

Determination of Heavy Metal Ions on Glassy Carbon Electrode Modified with Antimony

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Antimony film electrode formed by *ex situ* electro deposition on glassy carbon electrode substrate has been investigated by optimizing the suitable condition of voltammetric instrument and plating solution as well as characterizing metals. The electrochemical behavior of the film was studied by cyclic and differential pulse anodic stripping voltammetry using model samples of Pb^{2+} and Cd^{2+} ions. It was found that -500 mV depositions potential and 45 sec deposition time are optimized conditions for sensitive film fabrication. The detection limit for the characterizing metals was found to be 1.51 and 2.922 nM on antimony modified glassy carbon electrode for cadmium and lead with the linear range of 0.99523 and 0.995 respectively. The highest sensitivity with nano-molar detection limits were achieved on antimony film formed at constant potential for two model analytes. The concentration in real sample of water was recorded as 0.20097 μ M and 0.016 μ M for lead and cadmium respectively on modified surface. The modified electrode shows an excellent catalytic activity for the reduction of characterizing metals (Pb^{2+} and Cd^{2+} ions).

KEYWORDS: Lead, Cadmium, Antimony, Stripping Voltammetry, Glassy Carbon Electrode.

1. INTRODUCTION

The electrochemical sensors are very promising analytical instruments because of their high degree of selectivity and sensitivity. They are more useful and easy to determine the concentrations of various analytes in samples such as fluids and dissolved solid materials. They are frequently used in clinical diagnostics, occupational safety, medical engineering, process and environmental analysis.^{1,2} Voltammogram is one class of electrochemical sensor in which voltammetric measurement is made when the potential difference across an electrochemical cell is scanned from one pre-set value to another and the cell current is recorded as a function of the applied potential.^{3–5}

Stripping voltammetry is one of the most sensitive electrochemical methods for the determination of trace metals. The method is based on the preconcentration/stripping of an analyte in the sample solution.⁶ Especially differential pulse anode stripping technique is simple, fast and sensitive method for trace metal analysis in environmental sample.⁷ Stripping methods using chemically modified electrode (CME) has higher selectivity due to the ability of the modifier to capture the specific species ion via chemical reactions.⁸ For the analysis of trace metals, CME have

shown some advantages over other analytical methods and have been employed as powerful tools for concentration determination.⁹

One of the strategies for surface modification is to employ metals/semi-metals which deposited onto the electrode surface. Thin metal-film electrodes have become widespread in electrochemical stripping analysis due to their relatively simple fabrication and surface regeneration.¹⁰ When combined with advanced electrochemical stripping protocols, they offer almost unsurpassed analytical tools in terms of reliability, simplicity and flexibility. In the last six decades, mercury electrodes were the most extensively used for electrochemical stripping analysis of several metal ions and some selected organic species. Many other electrode materials have been suggested as substitutes for mercury, e.g., different modifications of carbon, gold, platinum, silver, iridium, several alloys and amalgams,¹¹ etc. But none of them approached mercury having an excellent electro analytical performance.

A decade ago, the bismuth film electrode was introduced and has proved to be a convenient alternative to its mercury counterpart. However, due to strict regulations and provisions concerning the use of mercury, there are still considerable efforts focused on new mercury free electrode materials which can be satisfactorily applied in modern stripping electro analysis.¹²

Recently, the *in situ* prepared antimony film electrode (SbFE) was suggested as another alternative that approaches the electro analytical performance of mercury

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and bismuth-based electrodes featuring some interesting characteristics, such as favorably negative overvoltage of hydrogen evolution, wide operational potential window, convenient operation in relatively strong acidic medium ($\text{pH} \leq 2$) and interestingly low stripping signal for antimony itself. Concerning antimony film electrodes (SbFEs) and their comparison with the bismuth analogues, they offer some specifics with effective use. At first, it has a better performance in more acidic solutions,^{13, 14} which can be appreciated in situations, when a wet acid-assisted digestion of the sample is required. In these cases, the residual of mineral acids remaining present after the decomposition process do not need to be extensively buffered or even removed by additional, usually complicated procedures and the proper specimen for analysis can be obtained by sole diluting the post-digestion solutions.^{15, 22} Second, the base-lines of SbFEs practically do not suffer from the large dissolution (stripping) signal of the Sb-film,¹⁶ which is quite advantageous for simultaneous co-deposition and the subsequent detection of some nobler metal ions, such as Cu(II), Hg(II), or even Bi(III).¹⁷ On the other hand, the individual variants of antimony-modified electrodes seem to be more sensitive towards the experimental conditions chosen especially, the actual pH has to be adjusted carefully and the use of antimony as such means the step backwards with respect to its less favorable toxicological classification.

The SbFE was prepared also *in situ* on a boron-doped diamond electrode exhibiting favorable electro analytical performance in even more acidic measurement solution of pH. However, in certain cases the application of the *in situ* prepared metal film electrodes is not convenient, undesired or even impossible, e.g., when performing measurements in environments where the antimony ions can not be added to the medium (natural waters), during *in-vivo* measurements, remote controlled measurements, and in solutions where the antimony ions are not stable. Thus, the possibility of simple electrochemical *ex situ* preparation of the SbFE on a suitable substrate electrode in a separate plating solution significantly extends the scope and applicability of the antimony film electrode to the abovementioned measurement conditions and to other more challenging environments. In particular, the *ex situ* preparation of the metal film paved the way towards measuring those metal ions and other selected compounds which are usually detected by anode stripping voltammetry. In addition, the metal film thickness and its related characteristics can be readily controlled via deposition time, concentration of metal ions,¹⁸ etc.

Anodic stripping voltammetry (ASV) is a powerful technique used for rapid determination of trace levels of metal ions.¹⁹ A bare glassy carbon (GC) electrode surface recommended for the analytical application of differential pulse anodic stripping voltammetry for the determination of heavy metal but is not much sensitive and selective for most elemental analysis.^{20, 21}

In this research work, we report the fabrication of SbFE which was prepared *ex situ* on the surface of a glassy carbon electrode for measuring trace heavy metals, i.e., Cd(II) and Pb(II).

2. MATERIALS AND METHODS

2.1. Reagents

All analytical grade chemicals were used. A stock solution of chloride, acetate and citrate buffer were made using equimolar mixture of 0.01 M HCl (RIEDEL DEHAEN, 37% PURE) and NaCl (NICE, 99% pure), 0.1 M CH_3COOH (LOBA CHEMIE, 99.5 PURE) and 0.1 M CH_3COONa (FINE, 99% PURE) and 0.1 M citric acid (WARDEL CHEMICAL LID., 99.5%) and sodium citrate (FENIKEM, 99%). Standard solutions of Sb^{3+} , Cd^{2+} and Pb^{2+} ion were prepared from their available salt.

2.2. Apparatus

Voltammetric technique was performed with a CV-50 W in connection with personal computer. Antimony coated glassy carbon electrode served as working electrode, with the Ag/AgCl (3 mol l^{-1} NaCl) and platinum wire acting as reference electrode and counter electrode, respectively. All electrochemical experiments were carried out in one-compartment voltammetric cells (10–20 mL) sample at room temperature. Stirring was carried out using a magnetic stirrer. All glassware were carefully cleaned by soaking in 0.1 mol l^{-1} HNO_3 over 48 h, followed by thorough rinsing with distilled water.

2.3. Preparation of Antimony Film Electrode (SbFE)

Glassy carbon electrode (GCE) surfaces was polished thoroughly with Al_2O_3 powder slurry on a polishing pad and then rinsed with double distilled water to remove alumina particles and other possible contaminants. After being dried, the GCE was immersed in a plating solution consisting of plating solution. This *ex situ* deposition of antimony was performed in optimized deposition potential, pH, concentration and deposition time. Deposition potential, deposition time, pH of plating solution and concentration were optimized. Similar parameters were optimized for model samples of Cd^{2+} and Pb^{2+} ion on antimony modified glassy carbon electrode except potential window instead of deposition potential and limiting concentration in the place of concentration of antimony.

2.4. Real Sample Determination

A 100 ml of tap water was digested with 5 ml concentrated nitric acid by boiling on a hot plate until its volume reduced to 50 ml. Then the volume of the sample adjusted to optimum pH and filled with acetate buffer until

its volume reached to 100 ml. Differential pulse anode stripping voltammetric (DPASV) measurements were performed in a solution of 0.01 M chloride and 0.1 acetate buffer containing lead and cadmium ions at various concentrations of these metals respectively at optimum conditions. After equilibration period, an anodic stripping voltammogram was recorded by applying a differential pulse potential scan. Before each measurement, a cleaning step was carried out by applying an optimized potential for stripping of each metal for 20 sec.

3. RESULT AND DISCUSSION

3.1. Cyclic Voltammogram of Antimony, Lead and Cadmium

In order to determine the redox electrochemical signal, cyclic voltammogram of cadmium, lead, and antimony were examined on glassy carbon electrode surface. As shown in Figure 1 the reduction potential of antimony, lead and cadmium gives maximum cathodic peak current at -350 , -550 and -960 mV respectively. This is very important to determine the optimum deposition potential required for thin film fabrication as well as metal deposition for the determination. Antimony film can be prepared on glassy carbon electrode by adjusting the reduction potential around the maximum reduction peak. Additionally cyclic voltammogram confirms antimony film is stable in negative potential window while its stability decreases towards the positive potential window.

3.2. Effect of Hydrogen Evolution

A greater challenge is inability to measure metal ions in which their reduction occurs at more negative potentials due to the evolution of hydrogen at most electrode materials. This evolution of hydrogen causes the decrease in peak height of analyte of interest. So in characterization of antimony modified glassy carbon electrode, it is very

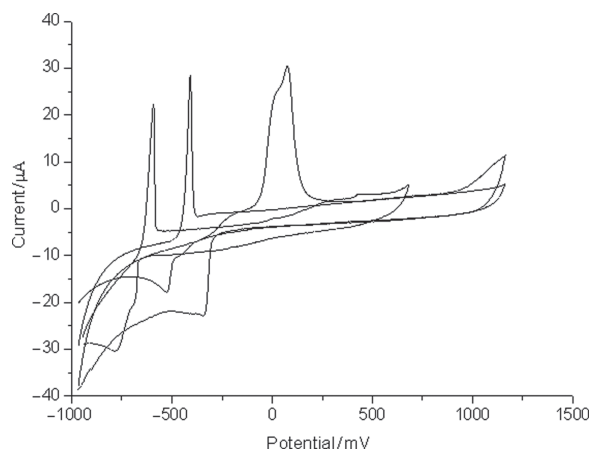


Fig. 1. Cyclic voltammogram of cadmium, lead and antimony on glassy carbon electrode.

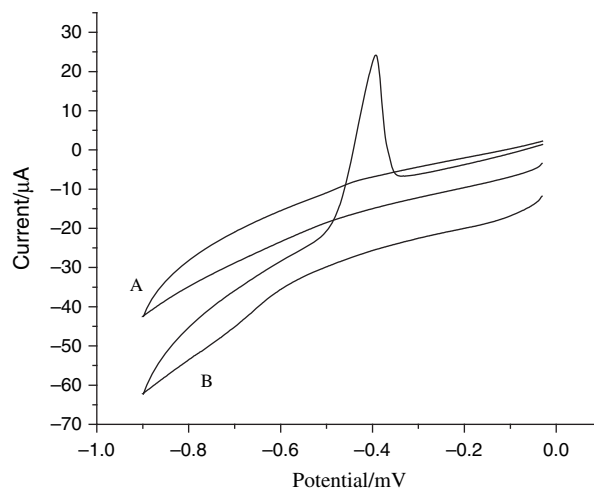


Fig. 2. Cyclic voltammogram of (A) supporting electrolyte, (B) lead at pH 2.5 on antimony modified glassy carbon electrode.

important, whether it has catalytic activity towards hydrogen absorption or not.

As shown in Figure 2(A) the reduction peak of the supporting electrolyte towards the negative potential window shows a slight increase on the antimony modified glassy carbon electrode at optimum pH for reduction of lead, when scanned from positive to negative direction. Similar property was observed for supporting electrolyte in the presence of analytes as shown in Figure 2(B). The effect of hydrogen evolution on the determination of lead increase when over potential becomes more negative. As the over potential become large, the hydrogen ion competition with metal ion increase on the same electrode surface and may cause the decrease in reduction of analytes. This implies that hydrogen evolution can reduce the surface activities of the electrode. Therefore the modified surface has catalytic activity for hydrogen gas evolution at higher negative potential.

In a similar way acetate buffer supporting electrolyte at pH 5.5 which is the optimum point for cadmium determination was run on antimony modified glassy carbon. Relatively the increase in hydrogen evolution was observed since the potential window is larger than the potential used for lead determination as indicated in Figure 3(A). A reduction peak was observed in the cyclic Voltammogram of cadmium at the same condition of the supporting electrolyte except the presence of the analytes as shown Figure 3(B). It is obvious that the reduction peak is due to the reduction of cadmium analytes.

Finally, it is possible to say antimony film modified glassy carbon electrode has higher catalytic activity for hydrogen evolution at larger negative potential and the reduction potential for lead and cadmium relatively low. So effect of hydrogen evolution on the determination of the two metals is minimal since the reduction potential for the two metals is less negative than hydrogen reduction potential.²³

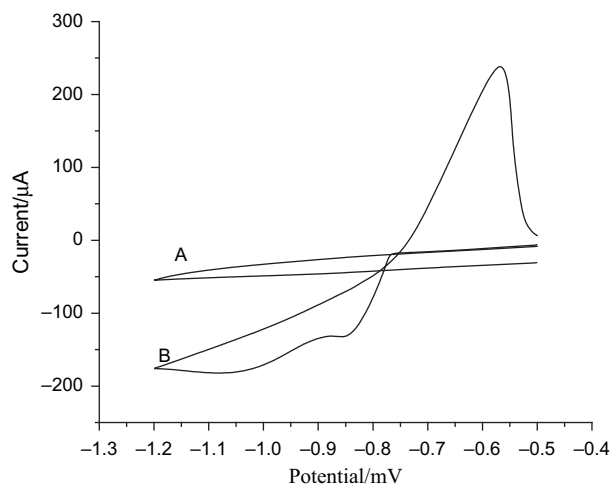


Fig. 3. Cyclic voltammogram of (A) supporting electrolyte, (B) cadmium at pH 5.5 on antimony modified glassy carbon electrode.

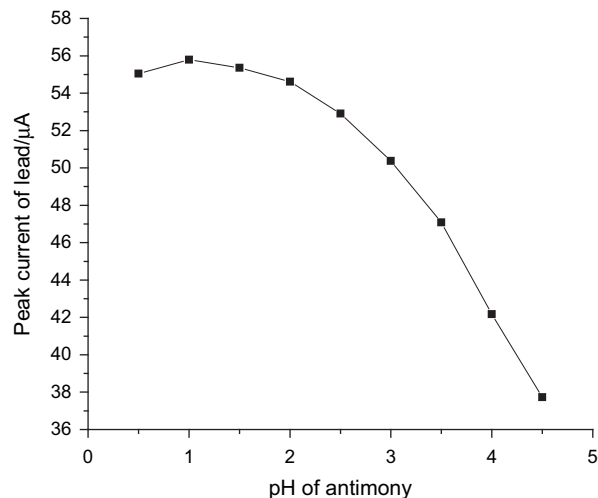


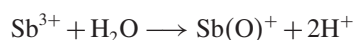
Fig. 4. pH dependent behavior of antimony film fabrication on glassy carbon electrode, keeping all variables constant (deposition potential of Sb = -450 mV, deposition time of Sb = 60 s, $[Sb^{3+}] = 0.66$ mmol/L).

3.3. Optimization of Parameters for Antimony Film Deposition

3.3.1. pH of Plating Solution (Antimony)

It is well known that many metallic compounds are soluble in an acidic environment. However, in alkaline environment cannot assure the complete solubility of heavy metals. This confirms that the electrolytic solution for antimony film fabrication is pH dependent. So evaluation of pH of the plating solution for thin film fabrication is an important parameter since free movement of ions is required for electrodeposition in electrolytic solution.

In order to determine the optimum condition at which the most sensitive thin film is fabricated, the effect of pH on differential pulse anode stripping voltammetric response of SbMGCE was studied by taking lead as thin film characterizer. By using a randomly selected reduction potential of -450 mV and 60 s deposition time, antimony was deposited by varying the pH using time base technique. The dependence of the peak current for 5 mg/L of antimony solution at various pH values is shown in Figure 4. As can be seen, the SbMGCE shows an optimum fabrication at $pH \leq 1.0$. But a slight decrease in peak current of lead above $pH = 1.0$ was observed. Most glassy carbon modified electrode studied previously like mercury and bismuth modified electrode have less stable if it is at lower pH.²⁴ But *ex situ* deposited antimony film is stable even at lower pH. It can be used for the determination of heavy metals at lower pH (≤ 2). Finally, the film fabrication was studied at pH of one. This is because the result at this pH shows a large peak current of analyte and increasing pH above this value causes precipitation formation due to hydrolysis reaction of antimony ion as shown below:



3.3.2. Deposition Time of Antimony Film

The deposition time is an important measurement parameter, which should be precisely controlled during the experiment. This is because large deposition time causes thick film production which has less sensitivity for analyte determination. In this study with a constant potential of (-450 mV), antimony was deposited by *ex situ* technique with different time. In each fabrication of the antimony film on GCE, lead was deposited and stripped by DPAS technique to determine the time required for the sensitive thin film formation. As shown in Figure 5 the peak current of lead during stripping increases which was deposited up to 45 s. But after this time it starts to decrease. This indicates that film thickness increases with time. As the film of antimony become thick its sensitivity becomes low. An attenuation of the electroanalytical

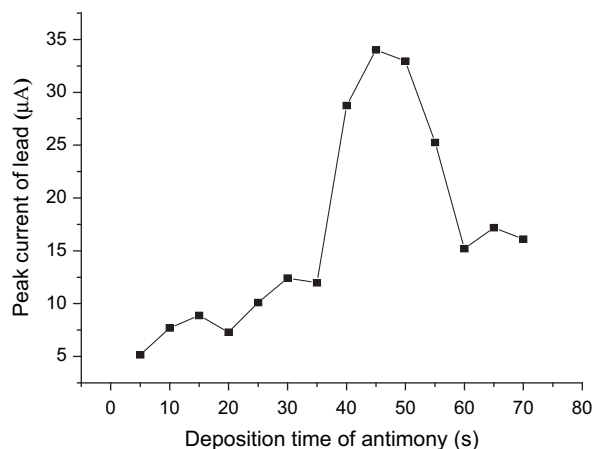


Fig. 5. Time dependent behavior of antimony film fabrication, keeping all variables constant (pH of Sb = 1.0 deposition potential of Sb = -450 mV, $[Sb^{3+}] = 0.005$ g/L).

performance of antimony film occurred at deposition times longer than 45 s, possibly as a consequence of thicker and less stable antimony film. This may be due to constituent atoms that have been deposited on glassy carbon substrate begin to wear out in to the composition bath (electrolytic cell) as the deposition time increases since the surface become saturated and the ions are unable to bind to the GCE surface. Thus, the adhesive force between the constituent atoms and the glassy carbon substrate weakens as the deposition time increases, which later resulted in low sensitivity and stability. In addition to this as the duration increases the size of crystal film increases and the sensitivity decreases. So from Figure 5 the most sensitive film was obtained at 45 s.

3.3.3. Deposition Potential of Antimony Film

The fabrication of thin film by electrochemical deposition for analysis of various analytes is usually done by forced chemical reaction. The deposition proceeds by applying an external potential. So applied potential (deposition potential) has superposition to control the thickness of the film during its fabrication. For this study, the effect of applied potential on the fabrication of antimony film on glassy carbon electrode by *ex situ* techniques from its nitrate salt solution was investigated using the range from -700 mV to -250 mV. This potential range was selected on the basis of the reduction potential which was obtained from cyclic voltamogram shown in Figure 1.

As shown in Figure 6, electrochemical peaks of lead were observed on the antimony thin film, which was recorded with various depositions potential, and constant times (45 s). The peak current of lead increases with increasing reduction potential of antimony up to -500 mV. But it decreases with more negative reduction potential below -500 mV. As the potential increases the amount of atoms that can be deposited increased and the size of the crystal increases. As the size of the film increases surface area to volume ratio become small and that the interaction

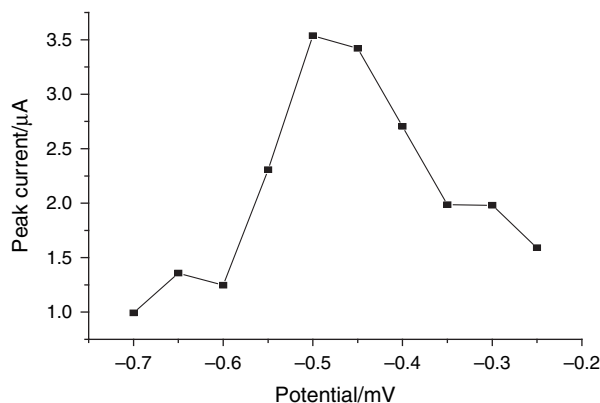


Fig. 6. Potential dependent behavior of antimony film fabrication, keeping all variables constant (pH of Sb = 1.0, deposition time of Sb = 45 s, $[Sb^{3+}] = 5$ mg/L).

between the film and the analytes decrease.²⁵ So from the graph shown in Figure 6, the optimum reduction potential for thin and sensitive antimony film fabrication was selected to be -500 mV.

3.3.4. Effect of Antimony Concentration on Film Formation

Cadmium and lead were deposited on the antimony surface fabricated at different concentration as shown in Figures 7(A) and (B) below, using the optimized deposition time and potential. The increase in concentration of antimony solution increases the sensitivity of metal to be determined. Further increase in the concentration of antimony plating solution causes decrease in response of the characterizing metal. This is due the increasing in film thickness of antimony. From Figure 7(A), the sensitivity of cadmium using differential pulse anode stripping

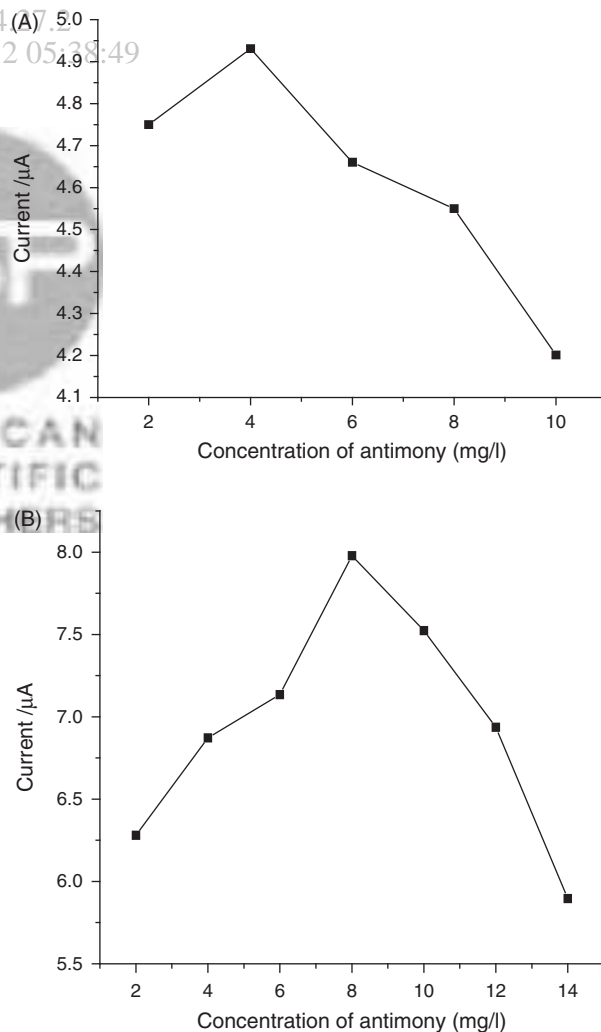


Fig. 7. Concentration dependent behavior of antimony film fabrication using (A) cadmium (B) lead characterizing metals, keeping all variables constant (pH of Sb = 1.0, deposition time of Sb = 45 s, deposition potential of Sb = -500 mV).

analysis increases up to 4 mg/L of Sb^{+3} and starting to decline above this concentration. Similarly, the concentration of lead increases up to 8 mg/L of Sb^{+3} and then starts to decline as shown in Figure 7(B). This is may be because lead is neither complete nor half-field. So it is active to capture electron from electron rich electrode and form amalgam with antimony surface, while cadmium ion is complete field so the activity towards antimony surface is less relative to lead ion during the reduction process. This means inter metallic bond on lead is stronger than cadmium due to the presence of unfilled d' electrons.²⁶

3.3.5. Determination of Film Thickness

The electric current flowing through the working electrode has two components. These are the first, the faradic current, which obeys the Faradays law and is due to the discharge of the electro active compound on the electrode surface and the second, the capacitive current (non faradaic current), which is produced by the growth of the double electric layer on the interface between the electrode and the solution. The non faradic current is due to the supporting electrolyte in the solution (as shown in Fig. 8). The total current flowing through the electrode is finally the sum of non faradic and the faradic current. The charge used for film formation on the GCE is only due to faradic charge which can be obtained by subtracting the non faradic charge from the total charge. The amount of mass deposited on glassy carbon is calculated. Finally, the thin sensitive antimony film fabricated on the glassy carbon electrode for lead and cadmium is calculated.

The thickness of the electrodeposited antimony film on the glassy carbon electrode is calculated by applying Faraday's equation for electrolysis.

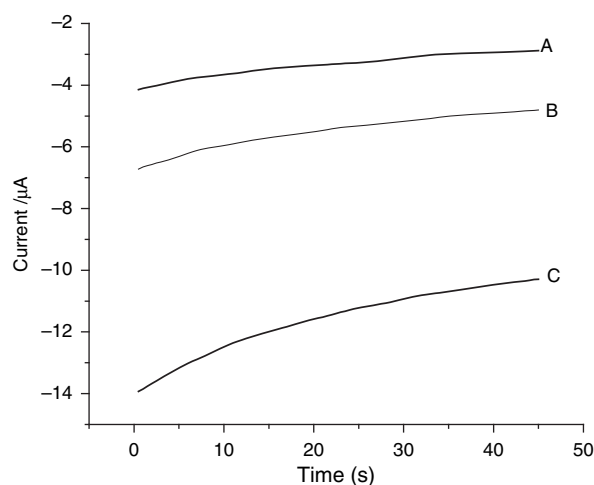


Fig. 8. Current versus time graph of (A) supporting electrolyte, (B) 4 mg/L antimony solution, (c) 8 mg/L antimony solution at optimum conditions.

The thickness of the deposited film required for lead and cadmium determination was calculated to be 4.58 μm and 0.826 μm respectively. So the film thickness required for metal determination varies with the characteristics of metals to be determined. It is clear that as film thickness increases signal of analyte decreases due to the increase in grain size of the film.

3.4. Optimization of Parameters for the Characterizing Metal on SbMGCE

In order to study the characteristics of the antimony modified glassy carbon electrode, optimizing the parameters for the deposition of characterizing metal on the modified surface is important.

3.4.1. pH of the Characterizing Metal

The solution pH was varied to determine its effect on the redox reaction of Pb^{2+} and Cd^{2+} at the antimony modified glassy carbon electrode in a separate electrochemical cell. As shown in Figure 9, in acidic solution at pH 1.5 to 2.5, it was observed that the oxidation current of Pb^{2+} increases linearly, while in the media more basic than pH 2.5, the peak current for the lead stripping peaks decrease in magnitude. The decrease in the current response of the electrode at higher pH is due to the formation of the lead hydroxide which causes a decrease in the concentration of lead in the solution used for accumulation on the electrode surface. On the other hand, the increase peak current towards lower pH values because of lead ions free from any precipitate formation and so the ions easily moves towards the active surface for reduction.^{27,28} Similarly as shown in Figure 10, the peak current of cadmium varies with change in pH. With increasing pH the peak current also increases, after pH 5.5, peak current decreases.

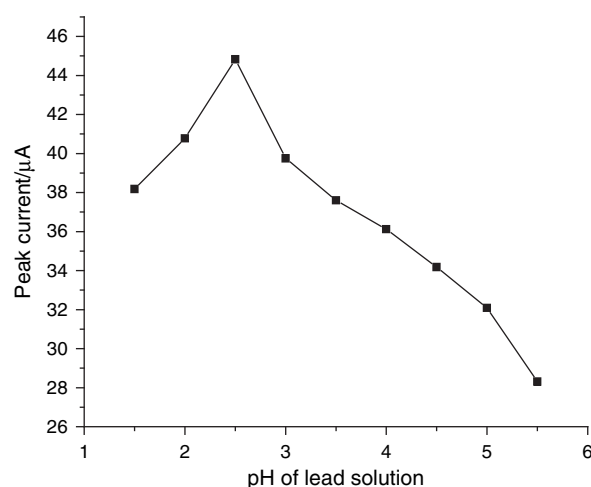


Fig. 9. pH dependent behavior of lead on an optimized antimony film, keeping all variables constant (deposition time of Pb = 60 s, scan rate of Pb = 50 mV/s, stripping potential of Pb = -900 to -30 mV, $[\text{Pb}^{2+}] = 1 \mu\text{M}$).

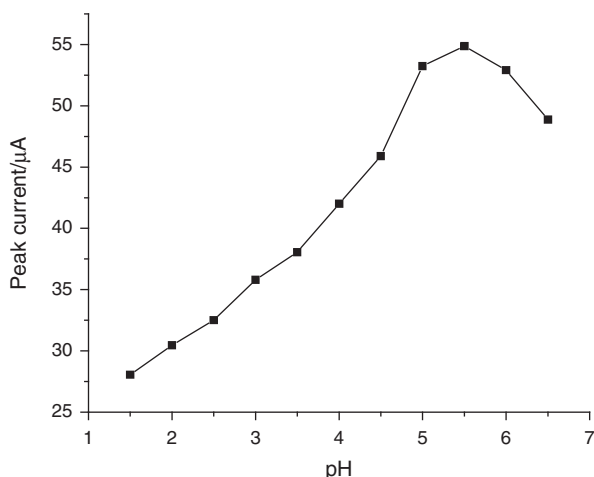


Fig. 10. pH dependent behavior of cadmium on an optimized antimony film, keeping all variables constant (deposition time of Cd = 60 s, scan rate of Cd = 50 mV/s, stripping potential of Cd = -1200 to -500 mV, $[Cd^{2+}] = 1 \mu M$).

This is because at higher pH above 5.5 cadmium starts to form cadmium hydroxide precipitate and thus the concentration of free cadmium ion decreased. As a result the amount of cadmium metal deposited at the specified condition become low. Finally the oxidation peak current decreased.²⁹ So the pH for deposition of lead and cadmium on the antimony thin film was adjusted to be 2.5 and 5.5 respectively for this study.

3.4.2. Scan Rate of Lead and Cadmium on the Antimony Surface

In the determination of any analyte from a given sample by DPAS techniques, the concentration of analyte in the sample directly related to the peak current. The influence of potential scan rate on the peak current of lead and cadmium were studied in the range of 10–100 mV s⁻¹. As shown in Figure 11, the electrochemical signals vary.

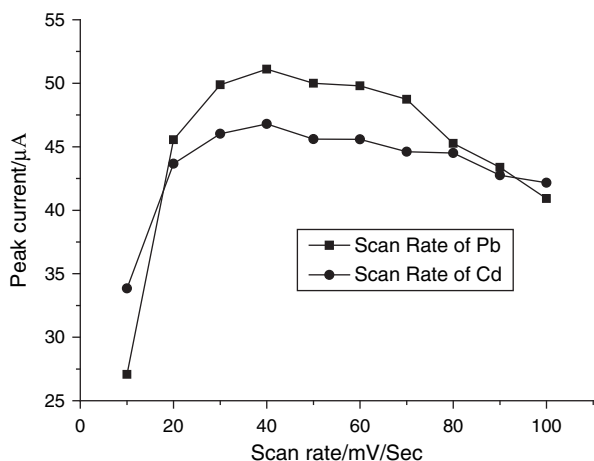


Fig. 11. Scan rate dependent behavior of lead and cadmium on an optimized antimony film, keeping all variables constant.

With increasing the scan rate from 10 to 40 mV s⁻¹, the peak currents increase linearly, whereas for a higher scan rate, the peak sizes of the signals becomes constant, due to the limitation of kinetics.³⁰

As shown in Figure 11, the peak current of cadmium at scan rate 40 mV/s is slightly larger than all electrochemical signals measured at various scan rates. Therefore, the optimum scan rate for cadmium determination selected to be 40 mV/s.

3.4.3. Deposition Time of Characterizing Metal

The result in Figures 12 and 13 shows the electrochemical signals obtained by varying the deposition time for DPASV analysis of a 1 μM Pb²⁺ and Cd²⁺ solution. Increasing the deposition time results in the increased signal intensities (electrochemical signals) for both lead and cadmium, due to the increased amount of metals deposited at the electrode surface. From, Figure 13(a) deposition time of 140 s is sufficient to obtain a well-defined stripping current profile of lead at this concentration. The longer the time for the reduction, the more cations reduced onto the sensor surface. Since more metal cation is reduced onto the surface of the sensor, an enhanced peak current was obtained due to an increased amount of metal cations that was stripped from the sensor surface. Ensuring that more metal cations were reduced would subsequently give an improved peak current until the surface is saturated and after saturation it becomes level.³¹ In addition to this an excessive deposition time would result in interference due to formation of intermetallic compounds and causes decrease in sensitivity. Obviously, the amount of metals plated into the SbMGCE film is directly proportional to the deposition time.

Similarly the effect of deposition time on the peak current of Cd²⁺ on antimony thin film fabricated on glassy carbon electrode was studied in the range of 30–180 s by fixing the differential pulse anode stripping potential

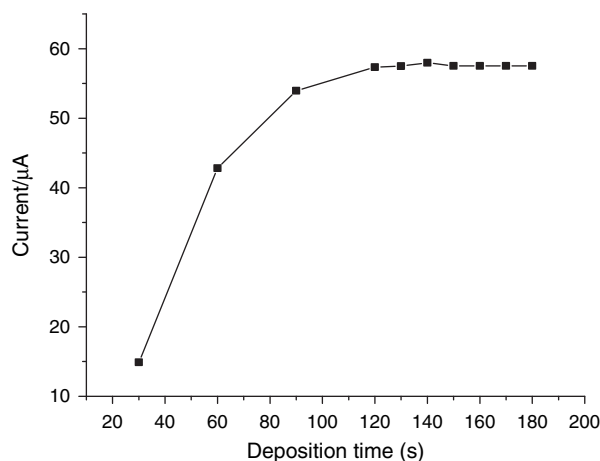


Fig. 12. Time dependent behavior of lead on an optimized antimony film, keeping all variables constant (pH of Pb²⁺ = 2.5, scan rate of Pb = 40 mV/s, stripping potential of Pb = -900 to -30 mV, $[Pb^{2+}] = 1 \mu M$).

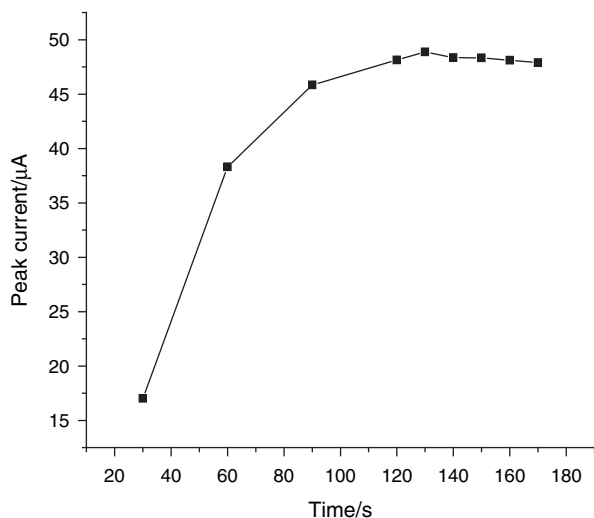


Fig. 13. Time dependent behavior of cadmium on an optimized antimony film, keeping all variables constant (pH of $\text{Cd}^{2+} = 5.5$, Scan rate of $\text{Cd} = 40$ mV/s, stripping potential of $\text{Cd} = -1200$ to -500 mV, $[\text{Cd}^{2+}] = 1$ μM).

window in the range -1200 to -500 mV. The peak current increases with the deposition time. For accumulation time higher than 130 s, the peak current becomes constant as shown in Figure 13. This is due to surface occupation of the active thin film of antimony and saturation.

3.5. Interference Studies

In order to evaluate the selectivity of the fabricated electrode, the influence of various interferences were examined. Under this study Hg^{2+} , Zn^{2+} , Cr^{3+} , Cu^{2+} , Co^{2+} and Cd^{2+} and Pb^{2+} were examined. Considerable interference can be caused by co-existing surface-active compounds capable of competing with the analyte of interest for the deposition site on the electrode surface, resulting in decreased peak height. The competitive co-deposition interference was evaluated in the presence of various substances. For these investigations, the interfering species were added at the same concentrations of the characterizing metal at optimized condition of lead and cadmium metals. The addition of 50 μM interfering metals like Hg^{2+} , Cr^{3+} , Cu^{2+} , Co^{2+} and Cd^{2+} caused to decrease the peak current of lead by about 12.2%, 2.5%, 21.82%, 0.8%, and 2.8%, respectively of its original peak current. Similarly, Zn^{2+} , Cr^{3+} , Cu^{2+} , Co^{2+} and Pb^{2+} decrease the original peak current of cadmium by 29.42%, 12.31%, and 23.02%, 3.82% and 21.57% respectively. This inhibition or surface competition could be caused by the working electrode surface blockage of the interferences or due to special interaction of the interferent to the analyte. Even if the concentration is the same for the analyte and the interferent, the fabricated electrode is highly selective for analyte since the decrease in peak current is low percent as the result indicated.

3.6. Calibration Curve and Detection Limit

To determine the sensitivity of the modified electrode in relative to the bare electrode from the calibration curve, knowing the relationship between the standard of the analyte and the voltammetric signal measurement is important. This is helpful to minimize error in addition to the quality of the reagent and glassware used to prepare the standards. For this investigation, differential pulse anode stripping measurement was carried out on bare and antimony modified glassy carbon electrode at various concentrations of lead and cadmium.

The detection limit of lead on bare and Antimony modified GCE was determined from the calibration curve using 0.1 M acetate buffer supporting electrolyte at pH 2.5. In this case the pre-concentration was carried out by holding the deposition potential at -900 mV and 140 s deposition time. Figure 14 display the plot for DPAS analysis of lead at the concentrations of 0.011, 0.081, 0.135, 0.27, 0.54, 1.08, 1.62, 2.16 and 2.70 μM Pb^{2+} ion on bare and Antimony modified glassy carbon. The linearity of the curve was found to be 0.9991 and 0.9996 on the two respective electrode surfaces. At the end the detection limit of Pb ion was determined by taking the minimum point from the calibration curve using five replicate measurements of the standard solution. The limit of detection of Pb ion was recorded as 8.06 and 2.992 nM on bare and modified GCE surface.

Similarly, the detection limit of cadmium on bare and modified GCE surface by DPAS Voltammetry was investigated using 0.1 M acetate buffer as supporting electrolyte at pH 5.5. Figure 15 shown are plots for the concentrations of 0.059, 0.074, 0.148, 0.295, 0.59, 1.18, 1.77, 2.36 and 2.95 μM Cd ion on bare and modified GCE orderly from DPAS response in -1200 mV deposition potential and 130 s deposition time. The linearity was found to be 0.9979 and 0.9981 on the bare and modified electrode surface. Finally, the detection limit of Cd was determined using five trials of the standard solution by taking the minimum point from the calibration curve under optimized experimental conditions. Then the limit of detection was

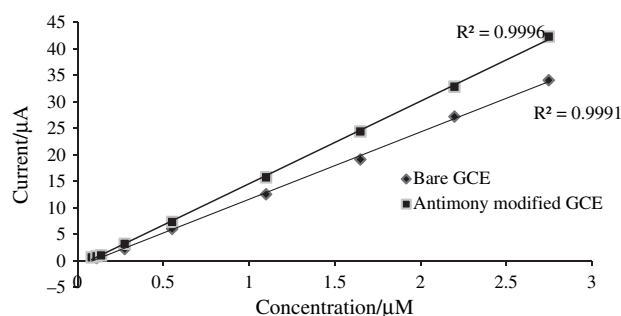


Fig. 14. Concentration dependent behavior of lead on bare and antimony modified GCE, keeping all variables constant (pH of $\text{Pb}^{2+} = 2.5$, scan rate of $\text{Pb} = 40$ mV/s, deposition time of $\text{Pb} = 140$ s, stripping potential of $\text{Pb} = -900$ to -30 mV).

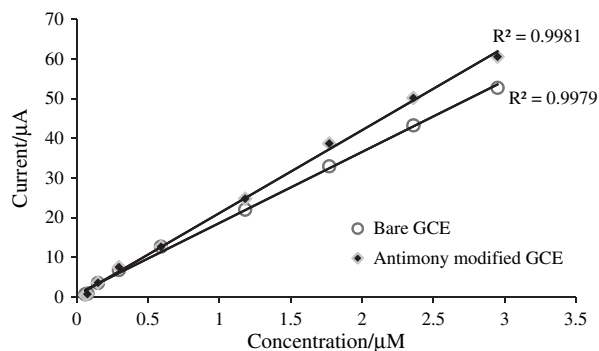


Fig. 15. Concentration dependent behavior of cadmium on bare and antimony modified GCE, keeping all variables constant (pH of $\text{Cd}^{2+} = 5.5$, scan rate of Cd = 40 mV/sec, stripping potential of Cd = -1200 to -500 mV).

determined to be 7.624 and 1.51 nM for the respective two electrodes.

We can summarize that it is possible to expect lower detection limit on deposition time longer 140 s and 130 s; and deposition potential more than -900 mV and -1200 mV for Pb and Cd respectively.

3.7. Determination of Lead and Cadmium in Real Sample

Different substances in the sample have their own effect on the determination of analyte from real sample. The method

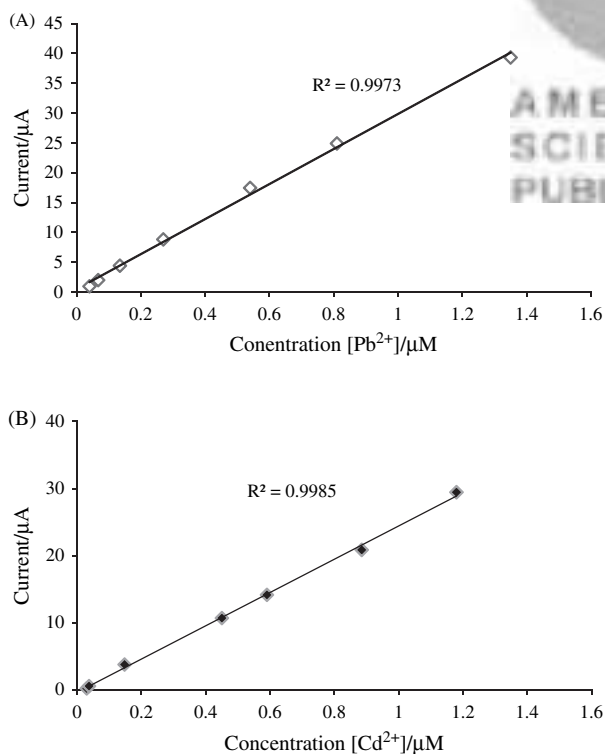


Fig. 16. Calibration curve (A), lead and (B) cadmium for real sample analysis at optimum conditions.

used for the determination should minimize effects caused by interference of electroactive species. Standard addition is an effective method to minimize the matrix effect during voltammetric determination of analyte of interest.

In this case, a series of Pb and Cd standard concentrations were added to equal volume of samples. In one of the samples, only 10 ml supporting electrolyte was added. This helps to balance the effect of supporting electrolyte in the determination of the analyte. Figures 16(A) and (B) show the voltammetric response of 10 ml spick with series concentrations of 0.081, 0.135, 0.27, 0.54, 1.08, 1.62, 2.16 and 2.75 μM Pb ion and 0.074, 0.148, 0.295, 0.59, 1.18, 1.77, 2.36 and 2.95 μM Cd ion. Then the analytes were determined from real sample based on the calibration equation set by the standard addition method. Finally, 0.20097 μM Pb and 0.016 μM Cd was obtained.²⁰ *Ex situ* fabricated Antimony modified glassy carbon electrode is interesting for the determination of heavy metals if all conditions are optimized according to the properties of the metal to be determined.

4. CONCLUSIONS

Antimony film modified glassy carbon electrode was prepared by *ex situ* electrode deposition on glassy carbon electrode at -500 mV applied potential and 45 second deposition time. The concentration of antimony ion required for film formation varies with type of analyte of interest. The fabricated film was studied voltammetrically using cyclic and differential pulse anode stripping techniques. Deposition time, pH and deposition potential have significant effect on sensitive film production. The detection limit of Pb and Cd is 8.06 and 7.624 nM on bare glassy carbon electrode respectively. While the detection limits of the two metals on modified electrode surface were 2.922 and 1.51 nM. The electro chemical responses of Pb and Cd were improved in comparison with bare glassy carbon electrode. The modified electrode is fast, selective, sensitive and can determine metals with high accuracy when connected with electro chemical stripping Voltammetry. It is also advantageous due to its suitable operation in acidic solution in the presence of dissolved oxygen. Low signal for hydrogen evolution also makes it better in electro chemical analysis.

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