

Experimental Setup of Square-Wave Anodic Stripping Voltammetry Measurement of Lead and Cadmium using Antimony Impregnated Activated Carbon Electrode

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Abstract— Heavy metals in human body cause chronic diseases when in excess like Parkinson's disease and cancer. Techniques are developed to detect small concentrations of heavy metals in water; one of them is stripping voltammetry. It involves current detection against the applied voltage. The resulting voltammograms are used to quantify the heavy metals present in the water body. The current work is about manufacturing of working electrode by impregnation method to increase the detection efficiency and other characteristics. Vacuum impregnation of antimony over activated carbon was done. Four samples having 2%, 3%, 4% and 5% antimony by weight were prepared. Working electrode was prepared by holding samples over a copper structure with the help of a paraffin binder. "Square-wave Anodic Stripping Voltammetry" tests were performed in electrochemical cell with an AUTOLAB potentiostat. The correct experimental setup was first devised using several experimental arrangements of the apparatus. The optimization of the working parameters was also performed. This setup obtained remarkable voltammogram peaks of both cadmium and lead equal to 29.2 and 49.4 μA respectively as compared to previous values of 6 and 3 μA respectively. These values are in 100 $\mu\text{g/L}$ of both cadmium and lead.

Keywords— Anodic Stripping Voltammetry; Working electrode; Antimony; Impregnation

I. INTRODUCTION

A. Heavy Metals

The term "Heavy Metal", unfortunately, is a misinterpretation, has contradictory definitions and lacks 'coherent scientific basis' as stated by an IUPAC report [1]. An alternative term known as "Toxic Metal" also exists for which no exact definition exists either. Several definitions have been proposed – some are based on physical properties as density, atomic number or atomic weight and some are based on chemical properties as toxicity etc. Covering all the bases, heavy metals have a general definition as: "Heavy metals are chemical elements having specific gravity at least 5 times that of water" [2], [3]. Specific gravity relates the density of a given amount of solid substance when it is compared to an equal amount of water. Thus, the specific gravity of water is equal to 1 at 4°C. Some well-known toxic heavy metals having specific gravity 5 or more times that of water are Cadmium - Cd (8.65), Lead - Pb (11.34), Mercury – Hg (13.546), Antimony – Sb (6.691), Arsenic – Ar (5.7) and Iron – Fe (7.9) [4]. All the values are reported at 20°C. Toxic

metals are those having no biological role, i.e. are not essential minerals for human body, or bonded in a harmful form. They form poisonous soluble compounds having harmful effects on humankind. A toxic metal having no biological role has no beneficial dose whatsoever. Aluminum is an element that has no biological role, still its classification as a toxic metal is controversial [5]. In renal impaired patients, accumulation in tissues and other significant toxic effects have been observed. However, individuals having healthy kidneys might be exposed to large amount of aluminum without any adverse effect, thus it is not categorized as dangerous to persons having normal elimination capacity. Similarly, barium can also be removed efficiently by the kidneys.

Generally, heavy metals are considered as members of subset of elements exhibiting metallic properties. Mainly the transition metals, some metalloids, lanthanides, and actinides are considered heavy metals. However, depending on the context, heavy metals can include elements lighter than carbon while some heavy metals may be excluded from the list [6]. Heavy metals are sometimes considered synonymous to toxic metals, but some lighter metals also have toxicity (e.g. beryllium – Be) on the other hand, not all heavy metals are particularly toxic, e.g. bismuth [5], [6]. Some heavy metals are in fact essential for human body, such as iron – Fe. In abnormally high doses, trace elements may become toxic. There are in total 35 toxic elements which are of concern due to occupational or residential exposure [2], [7]. Out of these 35 elements; 23 are heavy metals, namely: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc [8]. In European community the 11 elements of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and thallium, and their emissions are regulated in waste incinerators [6].

B. Occurrence of Heavy Metals

In ecosystem heavy metals occur naturally with large concentration variations over ages. However recently, pollution (an anthropogenic source) has also been introduced as a heavy metal source in this ecosystem [6]. This is because of the fuels that are derived from waste contain heavy metals, thus heavy metals are a major consideration in using waste as fuel. Another major pollution source arises from purification

of metals, e.g. preparation of nuclear fuels, smelting of copper and electroplating for chromium and cadmium. Heavy metal pollutants tend to localize and lay dormant through precipitation of their compounds or by ion-exchange into soils and muds [6]. Heavy metals do not decay unlike organic pollutants and thus pose a different kind of challenge for remediation. Still another threatening consequence of manufacturing and industrial practices (from textile working to metalworking operations) is the release of heavy metals in waterways. Those metals remain in low but dangerous concentrations for decades and sometimes even for centuries.

C. Removal Need

As discussed earlier, different living organisms require different amounts of heavy metals for proper growth. Human body requires iron, cobalt, copper, manganese, molybdenum, and zinc and still these can be dangerous at excessive levels. Other heavy metals such as mercury, plutonium, chromium, cadmium and lead are toxic even in minute amounts, having no vital or beneficial effect at all and their overtime accumulation in animal bodies can cause serious illnesses [6]. It is interesting to note that certain elements that are toxic for one organism might become beneficial for others under certain conditions.

Despite of the fact that some of the heavy metals in minute amounts are needed by human body (e.g. cobalt, copper, chromium, manganese and nickel), others are carcinogenic or toxic (e.g. manganese, mercury, lead and arsenic) affecting, among other, the central nervous system [9]. Still others affect kidneys and liver (e.g. cadmium, mercury, lead and copper) and skin, bones or teeth (e.g. nickel, cadmium, copper and chromium) [9]. Some diseases are specific towards certain heavy metals, such as, minamata disease is a result of mercury poisoning and itai-itai disease is from cadmium poisoning [6]. Exposure to mercury and lead can cause development of autoimmunity (in which a person's immune system starts attacking its own cells). This medical condition leads to joint diseases such as rheumatoid arthritis, and other diseases in the nervous system, human circulatory system and the kidneys.

Toxic heavy metals have the tendency to bio accumulate in the body and in the food chain. This is the reason why heavy metals' toxicity is characterized as chronic. Long-term exposure usually results in slowly progressing physical, neurological and muscular degenerative processes that mimic muscular dystrophy, Alzheimer's disease, multiple sclerosis and Parkinson's disease [2]. Allergies are also fairly common and repeated long-term contact with some of the heavy metals or their compounds may even cause cancer [10]. This trend is particularly notable in the case of radioactive heavy metals such as thorium. This element tends to imitates calcium to a point of being incorporated into human bone. Similar health implications are also found in mercury and lead poisoning. Heavy metal toxicity commonly results in lower energy levels, damaged or reduced mental and central nervous function and damage to blood composition, kidneys, lungs, liver and other vital organs.

Heavy metals are not only dangerous for human health but they are harmful for the environment too, e.g. mercury, cadmium, lead and chromium [7]. Some of them are corrosive in nature, e.g. zinc and lead. Some of them are

industrially harmful, e.g. arsenic pollutes catalysts. One of the biggest problems associated with heavy metals persistence is bioaccumulation and bio magnification potential. This phenomenon causes heavier exposure of heavy metals towards some organisms. For this reason, coastal fish (e.g. smooth toadfish) and seabirds (e.g. Atlantic Puffin) are monitored regularly for the presence of such contaminants.

The Agency for Toxic Substances and Disease Registry (ATSDR), in cooperation with the U.S. Environmental Protection Agency, compiled a priority list for 2001, called the 'Top 20 Hazardous Substances'. In this list, the heavy metals arsenic (1), lead (2), mercury (3), and cadmium (7) also appear [2]. The World Health Organization (WHO) has also implemented a standard for maximum permissible concentrations of certain heavy metals in drinking water as shown in TABLE I. [11].

D. Human Exposure

Heavy metals enter human body by three primary modes. 1) Intake via respiratory system or food chain (water, air and food products). 2) Absorption by skin (in agriculture, pharmaceutical, manufacturing, industrial, or residential settings). 3) Radiological procedure (usually inappropriate medical treatment). Of all the above listed sources of contact of heavy metals with human body, water contamination is by far the most usual cause of heavy metal poisoning in humans [12]. The major sources of water contamination by heavy metals are the industrial and manufacturing practices (from textile factories to metalworking operations), which release heavy metals in waterways. Other potential sources of heavy metal exposure to water bodies are waste disposal, nuclear fuels preparation and environmental pollution. These heavy metals can remain in water bodies for decades, even centuries, in low but still dangerous concentrations.

E. Removal Techniques

Large amounts of heavy metals are easily detected and removed [13]; however small amount (~ppm and ppb) imposes difficulties in their removal and detection. Heavy metals are present in ionic form and are dangerous even in this minute amount so need to remove the traces of them from drinking and other kinds of water is the need of the hour. Scientists and researchers around the globe have devised methods to detect the heavy metals ions in water in accurate amounts so they can be removed subsequently. Heavy metals detection techniques have developed rapidly in recent years. Portable equipment are available, which after simple tests, generate the results in real time. The different techniques of heavy metal detection are listed hereby: 1) Atomic Absorption Spectrometry (AAS), 2) Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), 3) Capillary Electrophoresis (CE), 4) X-Ray Fluorescence Spectrometry (XRF), 5) Optical Sensors, 6) Aptamers Sensors, 7) Quantum-Dot-Labeled Dnazymes, 8) Voltammetry.

The researcher has selected voltammetry as the detection technique for heavy metals in this work because of its superiority in terms of little pre-treatment requirement, the ability to reproduce results, the less amount of time and training required etc.

TABLE I. MAXIMUM PERMISSIBLE CONCENTRATIONS (MG DM⁻³) OF CERTAIN HEAVY METALS IN DRINKING WATER AS IMPLEMENTED BY WHO.

HEAVY METAL	PERMISSIBLE LIMIT (mg dm ⁻³)
Iron	0.30
Zinc	3.0
Nickel	0.02
Cadmium	0.003
Chromium	0.05
Cobalt	0.05

F. Voltammetry

As briefly described above, voltammetry is a category of electro analytical methods used in analytical chemistry and various industrial processes. It is the study of current as a function of applied potential. These curves $I = f(E)$ are called voltammograms. Among other applications, voltammetry can be used to identify and quantitate different species in solution. In this method, the potential is varied arbitrarily both step by step and continuously. During this, the actual current is measured as the dependent variable. Three-electrode system is commonly employed in voltammetry experiments. Heavy metal ions are present as positive ions in the water. The working electrode, which makes contact with the analyte, applies the required potential in a controlled way (usually by a potentiostat) and facilitates the transfer of charge to and from the analyte. This working electrode reduces the metal ions and deposits them on its surface in metallic form. A second electrode called the counter or auxiliary electrode, acts as the other half of the cell and it must balance the charge added or removed by the working electrode. It does not take part in the reaction and is made of some inert material e.g. C, Hg or Pt. The third electrode is called the reference electrode. This is basically a half-cell with a known reduction potential and performs the role of measuring and controlling the potential of the working electrode and at no point does it pass any current. These electrodes, the working electrode, the reference electrode, and the counter electrode make up the modern three-electrode system.

As discussed previously, small amounts of heavy metal ions are very difficult to detect. However, the detection of small amounts is facilitated by their adsorption at an engineered surface followed by a subsequent stripping step. This technique in essence makes stripping voltammetry a collect and disperse method. Heavy metal ions are initially dispersed in the sample solution. They are then made to accumulate on a common surface of the working electrode by the application of a deposition potential. During this accumulation step, the metal cations are reduced to metallic form and are deposited on the surface. After this, an equilibrium time period is provided which is followed by a stripping step in which the metal atoms are oxidized to metal ions. During this stripping step, the current is measured by a potentiostat and recorded in the form of a voltammogram.

Stripping voltammetry is further subdivided into anodic (ASV) and cathodic stripping voltammetry (CSV). In ASV, the electrodes are held at a potential sufficient to reduce any metal ion it encounters for about 60 seconds before the scan begins. This process has the effect of reproducibly concentrating the analyte in the vicinity of the electrode. Some analytes are coated on the surface of the working electrode; others are dissolved in the mercury. During the

voltage scan, all of the reduced analyte ions at the working electrode surface are re-oxidized, thereby giving a much larger signal than normal. This strategy is called anodic stripping voltammetry and it is considered one of the most widely acceptable strategies for the electrochemical determination of metal ions in waters. If the potential of electrode is held to cause analyte species oxidize and accumulate at electrode surface before potential is scanned to more negative direction, this technique is called "cathodic stripping voltammetry".

Several techniques of ASV have been developed with respect to the excitation potential that is provided during the scan. These excitation modes are named as follows: 1) Linear Sweep Voltammetry, 2) Staircase Voltammetry, 3) Squarewave Voltammetry, 4) Cyclic Voltammetry, 5) Alternating Current Voltammetry, 6) Rotated Electrode Voltammetry, 7) Normal Pulse Voltammetry, 8) Differential Pulse Voltammetry [14]

The square wave scan has several advantages over other types of excitation signals. They include: 1) The entire scan can be performed on a single mercury drop in about 10 seconds, as opposed to about 5 minutes for other techniques. 2) It saves time, reduces the amount of mercury used per scan by a factor of 100 in some instances. 3) If it is used in conjunction with a pre-reduction step, the limits of detection can reach up to 1-10 ppb. All of the above-mentioned factors lead to the selection of Square-Wave Anodic Stripping Voltammetry (SWASV) as the prime option for the detection of heavy metal ions in this research work.

II. LITERATURE REVIEW

Different techniques of voltammetry have been investigated in combination with various working electrodes and base materials. Remarkable lower limits have been obtained by different researchers. Following literature review covers the broad sense of the field of voltammetry.

Zhu et al. [15] utilized SWASV for the detection of lead and cadmium using gold nanoparticle-graphene-cysteine composite modified bismuth film working electrode on a glassy carbon base material. They obtained lower limits of 0.05 $\mu\text{g dm}^{-3}$ and 0.10 $\mu\text{g dm}^{-3}$ for lead and cadmium respectively. Zhou et al. [16] utilized cathodic adsorptive stripping for the detection of antimony using mercury drop electrode and obtained a lower limit of $7 \times 10^{-10} \text{ mol dm}^{-3}$. Adejolu and Young [17] utilized anodic stripping potentiometry for the detection of antimony using in-situ prepared mercury working electrode on a glassy carbon base material. They obtained lower limit of 0.9 $\mu\text{g dm}^{-3}$. Renedo and Martinez [18] utilized ASV for the detection of antimony using in-situ prepared gold working electrode on a carbon screen base material with a lower limit of $9.44 \times 10^{-10} \text{ M}$. Salaun et al. [19] utilized SWASV and differential ASV for the detection of antimony using gold film working electrode with a lower limits of 0.63 ppt. Brihaye et al. [20] utilized linear anodic stripping voltammetry for the detection of lead, cadmium and copper using mercury film working electrode on a glassy carbon base material. They obtained lower limits of 6 ng dm^{-3} , 8 ng dm^{-3} and 5 ng dm^{-3} for lead, cadmium and copper respectively.

Tesarova et al. [21] utilized ASV for the detection of lead and cadmium using in-situ prepared antimony film working electrode on a carbon paste base material. They obtained lower limits of $0.2 \mu\text{g dm}^{-3}$ and $0.8 \mu\text{g dm}^{-3}$ for lead and cadmium respectively. Hocevar et al. [22] utilized ASV for the detection of lead and cadmium using in-situ prepared antimony film working electrode on a glassy carbon base material. They obtained lower limits of $0.9 \mu\text{g dm}^{-3}$ and $0.7 \mu\text{g dm}^{-3}$ for lead and cadmium respectively. Tesarova et al. [23] utilized SWASV for the detection of lead and cadmium using in-situ prepared antimony film working electrode on a carbon paste base material. They obtained lower limits of $0.9 \mu\text{g dm}^{-3}$ and $1.4 \mu\text{g dm}^{-3}$ for lead and cadmium respectively.

Guzsvany et al. [24] utilized ASV for the detection of lead and cadmium using in-situ prepared antimony film working electrode on a glassy carbon base material. They obtained lower limits of $1.2 \mu\text{g dm}^{-3}$ and $1.4 \mu\text{g dm}^{-3}$ for lead and cadmium respectively. Jovanovski et al. [25] utilized ASV for the detection of lead and cadmium using ex-situ prepared antimony film working electrode and obtained lower limits of $0.3 \mu\text{g dm}^{-3}$ and $1.1 \mu\text{g dm}^{-3}$ for lead and cadmium respectively.

Voltammetry is a vastly investigated research area, almost all kinds of working electrodes are manufactured and investigated in the electrochemical experiments. In previous works, manufacturing and investigation of the working electrodes was done in a single step. On the contrary, in this research the working electrode will be prepared ex-situ in the first step. Investigating the effectiveness of this working electrode will be done in the second step. In this way, one mass transfer resistance will be eliminated. In addition, the surface characteristics of working electrode can be controlled. This will supposedly increase the detection efficiency.

In SWASV, there are two types of ions, analyte ions and the working ions. Analyte ions are those, which are unknown and are supposed to be detected by voltammetry. On the other hand, working ions are the heavy metal ions that are introduced into the solution by the analyst himself to facilitate the detection technique by amalgamation. So much work is already done in this field and researchers have managed to achieve high sensitivity in detection reaching up to nano-grams per liter concentrations; however, the technique used has several limitations. These conventional techniques include the analyte ions and the working ions to be introduced into the solution simultaneously and the deposition of both at the working electrode are done at the same time. So essentially these techniques rely on the in-situ preparation of the working electrode.

This work is mainly oriented towards the manufacturing of electrodes by an ex-situ working electrode preparation. This ex-situ preparation is done by impregnation of working ions over activated carbon. The selection of the working ion is another hurdle faced since mercury seems to be the obvious choice due to having the maximum deposition potential as compared to other toxic heavy metals. Despite of having this quality, mercury is replaced by the next available choice, i.e. Antimony (Sb). This replacement is done due to the highly toxic behavior of mercury and the tendency of it to getting dispersed into the sample solution and poison it. This ex-situ preparation helps in the development of a working electrode

with superior detection efficiency and surface characteristics. In this proposed research work, a novel method of electrodes preparation will be introduced. From the above discussion, it is quite clear that currently electrodes are prepared and investigated for effectiveness in a single experimental arrangement. Such a practice imposes two mass transfer resistances to the system. First one is the coating of the required heavy metal on the surface of the substrate and second is the stripping step which imposes its own mass transfer resistance. This work aims towards the elimination of the first mass transfer resistance of coating of the heavy metal ion. This target is achieved by preparing the electrode itself prior to carry out the voltammetry experiment. Further advantages of the proposed method supposedly include: 1) A non-toxic electrode. 2) Excellent detection limits. 3) Robust nature. 4) Enhanced surface characteristics. 5) Economical usage.

For the base material, activated carbon (AC) is selected because of having superior surface area than other materials. Analyte heavy metal ions to be investigated are selected to be Cadmium (II) – Cd^{2+} and Lead (II) – Pb^{2+} . Now the selection of the working ions is based upon the fact that Mercury (II) – Hg is a highly poisonous substance still it is used in various electrochemical researches as working ion [16], [17], [20], [26], [27]. It is clear that antimony is the next suitable choice for heavy metal ions detection because of having the next highest standard hydrogen reduction potential after mercury as shown in TABLE II.

III. EXPERIMENTAL

A. Electrode Preparation

In the preparation step, activated carbon (AC) is used as a support material on which antimony is impregnated. First, AC is regenerated and then antimony is impregnated over it, followed by drying and calcination step. The manufactured electrode is then characterized for the surface study. Various characterization techniques are employed e.g. TPR, CO titration, XPS, BET etc. and the results will be presented later. After characterization, the electrode is then tested in electrochemical system and its properties investigated for practical applications. Several electrochemical were performed including working configuration test, best electrode test, repeatability test, reproducibility test, minimum concentration test etc and the results will be presented later.

Following is the list of the chemicals used during the process of electrode manufacturing: 1) Activated Carbon (AC) from Norrit – As support material. 2) Antimony (III) Chloride (SbCl_3) from Sigma Aldrich – As precursor to Antimony working ions. 3) 37% Hydrochloric Acid (HCl) from Scharlau – As supporting electrolyte for electrochemical testing. 4) Paraffin (C14) – As binder material for granular AC to stick to electrode surface. The equipment utilized to carry out various manufacturing and testing are listed hereby: 1) ECF 12/4A Furnace from Lanten – For AC re-activation. 2) XA-43 Rotary Vacuum Evaporator from BIBBY – For vacuum impregnation of Sb over support. 3) JSON-150 Oven from JSR – For drying of antimony impregnated activated carbon (AIAC). 4) CTF 12/C5 Muffle Furnace from Carbolite – For calcination of AIAC. 5) PG STAT-101 Potentiostat from AUTOLAB powered by NOVA – For electrochemical testing of AIAC.

TABLE II. STANDARD REDUCTION POTENTIALS OF VARIOUS HEAVY METAL IONS WITH RESPECT TO HYDROGEN STANDARD REDUCTION POTENTIAL OF 0.

HALF-REACTION	E° (V)
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}(\text{s})$	+0.159
$\text{Sb}^{3+} + 3\text{e}^- \rightarrow \text{Sb}(\text{s})$	+0.204
$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$	+0.70

B. Electrochemical Testing

The catalyst samples prepared were reduced at 600°C and tested in an electrochemical cell. Paraffin (C14) as a binder was used to hold the catalyst powder over a specially developed copper-plastic piston-working electrode. Copper was used as the base material due to having an excellent electrical conductivity, a property much needed in electrochemical testing. Teflon tape was wrapped around the copper electrode to make sure that only surface area exposed to the analyte solution was the circular area of the tip on which the AIAC was applied as paste. A layer of activated carbon was introduced between the AIAC paste and copper to prevent any short-circuiting to happen by isolating the copper surface and the analyte solution in the electrochemical cell. This whole working electrode structure was wrapped in a non-conductive plastic assembly for protection and prevention of direct contact of copper with the solution. Carbon was used as a counter electrode and reference electrode was Ag/AgCl. Analyte solution consisted of 100 µg Pb⁺² and Cd⁺² (precursors: Lead Nitrate and Cadmium Chloride Monohydrate from Loba Chemie) supported in a 0.01 M HCl solution (pH = 2) to remove the effect of migration current. The electrochemical tests were performed on PG STAT-101 potentiostat provided by AUTOLAB and powered by NOVA software. Deposition potential of -0.1 V was given to the solution with a deposition time of 10 minutes. Stepping potential was set to 4 mV, frequency was set to 30 Hz, amplitude to 50 mV and stopping potential to +0.5 V. During deposition, the working electrode acts as a cathode and reduces the metal ions to metal atoms. The counter electrodes completes the other half-cell by working as an anode and dissociates water molecules to liberate oxygen. During stripping step, the working electrode acts as an anode and oxidizes the metal atoms back to metal ions while the counter electrode becomes cathode and completes the other half cell by hydrogen ions reduction to hydrogen gas.

C. Electrochemical Cell

0.0179 g of cadmium chloride (CdCl₂) from Loba Chemie was dissolved in 1000 ml of distilled water. Out of this solution, 1 ml was taken and diluted to 10 ml. Again 1 ml was taken to equal the amount of 100 µg cadmium (1.79x10⁻⁴ g cadmium chloride). Similarly, 1.59 g of Lead Nitrate (PbNO₃) from Loba Chemie was dissolved in 1000 ml of distilled water. Out of this solution, 1 ml was taken and diluted to 10 ml. Again 1 ml was taken to equal the amount of 100 µg lead (1.59x10⁻⁴ g PbNO₃). Now 0.828 ml of stock HCl was taken and diluted to 250 ml with distilled water. The two, previously prepared solutions of lead and cadmium were added to it and then the total solution was made equal to 1 L. This is a 0.01 M HCl solution (pH = 2) containing 100 µg of Pb⁺² and Cd⁺² metal analyte ions.

D. Setup Testing

Configuration test was performed to establish the correct working combination of the primary working electrode. It took major time of the research work to get the desired results. Once the configuration was properly determined, results were obtained quite instantly. 3% AIAC was selected to investigate following configurations: 1) Metallic gauge. 2) Cotton cloth. 3) Binder without carbon layer. 4) De-aerated solution. 5) Aerated solution. 6) Carbon layer without pressing. 7) Carbon layer with pressing. All of these configurations are shown in Fig. 1.

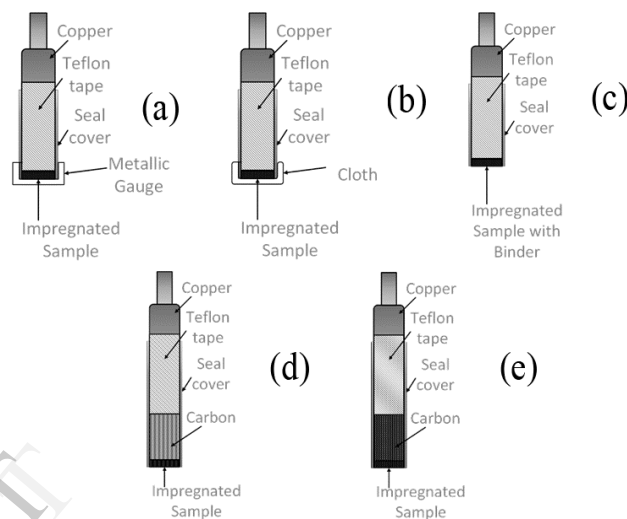


Fig. 1. Various configurations employed to carry out SWASV analysis on the antimony impregnated activated carbon working electrode, including metallic gauge (a), cotton cloth (b), binder (c), uncompresses binder (d) and compressed binder (e) configurations.

IV. RESULTS AND DISCUSSION

To investigate the best configuration of the working electrode, several experimental setups were tested. Metallic gauge was used initially to hold the impregnated sample over the copper electrode surface during stripping voltammetry. However, due to the conductive nature of the metallic gauge, short-circuiting of copper structure from the metallic gauge and the analyte solution occurred and no voltammogram was obtained as shown in **Error! Reference source not found.**

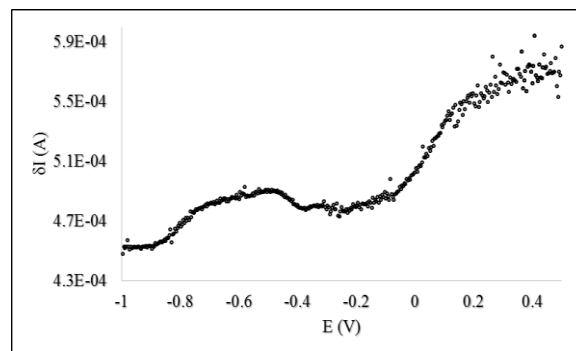


Fig. 2. SWASV of 100 µg/L Cd(II) and Pb(II) at the ex situ prepared 3% AIAC electrode in metallic gauge configuration. Solution: 0.01 M HCl (pH 2), deposition at -0.1 V for 10 min with a frequency of 30 Hz, amplitude of 50 mV and a potential step of 4 mV.

Secondly, a cotton cloth was used to act as an insulator barrier between activated carbon and the analyte solution, however, the cotton cloth imposed major resistance to current flow between the analyte solution and the AIAC that the test did not obtain an acceptable voltammogram as shown in Fig. 3.

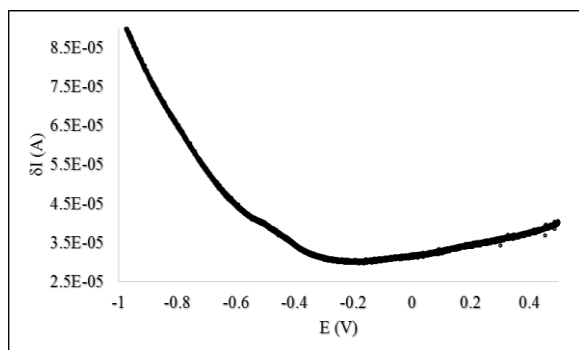


Fig. 3. SWASV of 100 $\mu\text{g/L}$ Cd(II) and Pb(II) at the ex situ prepared 3% AIAC electrode in cotton cloth configuration. Solution: 0.01 M HCl (pH 2), deposition at -0.1 V for 10 min with a frequency of 30 Hz, amplitude of 50 mV and a potential step of 4 mV.

Then paraffin (C14) was used as binder to hold the AIAC impregnated sample over the copper base-electrode surfaces. However, the thin carbon layer was not enough to isolate this copper base from coming in contact with the analyte solution directly, resulting in the short-circuiting of current and failure of experimental setup as shown in Fig. 4.

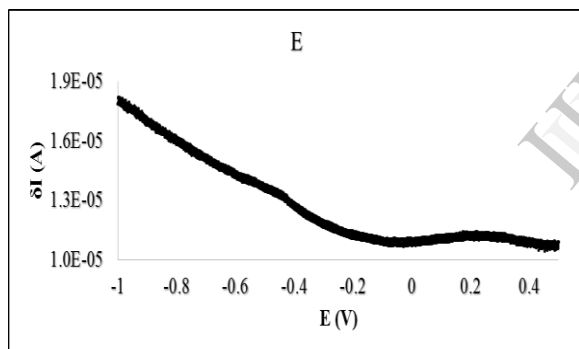


Fig. 4. SWASV of 100 $\mu\text{g/L}$ Cd(II) and Pb(II) at the ex situ prepared 3% AIAC electrode in binder configuration. Solution: 0.01 M HCl (pH 2), deposition at -0.1 V for 10 min with a frequency of 30 Hz, amplitude of 50 mV and a potential step of 4 mV.

Solutions were then de-aerated and aerated to make sure the presence or absence of air is not imposing problem over the electrochemical analysis, but results were not favorable. Then a setup was introduced involving an insulating activated carbon layer between the copper base structure and the AIAC impregnated sample with. This time the results were not acceptable because the insulating activated carbon layer has a high void volume due to its incredible surface area. This leads to reduced electrical conductivity and thus voltammograms obtained were not acceptable as shown in Fig. 5.

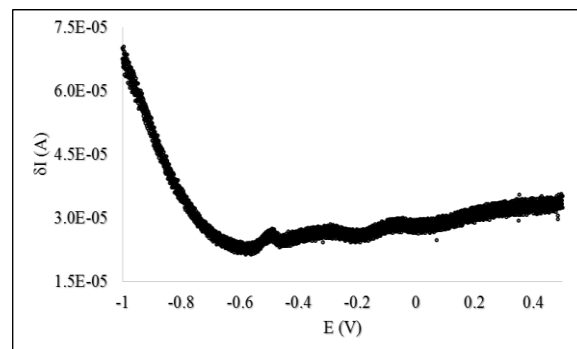


Fig. 5. SWASV of 100 $\mu\text{g/L}$ Cd(II) and Pb(II) at the ex situ prepared 3% AIAC electrode in un-pressed AC configuration. Solution: 0.01 M HCl (pH 2), deposition at -0.1 V for 10 min with a frequency of 30 Hz, amplitude of 50 mV and a potential step of 4 mV.

The above-mentioned limitation was overcome by pressing the insulating AC layer and the resulting voltammograms showed excellent results as shown in Fig. 6. This configuration of pressed insulating carbon layer between copper base and AIAC impregnated carbon layer was selected as the finalized setup for further electrochemical testing.

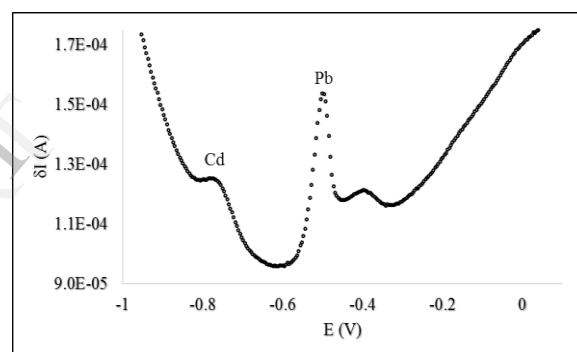


Fig. 6. SWASV of 100 $\mu\text{g/L}$ Cd(II) and Pb(II) at the ex situ prepared 3% AIAC electrode in pressed AC configuration. Solution: 0.01 M HCl (pH 2), deposition at -0.1 V for 10 min with a frequency of 30 Hz, amplitude of 50 mV and a potential step of 4 mV.

V. CONCLUSION

Square-wave anodic stripping voltammetry (SWASV) was carried out for a novel working electrode. Activated carbon was vacuum impregnated with antimony to act as working ions for the detection of lead and cadmium ions in the water sample. The experimental setup was optimized for working parameters as well as the appropriate working configuration. It was found that the copper base must be properly insulated from the test sample to avoid short-circuiting. This can be made sure by utilizing a compressed insulating carbon layer between the copper base and the impregnated sample. The results obtained were remarkable and better than the previously reported values.

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