction of Hg(II) ions are not available for the reduction at the preconcentration step. However the presence of same chelating agents below $1 \times 10^{-6} \text{ M}$ had negligible influence on the peak intensity of Hg(II) ions.

8.1.5 Conclusion

A new chemically modified CPE has been developed using BHP for the determination of Cd(II), Pb(II) and Hg(II) ions at trace levels. The new electrode (BHP-CPE) has an advantage of being toxic-free, low-cost and highly stable. The modified electrode shows good voltammetric responses in presence of many interfering ions and surfactants. Also there is no leaching of the electrode materials because of the low solubility of BHP in aqueous solutions and hence a single electrode surface can be used for the multiple analysis over several weeks.
Electrochemical determination of Pb(II), Cd(II) and Hg(II) ions using SHP modified carbon paste electrode

8.2.1 Characterization of strontium hydrogen phosphate (SHP)

The synthesized SHP particles were subjected to XRD and SEM analysis. Figure 8.2.1 shows the XRD pattern of SHP. This pattern can be readily indexed according to the reported crystal structure of SrHPO$_4$ in JCPDS file (PDF: 120368). The peaks observed at 2θ values 15.5°, 19.4°, 24.3°, 24.7°, 27.3°, 28.4°, 29.5°, 31.3°, 39.6° and 49.7° were in good agreement with the reported crystal structure of SrHPO$_4$.

Figure 8.2.1: XRD pattern of strontium hydrogen phosphate (SHP).
The scanning electron micrographs of SHP are shown in Figure 8.2.2. At high magnification, flake like structures of approximately 1μm size can be seen.

**Figure 8.2.2:** SEM images of SHP at different magnifications: A) 5000X B) 10000X.

### 8.2.2 Electrochemical characterization of CPE and SHP-CPE

#### 8.2.2a Cyclic voltammetric behavior of $K_3[Fe(CN)_6]$ $[Fe(CN)_6]^{3-/4-}$ couple was used as the electrochemical redox probe to investigate the electrochemical properties of CPE and SHP-CPE. Cyclic voltammograms of 5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl at CPE and SHP-CPE are shown in Figure 8.2.3.

The $[Fe(CN)_6]^{3-/4-}$ couple shows well defined redox peaks with peak to peak separation ($\Delta E_p$) of 120 mV at SHP-CPE and nearly 400 mV at CPE. This suggested the faster electron transfer kinetics and more reversible behavior of $[Fe(CN)_6]^{3-/4-}$ couple at SHP-CPE. The decrease in the peak to peak potential ($\Delta E_p$) and increased peak current intensity is attributed to the catalytic effect of SHP.
8.2.2b EIS Studies of K₃[Fe(CN)₆]

Electrochemical impedance spectroscopy (EIS) is an effective method to probe the characteristic features of modified electrode. EIS was performed to observe the change in impedance at the electrode surface in the frequency range of 1 Hz to 10 kHz. The electrochemical impedance spectra at CPE and SHP-CPE for 5 mM [Fe(CN)₆]³⁻⁻/⁴⁺ couple in 0.1 M KCl were measured at the formal redox potential and shown in Figure 8.2.4.

It can be seen that for CPE, the plot is a semicircle with a considerable radius (curve-a). The electron-transfer resistance ($R_{et}$) was determined from the Randle's circuit and was found to be 8.5 kΩ at CPE. The SHP-CPE shows a semicircle with decreased radius implying that the resistance towards rate of electron transfer is decreased with $R_{et}$ 2.15 kΩ (curve b). The decrease in the charge transfer resistance may be ascribed to the catalytic behavior of SHP. This implied that the lesser
Chapter 8.2  Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

electron-transfer resistance to the redox couple dissolved in the electrolyte solution.

These Nyquist plots are in good agreement with the CV behavior of $[\text{Fe(CN)}_6]^{3-/4-}$ couple.

![Figure 8.2.4: Nyquist plots of 5 mM $\text{K}_3[\text{Fe(CN)}_6]$ in 0.1 M KCl on CPE (a) and SHP-CPE (b) (pH: 7.0; Frequency range: 10 kHz - 1 Hz).](image)

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

8.2.3a Differential pulse voltammetric response of Cd(II) and Pb(II) ions

Figure 8.2.5 shows the differential pulse anodic stripping voltammograms for $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions at CPE and SHP-CPE. A very small stripping current was observed at CPE, whereas, after modification with SHP the signal current increased remarkably for both the ions. The increase in peak current intensity after modification is probably due to the catalytic effect of SHP, which provides a host matrix to accommodate the charged species and hence increased rate of mass transfer at the electrode/solution interface.
8.2.3b Effect of preconcentration Potential

It is well known that in stripping analysis, the application of adequate deposition potential is very important to achieve the best sensitivity and selectivity. Thus the influence of electrolysis potential on the anodic peak current of $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions was studied by varying the reduction potential from -0.9 to -1.5 V (vs. SCE). When the potential was increased to -1.2 V, a well defined peak with the highest peak current was obtained. Further increase in the reduction potential from -1.2 to -1.5 V led to decreased peak currents. This is mainly due to hydrogen evolution at such higher potential. Hence, the selected optimum reduction potential for further studies was -1.2 V.

8.2.3c Effect of Preconcentration Time

The effect of preconcentration time on the anodic peak current for $1 \times 10^{-8}$ M Cd(II) and Pb(II) ions was examined. As shown in Figure 8.2.6, the peak current was
found to increase linearly with increase in preconcentration time up to 300 s and then attained a constant value. Therefore, a 300 s preconcentration time was used for all subsequent measurements. The decreased peak current with increase in preconcentration time is probably due to the rapid surface saturation of the electrode.

![Figure 8.2.6: Effect of preconcentration time on stripping current intensity of 1×10^{-6} M Cd(II) and Pb(II) ions.](image)

8.2.3d Effect of pH

![Figure 8.2.7: Effect of pH on peak current of 1×10^{-6} M Cd(II) and Pb(II) ions.](image)
The effect of solution pH on the peak intensity of $1 \times 10^{-6}$ M Cd(II) and Pb(II) ions solution was studied in the pH range 3.0-7.0. As can be seen from the Figure 8.2.7, the peak current increased with increase in pH up to 7.0. At pH greater than 7.0 the peak current of Pb(II) decreased to some extent. The decrease in the peak intensity may be due to the formation of insoluble metal hydroxides, which are not available for the deposition process during preconcentration. Hence, subsequent studies were carried out at pH 7.0.

8.2.3e Calibration curve, detection limit and reproducibility of the electrode

Figure 8.2.8 shows the DPASVs for different concentrations of Cd(II) and Pb(II) ions. It was observed that the peak current increased with increase in concentration of Cd(II) and Pb(II) ions under the optimized conditions.

![Figure 8.2.8: DPASVs of 1 to $8 \times 10^{-8}$ M Cd(II) and Pb(II) ions in 0.1 M KCl at SHP-CPE.](image-url)
Chapter 8.2 Electrochemical determination of Cd(II), Pb(II) and Hg(II) ions

The calibration plots have been generated and shown in Figure 8.2.9. The correlation coefficients of linear calibration curves were 0.9932 and 0.9908 for Cd(II) and Pb(II) ions respectively. The sensitivity of the electrode calculated from slopes of linear calibration curves was 0.48×10⁻⁸ A/nM and 0.4×10⁻⁸ A/nM for Cd(II) and Pb(II) ions respectively. The detection limits observed on SHP-CPE for the determination of Cd(II) and Pb(II) ions with the above mentioned optimized experimental conditions were 5.5×10⁻⁹ M and 7×10⁻⁹ M respectively.

Figure 8.2.9: Calibration plots of Cd(II) and Pb(II) ions at SHP-CPE.

The reproducibility of the electrode was checked for Pb(II) and Cd(II) ion determinations. The RSD values of 4.7 % and 6.0% were obtained for repeated experiments with six different solutions containing 1×10⁻⁶ M Pb(II) and Cd(II) ions, respectively. Also, when a new electrode was used, reproducibility was good (RSD < 5.6 %). The sensitivity of the electrode did not change significantly during the analysis for a period of two months. This furnished the chemical stability of electrode. However, when not in use the electrode was stored in desiccator.
8.2.3f Interference studies

Chemically modified electrodes have significant analytical potential to enhance sensitivity and selectivity of determination because of the modifier-analyte interaction. The use of selective or specific modifier helps to overcome interferences from coexisting ions. But those metal ions which compete for complexation with the modifier and binding sites on the modified electrode surface would interfere significantly in the determination of the analyte. Anions which form stable complexes with the metal ion to be determined can also interfere.

Coexisting metal ions can interfere with the determination of Cd(II) and Pb(II) if they are in the concentration range which competes with the active site of the electrode surface. The examined ions, such as Fe(III), Al(III), Na⁺, Ca⁺, Mg²⁺, Ba²⁺, Sr²⁺, Al³⁺, NH₄⁺, NO₃⁻ and SO₄²⁻ in 1000-fold excess, and Fe(II), Zn(II), Mn(II), in 100-fold excess did not cause any interference. However, it was observed that the presence of 25-fold excess Cu(II) ions decreased the peak currents of Cd(II) and Pb(II) ions by 60%, which may be due to the formation of inter-metallic compound between copper and cadmium deposited on the electrode surface. In equal concentration of Hg(II) ions, the Cd(II) and Pb(II) ions peak current increased by 50% and similar results were observed in presence of Bi(III) ions. This may be due to the in-situ formation of mercury and bismuth film on the electrode during preconcentration. In a 100 fold excess of Ni(II) interpretation of the Cd(II) and Pb(II) signal was found to be very difficult.

The surface-active compounds are usually a source of strong interferences in voltammetric methods. An anionic surfactant (sodium dodecyl sulphate), nonionic surfactant (Triton X-100) and cationic surfactant (cetyltrimethylammonium bromide)
were investigated in this respect. The presence of $1 \times 10^{-5}$ M TritonX-100 suppressed the signal intensity of Cd(II) and Pb(II) ions by 40%. Higher concentration of Triton X-100 caused major suppression in the signal. The addition of $1 \times 10^{-5}$ M sodium dodecyl sulphate and cetyltrimethylammonium bromide have not influenced the peak intensity of Cd(II) and Pb(II) ions.

8.2.4 Determination of Hg(II) ions from aqueous solutions

8.2.4a Differential pulse voltammetric studies of Hg(II) ions on CPE/SHP-CPE

Figure 8.2.10 shows the DPASVs of 1 to $8 \times 10^{-8}$ M Hg(II) ions at the CPE and SHP-CPE. In Figure, relatively very poor current was observed at CPE (dotted line). However, the stripping peak current of Hg(II) ions at the SHP-CPE (curve a-f) were greatly enhanced. This may be due to the increased surface area because of the incorporation of SHP in carbon paste, which might have provided the host matrix to adsorb more Hg(II) ions from the solution during preconcentration.

**Figure 8.2.10:** DPASVs of 1 to $8 \times 10^{-8}$ M Hg(II) ions in 0.1 M KNO₃ at CPE (dotted line) and SHP-CPE (solid lines-a to h). (Preconcentration time: 300s; Preconcentration potential: -0.2 V).
8.2.4b Effect of preconcentration time

The effect of accumulation time on peak current of $10 \times 10^{-8}$ M Hg(II) ions is as shown in Figure 8.2.11A. In the beginning, the peak current increases with increase in accumulation time. Longer accumulation time, resulted in the increased reduction of more Hg(II) ions on electrode and the peak current becomes larger. However, after a specific accumulation period of 600s, the peak current tends to level off. Hence, 600 s of deposition time was applied during subsequent studies.

8.2.4c Effect of preconcentration potential

The effect of preconcentration potential on peak current of $10 \times 10^{-8}$ Hg(II) was investigated over the range -0.1 to -0.5 V versus SCE. It can be seen from the Figure 8.2.11B that the peak current increased with change in potential from -0.1 V to -0.5V and further increase in the predeposition potential decreased the peak current. The peak current increased with increase in the deposition potential. However, a well defined peak was observed when the applied predeposition potential was -0.2 V. Hence, -0.2 V of accumulation potential was selected for further studies.

![Figure 8.2.11: Effect of preconcentration time (A) and preconcentration potential (B) on the stripping current of Hg(II) ions.](image)
8.2.4d Effect of pH

The influence of pH on peak current of $10 \times 10^{-8}$ M Hg(II) ions was studied in the pH range of 3.0-7.0 and shown in the Figure 8.2.12. It was found that the peak current increased with increase in pH and the maximum current was obtained at pH 7.0. The effect of pH on the stripping current of Hg(II) ions was not studied below pH 3.0 and above pH 7.0, because of the solubility of SHP at lower pH and the formation of metal hydroxide at higher pH.

![Figure 8.2.12: Effect of pH on the stripping current of $10 \times 10^{-8}$ M Hg(II) ions.](image)

8.2.4e Calibration curve, detection limit and reproducibility of the electrode

The dependence of DPAS voltammetric peak current on the concentration of Hg(II) ions was investigated. As shown in Figure 8.2.10, the voltammetric signals intensity increased with increase in the concentration of metal ions. The calibration curve constructed is shown in the Figure 8.2.13. The dependence of peak current on the initial concentration was linear with high regression coefficient 0.9948. The sensitivity of electrode calculated from slope of the calibration curve was found to be
5.1×10^{-8} \text{ A/nM} and the limit of detection obtained under the optimized condition was 5.5×10^{-9} \text{ M.}

The reproducibility of Hg(II) ions analysis was examined with five identical SHP-CPE electrodes in 10×10^{-8} \text{ M Hg(II) ions solution. Under the optimized conditions the corresponding stripping currents were in the range 3.7 to 4.0 \text{ µA}, which shows that the reproducibility is higher than 90\% in both preparation and sensing processes. Ten consecutive analyses of Hg(II) ions carried out in 10×10^{-8} \text{ M solution using the same modified electrode, produced relative standard deviation of 8.4\%. After each determination, regeneration of the metal free SHP-CPE electrode was achieved by holding the electrode at higher oxidation potential in order to ensure the complete removal of deposited Hg.

![Figure 8.2.13: The calibration plot of 1 to 8×10^{-8} \text{ M Hg(II) ions on SHP-CPE.}](image)

The lifetime of SHP-CPE was studied by periodically recalibrating the DPASV response to Hg(II) ions. After the conditioning step, the electrode was repeatedly calibrated three times during a period of one month. No significant change in the performance of the electrode was observed. This shows that the lifetime of
proposed electrode was longer than several months. The stability of the electrode may be due to the presence of stable structure of SHP which is passive to the areal oxidation and the leaching effect.

8.2.4f Interference studies

The influence of other ions on the peak current of Hg(II) ions was evaluated. The interference study was considered by adding various foreign substances into a standard solution containing $1 \times 10^{-6}$ M Hg(II) ions under the optimized conditions. When the change of peak current exceeds 5.0% relative error, it is considered that this substance causes obvious interference, and the corresponding concentration was defined as tolerance level. Most of the foreign ions such as Na$^+$, K$^+$, Ca$^{2+}$, NH$_4^+$, SO$_4^{2-}$, NO$_3^-$ and Cl$^-$ which exceed 100-fold concentration have no interference to the determination of target metal ions. However, 10-fold concentration of Cu(II) and Ag(I) ions significantly influence the determination of Hg(II), because of their close oxidation peak potentials. No significant change is observed in the oxidation peak of Hg(II) in presence of 50-fold excess Pb(II), Zn(II), Cd(II), Fe(II), Ni(II) and Bi(III) ions.

The presence of more than $1 \times 10^{-5}$ M EDTA, thiourea, 1-10 phenanthroline and SCN$^-$ suppressed the Hg(II) ions peak intensity. The suppression in the peak current in presence of chelating agents is due to the formation of complexes. Generally strong chelates form stable complexes with Hg(II) ions which hinder the release of free Hg(II) ions at electrode surface for the process of reduction. Hence, the bound fraction of Hg(II) ions is not available for reduction during the preconcentration step. However, the presence of same chelating agents below $1 \times 10^{-6}$ M had negligible influence on the peak intensity of Hg(II) ions.
8.2.5 Conclusion

A new chemically modified carbon paste electrode was prepared using the strontium hydrogen phosphate and used for the determination of Hg(II), Cd(II) and Pb(II) ions. This electrode was successfully used for selective preconcentration and sensitive determination of heavy metal ions. The detection limits obtained on SHP-CPE were in nano moles and satisfying compared to other modified electrodes reported elsewhere. The sensitivity of the modified electrode was free of interference from other ions and less prone to the interference by surfactants. The electrode has got good stability over a period of several months and hence same electrode may be used for the determination of heavy metal ions, without significant analytical error.
References: