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DETERMINATION OF THE LEVEL OF LEAD AND CADMIUM IN GROUND WATER BY SQUARE WAVE ANODIC STRIPPING VOLTAMMETRIY (SWASV) USING CARBON PASTE ELECTRODE

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Wisdom at the source of the Blue Nile

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Abstract

Heavy metals can be very harmful to human health if drinking water is contaminated with toxic metals. Severe effects include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. In the present study a direct determination of Cd and Pb metal was carried out from ground water collected in some selected areas of N/Gondar administrative zone Ethiopia, using a square wave anodic stripping Voltammeter (SWASV) at carbon past electrode. Determination of Cd and Pb was done after optimizing of working parameters. The optimized parameters for this are pH value 2 with a sweep rate (scan rate) of 100 mV/s and amplitude 30 mV. The solution was pre-concentrated at -0.8 V (vs. Ag/ AgCl) for 20 seconds and the potential was scanned from -1.4 V to +0.6 V (vs. Ag/AgCl). The concentration of Cd was not detected in this work that may be the amount of Cd is below the detection limit of the instrument. On the other hand, the amount of Pb in the ground water collected from azezo kebele, N/Gondar was determined and found to be 1.8 mg/l in shinta and 2.499 mg/l in boyit ground water. Based on the results obtained, both sampling areas ground water are polluted with Pb and are not safe for peoples living around. This is because the concentration of Pb in both sampling area ground water was above the safe limit of WHO.

Key words: *Anodic stripping Voltammetry, carbon past electrode, Heavy Metals, Cadmium, Lead, ground water.*

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LIST OF ABBREVIATION/ ACRONYMS

AAS-----------------------Atomic Absorption Spectro Photometry

ADSV----------------------Adsorptive Stripping Voltammetry

ASV----------------------- Anodic Stripping Voltammetry

CPE------------------------Carbon Paste Electrode

CSV------------------------Cathodic Stripping Voltammetry

CV--------------------------Cyclic Voltammetry

DCE------------------------Doping Carbon Electrode

DME-----------------------Doping Carbon Electrode

DPV ----------------------- Differential Pulse Voltammetry.

E_{Pa} ------------------------Anodic Peak Potential

E_{PC} ----------------------- Cathodic Peak Potential

GW-----------------------Ground Water

ICO-OES------------------Inductively Coupled Plasma Optical Emission spectrometry

I_{Pa} --------------------------Anodic Peak Current

I_{PC} --------------------------Cathodic Peak Current

NPV-----------------------Normal Pulse Voltammetry

SCE------------------------Standard Calomel Electrode

SWASV-------------------Square Wave Anodic Stripping Voltammetry

SWV ----------------------Square Wave Voltammetry

WHO----------------------World Health Organization

1. INTRODUCTION

1.1 Ground Water

Groundwater comes from surface water percolating through overlying soils and it resides in the pore spaces between particles of soil and other geologic materials. Formations that have all the pore spaced saturated with water are called saturated zones or aquifers. The top of the aquifer is called the water table. Aquifers typically consist of gravel, sand, sandstone, or fractured rock, like limestone. These materials are permeable because they have large connected spaces that allow water to flow through. The amount of ground water and the speed at which groundwater flows depends on the size of the spaces in the soil or rock and how well the spaces are connected [1].

Groundwater is located in an underground, saturated zone but can intercept surface water. Water wells extend into aquifers to allow water to be collected and pumped to the surface. Groundwater does not (generally) exist as underground rivers or pools − instead it is captured between particles above an impermeable layer that restricts water movement further downward. The quality of ground water is the resultant of all the processes and reactions that act on the water from the moment it condensed in the atmosphere to the time. It is discharged by a well or spring and varies from place to place and with the depth of the water table with sufficient water infiltration, soil contaminants such as heavy metals can leach to underlying ground water [2]. Unconfined aquifers are especially vulnerable to various contaminants and sediment loads (including microscopic bacteria, viruses and protozoa) [3].

Contamination of the groundwater by domestic, industrial effluents and agricultural activity is a serious problem facing by the developing countries. The industrial wastewater, sewage sludge and solid waste materials are currently being discharged into the environment indiscriminately. These materials enter subsurface aquifers, resulting in the pollution of irrigation and drinking water [4].

1.2 Water Pollution

Water is a unique substance, because it can naturally renew and cleanse itself, by allowing pollutants to settle out (through the process of sedimentation) or break down, or by diluting the pollutants to a point where they are not in harmful concentrations. However, this natural process

takes time, and is difficult when excessive quantities of harmful contaminants are added to the water. Water pollution includes all of the waste materials that cannot be naturally broken down by water.

Water pollution is the contamination of water bodies (e.g. lakes, rivers, oceans and groundwater). Water pollution occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds. Water pollution affects plants and organisms living in these bodies of water. In almost all cases, the effect is damaging not only to individual species and populations, but also to the natural biological communities.

It has been suggested that water pollution is the leading worldwide cause of deaths and disease and that it accounts for the deaths of more than 14,000 people daily [5]. In addition to the acute problems of water pollution in developing countries, industrialized countries continue to struggle with pollution problems as well. Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish. Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water.

1.3 Sources of Water Pollution

Surface water and groundwater have often been studied and managed as separate resources, although they are interrelated [6]. Surface water seeps through the soil and becomes groundwater. Conversely, groundwater can also feed surface water sources. "Industrial and household waste discharges, may be directly or indirectly through leakages in sewage systems into water sources, cause excessive pollution in surface and underground water" [7].

Sources of surface water pollution are generally grouped into two categories based on their origin.

1.3.1 Point Sources

Point source water pollution refers to contaminants that enter water away from a single, identifiable source, such as a pipe or ditch. Examples of sources in this category include discharges from a sewage treatment plant, a factory, or a city storm drain. The U.S. Clean Water Act (CWA) defines point source for regulatory enforcement purposes. The CWA definition of

point source was amended in 1987 to include municipal storm sewer systems, as well as industrial storm water, such as from construction sites [7].

1.3.2 Non–point Sources

Non–point source pollution refers to diffuse contamination that does not originate from a single discrete source. NPS pollution is often the cumulative effect of small amounts of contaminants gathered from a large area. Contaminated storm water washed off of parking lots, roads and highways, called urban runoff, is sometimes included under the category of NPS pollution.

However, this runoff is typically channeled into storm drain systems and discharged through pipes to local surface waters, and is a point source. However where such water is not channeled and drains directly to ground it is a non-point source. Highways, called urban runoff, are sometimes included under the category of NPS pollution [7].

Contaminated food and water are sources of illness in human body. Among various pollutants in the environment, heavy metals are directly related to health diseases in human [8, 9, 10].

The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years, because they are indestructible and most of them have toxic effects on organisms [11].

1.4 Statements of the Problem

Industrial waste discharges causes' excessive pollution in surface and underground water. The contamination of, for example ground water with heavy metals needs a threat to its quality and safety because the excessive content of heavy metals in ground water is associated with etiology of a number of diseases. In the study area which is in N/ Gondar around azezo kebele, the use of ground water has met the ever increasing water demand in the kebele and ground water in this kebele is the major source of drinking water. The study area of ground water is located in around Shinta River; it flows down to the study area through around the factory (Dashen Brewery and other industries). The researcher has a surmise that the ground water of the study area may be polluted with toxic metals because it is located in low land than that of the factory location. So it is necessary to determine toxic metals accumulation in aquatic environment, particularly in ground water, which is one of the major sources of drinking water in that area. Thus, there is the need to continuously assess the quality of ground and surface water sources.

1.5 Significance of the Study

The quality of drinking ground water changes in relation to chemical, physical and biological component of water. Knowledge of the free metals in water is essential to understand the role nutrient and the pollutant elements [12]. The effect of some metal ranges from beneficial to highly toxic, depending on their concentration in water. Peoples living in the study area of this work have been using ground water as a major source of drinking water. Therefore, the investigation of trace metals such as Pb and Cd in drinking ground water plays a special importance to avoid/reduce health hazards.

1.6 Objective of the Study

1.6.1. General Objective

- The main objective of this study is to determine the concentration of toxic metals (Pb and Cd) in ground water.

1.6.2 Specific Objectives
- To compare the concentration of lead and cadmium in the selected area of ground water sample with that set by WHO.
- To investigate the effect of parameters (frequency, amplitude, deposition time and step potential) on the peak current of Pb and Cd.
- To compare the contamination level of the ground water at the two study sites.

2. LITERATURE REVIEW

2.1 Heavy Metals

Metals are elements, present in chemical compounds as positive ions, or in the form of cat-ions (+ ions) in solution. Metals, which have a high atomic weight and a density (at least 5 times) than water, are known as heavy metals. Knowledge of free metal in ground water is very much helpful in understanding the role of pollutant and nutrient elements [12].

Heavy metals enter the environment by natural and anthropogenic means. Such sources include: natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents and pest or disease control agents applied to plants, air pollution fallout [13]. Among environmental pollutants, metals are of particular concern due to their potential toxic effect and ability to bio accumulates in aquatic ecosystems [3]. Heavy metals are grouped within the category of environmental toxins and the investigations of these toxic heavy metals such as As, Cd, Cr, Hg, Ni, Pb, Sb, and Se, Fe, Mn, Cu, Zn, Co, Ba, and Ag, place special importance on environmental samples [14, 15].

2.1.1 Chemistry of Lead and Cadmium

2.1.1.1 Lead

Lead (Pb) has an atomic number of 82 and atomic mass of 207.2. It is the heaviest non-radioactive metal that naturally occurs in substantial amounts in the earth's crust. Lead has two oxidation states Pb^{2+} and Pb^{4+}. Pb^{2+} dominates environmental chemistry. There is a great similarity in the ionic sizes of Pb^{2+} and Ca^{2+} such that Pb^{2+} may proxy for Ca^{2+} [16]. It is a bright and silvery metal with a very slight shade of blue in a dry atmosphere. It has a density of 11.34 g/cm^3, melting point of 327.46 ˚C and a boiling point of 1749 ˚C.

2.1.1.2 Cadmium

Cadmium has an atomic number 48 and relative atomic mass of 112.40. It has an estimated half-life of between 15 and 1100 years implying that it is a long-term problem in humans [16]. It is a silvery grey solid in nature at 298 k. It has a density of 8.65 g/cm^3, melting point of 320.9 ˚C and a boiling point of 767 ˚C at 100 kPa.

2.1.2 Source of Lead and Cadmium

2.1.2.1 Sources of Lead

There is lead in a car battery , ceramics, juices in cans, cigarette ashes, car exhaust, leaded gasoline, hair color, insecticides, mascara eyelash, snow, alloy solder, to paint, city water or well, wine and pipes [17].

2.1.2.2 Sources Cadmium

There is cadmium in dental alloys, batteries, engine oil, seafood, ceramics, smoke, tea and coffee, fertilizers, Soldering Alloy, Galvanized pipe, water pipes or wells, Welding electrodes, smoke from burning tires plastics and no grains and bran [18].

2.1.3 Toxicity of Cadmium and Lead

Heavy metals like Lead and cadmium don't have any useful biological role and they are considered among the most important contaminants of the environment and are highly toxic even at relatively low concentration [19].

The toxicity of these metals has two main aspects: (a) the fact that they have no known metabolic function, but when present in the body they disrupt normal cellular processes, leading to toxicity in a number of organs; (b) the potential, particularly cadmium and lead, to accumulate in biological tissues, a process known as bioaccumulation. This occurs because the metal, once taken up into the body, is stored in particular organs, for example the liver or the kidney, and is excreted at a slow rate compared with its uptake. This process of bioaccumulation of metals occurs in all animals, including food animals such as fish and cattle as well as humans. It is therefore necessary to control the levels of these toxic metals in foodstuffs in order to protect human health [20].

2.1.3.1 Lead Metal Contamination and Toxicity to Human Beings

Short-term exposure to high levels of lead can cause brain damage, paralysis (lead palsy), anemia and gastrointestinal symptoms. Longer-term exposure can cause damage to the kidneys, brain, red blood cell, reproductive and immune systems in addition to effects on the nervous system [20]. The most critical effect of low-level lead exposure is on intellectual development in young children and it crosses the placental barrier and accumulates in the fetus. Excessive lead accumulation in children is known to cause hyperactivity, a reduced intelligence and anti-social

behavior. Traditional sources of lead poisoning such as paint flakes and home dirt are usually ingested by small children at an age when iron deficiency is very common. Consumption of food containing lead is the major source of exposure for the general population [19, 20].

 An estimated 99% of the Pb that enters the adult human body and 33% that enters a child's body are excreted in about two (2) weeks. As a result of this, Pb poisoning is of much concern in children because they are susceptible to developmental delays secondary to Pb toxicity [21]. There is substantial evidence that a high Pb level in the environment could affect blood Pb level, intelligence and behavior. Pb poisoning in young children may cause permanent damage to the central nervous system and reduces intellectual capabilities. It also causes high blood pressure and hypertension in adults [22].

2.1.3.2 Cadmium Metal Contamination and Toxicity to Human Beings

The principal toxic effect of cadmium is its toxicity to the kidney, although it has also been associated with lung damage and skeletal changes in occupationally exposed populations [20].

Cadmium poisoning is known to cause liver damage, kidney failure, and pulmonary diseases. Cadmium also appears to be a contributing factor in high blood pressure, bone diseases, anemia, pulmonary fibrosis, prostates cancer, lung cancer, and yellow discoloration of the front teeth near gum line. The mechanism of cadmium poisoning my involve substitution insertion of cadmium in place of zinc in enzymes [23].

Acute doses (10-30 mg/kg per day) of Cd can cause severe gastrointestinal irritation, vomiting, diarrhea and excessive salivation, and doses of 25 mg/kg body weight can cause death [21]. The excessive content of a metal like Cd in food is associated with etiology of a number of diseases, especially with cardiovascular, kidney, nervous as well as bone diseases [24]. Cd increases in content with age and is estimated to peak at 40 mg in the human body at 50 years of age [22].

2.2 Review of Some Methods Used For Metal Analysis in Ground Water

Atomic Absorption Spectrophotometer (AAS) technique has been widely accepted as the standard technique for metals determination since they offer satisfactory sensitivity and fairly low acquisition cost [26, 27]. However, the majority of equipments can measure only one element at a time. Inductively coupled plasma optical emission spectrometry (ICP-OES), on the other hand, offers multi-element analysis [26, 28]. But this technique is not yet extensively used due to their high implementation and maintenance costs [26]. These constraints justify the search for improved methods and suggest that the electrochemical analytical method for metal ions is still indispensable. Some advantages of electrochemical analytical methods can be pointed out for the analysis of metal ions such as high sensitivity, selectivity, simultaneous de- termination, simplicity and relatively low cost[26,29]. Anodic stripping voltammetry (ASV) is an established method for trace metal ion analysis in contaminated water samples. ASV involves a two-step measurement sequence: (i) electro-reducing the ions at a negative potential to form metal deposits on the electrode surface, there by pre concentrating the analyte, and (ii) selectively electro-oxidizing each metal during a slow potential scan toward positive potentials [30]. The method, when coupled with an appropriate electrode material, generally provides low detection limits for many metal ions with a wide linear dynamic range and good response precision.

In the present study, an electrochemical technique called square wave anodic striping voltammetry (SWASV) was used for the determination of Cd and Pb in ground water that are the major source drinking water in the study area.

2.3 Electrochemical Techniques

Voltammetry belongs to a class of electrochemical methods which can be used to study solution composition through current-potential relationships at the electrode surface. The potential is varied in some systematic manner to cause electroactive chemical species to be reduced or oxidized at the electrode. This produces a current (I) that is proportional to the concentration of chemical species. This resulting current potential plot is known as a voltammogram [31, 32].

The common characteristic of all voltammetric techniques is that they involve the application of a potential (E) to an electrode and the monitoring of the resulting current (i) flowing through the electrochemical cell. In many cases the applied potential is varied or the current is monitored

over a period of time (t). Thus, all voltammetric techniques can be described as some function of E, i, and t. They are considered active techniques (as opposed to passive techniques such as potentiometer) because the applied potential forces a change in the concentration of an electro active species at the electrode surface by electrochemically reducing or oxidizing it.

The analytical advantages of the various voltammetric techniques include excellent sensitivity and selectivity with a very large useful linear concentration range for both inorganic and organic species (10^{-12} to 10^{-1} M), fast response, as well as simplicity of the analytical procedure, low cost, a large number of useful solvents and electrolytes, and simultaneous determination of several analyte. That is why; they are applied to the qualitative and quantitative assessment of food additives, ingredients and contaminants [33, 14, 35].

The electrochemical cell, where the voltammetric experiment is carried out, consists of a working (indicator) electrode, a reference electrode, and usually a counter (auxiliary) electrode.

In general, an electrode provides the interface across which a charge can be transferred or its effects felt. Because the working electrode is where the reaction or transfer of interest is taking place, whenever we refer to the electrode, we always mean the working electrode. The reduction or oxidation of a substance at the surface of a working electrode, at the appropriate applied potential, results in the mass transport of new material to the electrode surface and the generation of a current. Even though the various types of voltammetric techniques may appear to be very different at first glance, their fundamental principles and applications derive from the same electrochemical theory [36, 37].

2.3.1 Voltametric Measurement

2.3.1.1 Electrode Used In Voltametric Techniques

Voltametric techniques make use a three electrode system: working electrode, reference electrode and auxiliary electrode. The whole system consists of voltametric cell with various volume capacities and blanking the electrolyte solution.

A. Working Electrode

Working electrode is an electrode where the redox reaction of electro active species takes place and where the charge transfer occurs. It is made of several materials and performance of voltammetry is strongly influenced by the working electrode.

Electrochemistry properties of an ideal electrode consists of properties like high electrical conductivity, hard and durable, homogeneous micro structure throughout the bulk, reproducible physical, chemical and electronic properties, good chemical inertness, low and stable back ground current[38].

Carbone electrode: - carbon exists in various conducting forms, electrochemical reaction are normally slower at carbon than metallic electrodes, the electron transfer kinetics being dependent on the nature and surface preparation. Carbon has a high surface activity, which explains its susceptibility to poisoning by organic compounds. Bonds with hydrogen, hydroxyl and carboxyl groups and sometimes quoin ones can be formed at the carbon surface. The presence of these groups signifies that the behavior of these electrodes can be pH sensitive.

Various types of carbon are used as electrode. In 1958, R.N. Adams discovered a new type of electrode by using a mixture of carbon powder with a liquid non-electro active binder and called it as carbon paste. His original idea was to develop a dropping carbon electrode (DCE) that could be constructed similarly like the drooping mercury electrode (DME). Although practical experiments with DCE failed, the mixture of carbon powder and a binder prepared in thicker consistency was presented as a new type of electrode material [39].

Binary Mixtures prepared from carbon powder and organic liquid of non electrolytic character are known as bare or virgin or plain or unmodified carbon pastes [39]. As non electrolytic binders paraffin oils are commonly used. These non polar pasting liquids should be chemically inert, insulating, nonvolatile, water immiscible and forming paste mixtures of fine consistency [39]. Silicone oils also represent common type of pasting liquids, especially when the problem of paraffin oils vulnerability in media with organic solvents is considered. Another group of binders is some liquid organophosphates. Their attractive property is a high ion-pairing ability [39]. The electric conductor in carbon pastes is graphite powder with micrometric particles.

Carbon paste electrodes offer an easily renewable surface, low cost and very low background currents especially in the anodic region [39]. A disadvantage of carbon pastes is the tendency of the organic liquid binder to dissolve in solutions containing an appreciable fraction of organic solvents. And also, the conventional paste mixtures from spectroscopic graphite powder and

paraffin oil suffer from interferon's when being polarized cathodically, and consequently they have been used mainly for the determination of easily oxidizable organic compounds [39].

B. Reference Electrode

It is used to give a value of potential to which the working electrode potential can be referred in terms of the potential difference. The potential can only be registered as difference with respect to a choose reference value. Thus, a good reference electrode needs to have a potential that is stable with time and with temperature and not alerted by perturbations to the system. There are three types of electrode, standard hydrogen electrode (SHE), standard calomel electrode (SCE) and silver Ag/AgCl/ electrode.

Standard hydrogen electrode is a primary electrode used to define scale of standard potential in aqueous solution. The half-reaction potential of the electrode is 0.00 V at 25^oC. The electrode commonly consists of a platinum foil, the surface of which is able to catalyze the reaction.

$$AgCl_{(aq)} + 2e\text{-} \longleftrightarrow H_{2(g)} + H_2O \qquad\qquad E= +0.00\ V$$
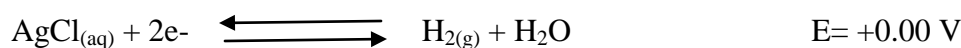
Silver /silver chloride/ is the most reproducible electrode next to hydrogen electrode. It is reliable and the most convenient electrode to construct and use. When prepared using a standard solution of KCl, the Ag/AgCl electrode has a potential of +0.197V at 25^oC. The Ag/AgCl electrode has the advantage of being useful at higher temperature.

$$AgCl(S) + e^- \longleftrightarrow Ag(S) + Cl^- \qquad\qquad E= +0.197\ V$$
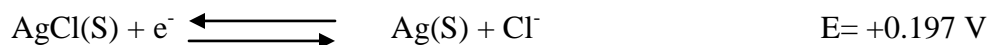
Standard calomel electrode /SCE/, which is constructed using an aqueous solution saturated with KCl, has a potential of +0.2444 V at 25^OC. A typical SCE consists of a paste of Hg/Hg_2Cl_2, and saturated KCl. The SCE has the advantage of constant concentration of Cl^- and the potential of the electrode remains constant even if the KCl solution partially evaporated remains constant even if the KCl solution partially evaporates. On the other hand, a significant disadvantage of the SCE is that the solubility KCl sensitive to a change in temperature. At higher temperature, the concentration of Cl^- increases and the electrodes potential decreases [40, 41].

$$Hg_2Cl_2 + 2e^- \longleftrightarrow 2Hg_{(l)} + 2Cl^- \qquad\qquad E= +0.2444\ V$$

C. Auxiliary Electrode

It is an electrode used in voltammetric system and its function is to complete the circuit and allowing charge to flow. This electrode does not need to have a constant or reproducible potential and usually made of an inert conducting material typically a platinum electrode wire,

graphite and mercury pool. It does not need special care, such as polishing. In order to need support current generated at working electrode, the surface area of the auxiliary electrode must be equal or greater than the working electrode.

2.3.1.2 Electrolyte

All electro chemical reaction and phenomena occurs in a medium, usually a solvent containing dissolved ions (often called supporting electrolyte) which are mobile and able to support current flow. The properties of this medium (the electrolyte) are critically important to any electro chemical experiment. A medium containing mobile ions must exist between electrodes in an electrochemical cell to allow for control and/or measurement of electrode potential in the cell, which is required in nearly all electrochemical experiments. A medium with good solvating power is needed to dissolve reactants and products for the electrode reaction, and the ones with reasonably low viscosity are often needed to allow for rapid transport of reactants and products to and from electrodes [42]. Supporting electrolyte is used to decrease the resistance of the solution, to eliminate electro migration effects, and to maintain constant ionic strength. The selection of electrolyte salt is from 100 to 1000 times that of the electrolyte and the minimum concentration of the analyte is usually 1.0 mM.

2.3.2 Cyclic voltammetry

Cyclic voltammetry (CV) offers a qualitative approach to study behavior of an electrochemical system. Cyclic voltammetry is often the first experiment performed in an electro analytical study. In particular, it offers a rapid location of redox potentials of the electro active species, and convenient evaluation of the effect of media upon the redox process [43].

 Its primary advantage comes from the fact that it gives insight into both the half-reactions taking place at the working electrode, providing at the same time information about the chemical or physical phenomena coupled to the studied electrochemical reaction. In cyclic voltammetry, starting from an initial potential E_i, a staircase potential sweep (or linear sweep in older Potentio states) is applied to the working electrode. After reaching a switching potential E_f, the sweep is reversed and the potential returns to its initial value [44]. Cyclic voltammetry is carried out in quiescent solution to ensure diffusion control. The important parameters in a cyclic voltammogram are the peak potentials (Epc, Epa) and peak currents (ipc, ipa) of the cathodic and anodic peaks, respectively. If the electron transfer process is fast compared with other processes

(such as diffusion), the reaction is said to be electrochemically reversible, and the peak separation is

$$\Delta E_P = |E_{Pa} - E_{Pc}| = \frac{2.303RT}{nF} \quad \text{-----------------------------------1}$$

Where n is the number of electrons transferred and E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively, in Volts. Thus for a reversible redox reaction at 25 ^{0}C with n electrons ΔE_p should be 0.0592/nV or about 60 mV for one electron.

The formal reduction potential (E^0) for a reversible couple is given by the formal reduction potential (E^0) for a reversible couple is given by

$$E^0 = \frac{E_{pa} - E_{pc}}{2} \quad \text{--2}$$

Randles-Sevcik equation is an equation that correlates the peak current (Ip) with concentration (C), I_p = k C, where k is a constant that includes different cell parameters such as transfer coefficient, number of electrons involved in the reaction, electrode area, diffusion coefficient and scan rate.

$$i_p = 2.69x10^5 n^{3/2}ACD^{1/2}v^{1/2} \quad \text{----------------------------------3}$$

where i_p is the peak current in ampere, A is the electrode area (cm^2), D is the diffusion coefficient (cm^{2}s^{-1}), C is the concentration in mol cm^{-3}, n is the number of the electrons exchanged and v is the scan rate in V S^{-1} [34].

2.3.3 Stripping Voltammetry

Voltammetric stripping analysis is a powerful technique in quantifying trace levels of organic and inorganic species, especially metals. Its high sensitivity is attributed to a combination of effective pre-concentration methods and high signal-to-noise ratio measurement techniques [45].

The three most commonly used variations are anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), and adsorptive stripping voltammetry (AdSV).

Even though ASV, CSV, and AdSV each have their own unique features, all have two steps in common. First, the analyte species in the sample solution is concentrated onto or into a working electrode. It is this crucial pre concentration step that results in the exceptional sensitivity that can be achieved. During the second step, the pre concentrated analyte is measured or stripped

from the electrode by the application of a potential scan. Any number of potential waveforms can be used for the stripping step (that is, differential pulse, square wave, linear sweep, or staircase). The most common are differential pulse and square wave due to the discrimination against charging current.

However, square wave has the added advantages of faster scan rate (speed), increased sensitivity and the square-wave currents are 4 and 3.3 times higher than relative to differential pulse [35].

Anodic Stripping Voltammetry (ASV) is most widely used for trace metal determination and has a practical detection limit in the part per-trillion range. This low detection limit is coupled with the ability to determine simultaneously four to six trace metals using relatively inexpensive instrumentation. Metal ions in the sample solution are concentrated into a working electrode during a given time period by application of a sufficient negative potential. These concentrated metals are then stripped (oxidized) out of the working electrode by scanning the applied potential in the positive direction. The resulting peak currents, i_p, are proportional to the concentration of each metal in the sample solution, with the position of the peak potential, Ep, specific to each metal. With more than one metal ion in the sample, the ASV signal may sometimes be complicated by formation of inter metallic compounds, such as Zn and Cu. This may shift or distort the stripping peaks for the metals of interest. These problems can often be avoided by adjusting the deposition time or by changing the deposition potential [46].

Cathodic Stripping Voltammetry (CSV) is used to determine many of organic and inorganic compounds that forms insoluble salts with electrode material. It involves positive deposition of the analyte when anodic potential is applied to the working electrode followed by stripping in a negative-going potential scan [35].

Adsorptive Stripping Voltammetry (AdSV) is quite similar to anodic and cathodic stripping methods. The primary difference is that the pre concentration step of the analyte is accomplished by adsorption on the electrode surface or by specific reactions at chemically modified electrodes rather than accumulation by electrolysis [34].

2.3.4 Pulse Methods

The deposition of potential pulse to the electrode leads to in most experimental situations to a considerable improvement (increase) in the ratio of the charging and faradic currents compared to linear scan voltammetry. This is because the faradic current usually decreases with $1/t^{1/2}$ while

the charging current decreases much faster. In consequence, decreased lower limits of detection are obtained [34, 47].

2.3.4.1 Normal pulse voltammetry (NPV)

This technique uses a series of potential pulses of increasing amplitude. The current measurement is made near the end of each pulse, which allows time for the charging current to decay. It is usually carried out in an unstirred solution. The potential is pulsed from an initial potential E_i. The duration of the pulse is usually 1 to 100 ms and the interval between pulses is typically 0.1 to 5 sec. The resulting voltammogram displays the sampled current on the vertical axis and the potential to which the pulse is stepped on the horizontal axis [5, 34]

2.3.4   Differential Pulse Voltammetry (DPV)

In DPV the potential is changed from an initial potential in small steps (2–5 mV) and a voltage pulse of a short duration (50 ms) is superimposed at the end of a long step (500–5000 ms). The current is sampled before the beginning of the pulse and near the end of the pulse [48]. Differential-pulse voltammetry is an extremely useful technique for measuring trace levels of organic and inorganic species. The current is sampled twice, just before the pulse application and again late in the pulse life (after~40 ms, when the charging current has decayed). The first current is instrumentally subtracted from the second, and this current difference [$\Delta i = I(t_2) - I(t_1)$] is plotted versus the applied potential.

The peak potential (E_p) can be used to identify the species, as it occurs near the polarographic half-wave potential:

$$E_P = E_{1/2} - \Delta E/2$$ ---4

Where $E_{1/2}$ is half peak potential ΔE is the pulse height [7].

The advantage of DPV is the reduction in capacitance current realized by taking the current difference over a small potential change. The increase in faradic/charging ratio is manifested in a lower detection limit of 10^{-8} M of redox species for a reversible couple in a suitable supporting electrolyte. The sensitivity of DPV can be increased by increasing the voltage pulse, however, with some decrease in resolution.

2.3.5   Square-Wave Voltammetry (SWV)

Square-wave voltammetry is a large-amplitude differential technique in which a waveform composed of a symmetric square wave, superimposed on a base staircase potential, is applied to the working electrode. A potential, consisting of symmetrical square-wave pulses superimposed on a staircase-wave form is applied to the working electrode. The current is sampled twice during each square-wave cycle, once at the end of the forward pulse and once at the end of the reverse pulse. The difference between the two measurements is plotted versus the base staircase potential. The peak height is directly proportional to the concentration of the electro active species and direct detection limits as low as 10^{-8} M is possible [49].
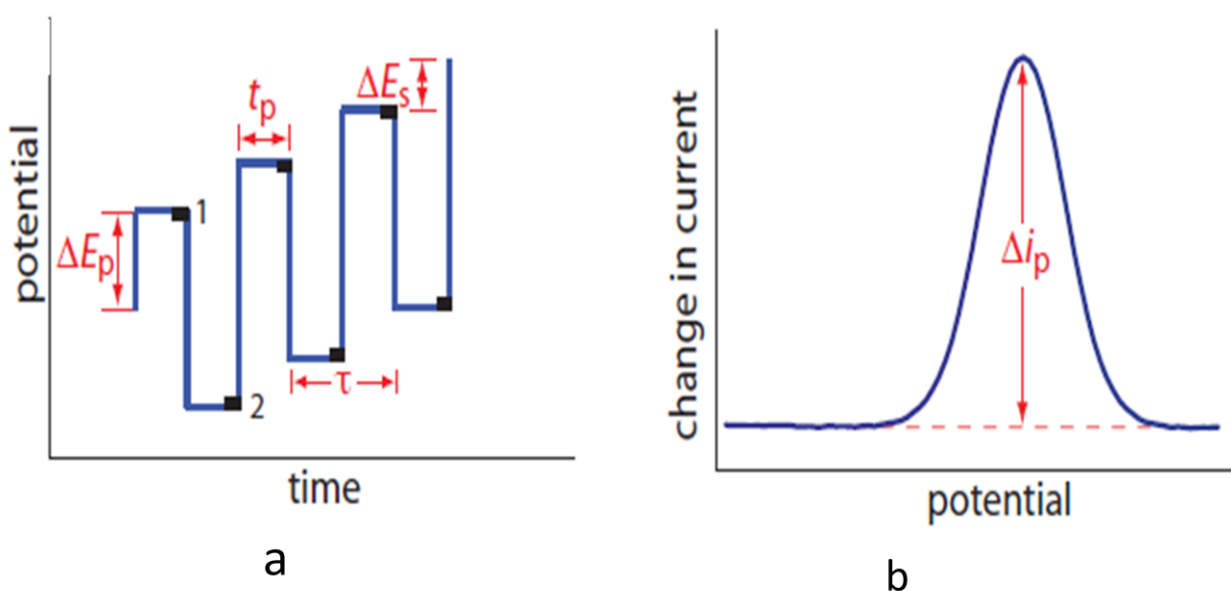
Figure 2.1: Excitation waveform of Square-Wave voltammetry (a), voltammogram (b)

Square-wave voltammetry has several advantages. Among these are its excellent sensitivity, speed and the rejection of background currents.

Applications of square-wave voltammetry include the study of electrode kinetics with regard to proceeding, following, or catalytic homogeneous chemical reactions, determination of some species at trace levels, and its use with electrochemical detection in HPLC [35].

Most Important Parameters in Square Wave Voltammetry includes:

    i. **Square Wave Frequency**

An increase in square wave frequency results in an increase in the scan rate which in turn increases the peak current. However, at very high frequency, the peak current may become unstable and be obscured by a large residual current. On the other hand very low frequency gives a low but narrow signal, and increases the total analyses time. Hence, the selection of frequency usually requires a compromise among sensitivity, resolution and speed [34].

ii. Square Wave Amplitude

In square wave voltammetry, the peak currents usually increase with increasing amplitude. However, the width of the peak also increases as the square wave amplitude grows larger and normally one refrains from increasing the square wave amplitude, because resolution may be degraded unacceptably [34].

iii. Square Wave Step Potential

The square wave voltammetric peak current usually increases as the step potential increases with an accompanying peak broadening. At higher step heights, too few points are sampled, thus affecting the reproducibility of the detection [34].

2.4. Carbon Paste Electrode

Carbon paste electrodes (CPEs) belong to promising electrochemical or bio-electrochemical sensors of wide applicability. CPEs are widely applicable in electrochemical studies due to their low background current (compared to solid graphite or noble metal electrodes), long-time stability, low cost, easy preparation, simple renewal of their surface (providing a fresh surface unaffected by electrode history), individual polarizability, easy to apply modifications (suitable for preparing an electrode material with desired composition) and possibilities of miniaturization. The disadvantage of CPE is the tendency of the organic binder to dissolve in solutions containing an appreciable fraction of organic solvent [35].

2.5. Analytical parameters

2.5.1. Limit of detection (LOD)

Limit of detection or detection limit, is the lowest concentration level that can be determine to be statistically different from a blank [50].

$$LOD = 3 \ S/m \quad \text{-- (5)}$$

2.5.2. Limit of quantification (LOQ)

Limit of quantification or lower limit of quantification is the level above which quantitative results may be obtained. The LOQ is mathematically defined as equal to ten times the standard deviation of the results for a series of replicates used to determine a justifiable limit of detection. Limit of quantification are matrix, method, and analyte specific [51].

$LOQ = 10S/m$ --- (6)

2.5.3. Percent Recoveries

One of the drawbacks of the method detection limit is that it doesn't take in to account the effect of high or low bias in a serious of measurements. Bias can be measured by the average percent recovery of a serious of samples. In order for the method detection limit to be realistic, the average percent recovery for the sample should be reasonable [50].

% recovery= <u>spiked - unspiked result</u>   x 100------------------------------------- (7)

Analyte

The recovery of analyte in an assay is the detector response obtained from an amount of analyte added to and extracted from biological matrix, compared to the detector response obtained for the true concentration of the pure authentic standard.

3. EXPERIMENTAL PART

3.1 Chemicals Used

The chemicals used for the analysis of lead and cadmium in ground water were concentrated HNO_3, Pb $(NO_3)_2$ (blulux), Cd $(NO_3)_2.4H_2O$ (blulux), Na_2HPO_4 (blulux), $NaH_2PO_5.4H_2O$ (blulux), NaOH (blulux), graphite powder (blulux), paraffin oil (carelabmed), and HCl (blulux).

3.2. Apparatus

Voltammetric determination of lead and cadmium were performed in electrochemical analyzer with three electrode system consisting of carbon paste working electrode (CPE: 3 mm in diameter and 7mm in depth), platinum wire auxiliary electrode and Ag/AgCl reference electrode. Whitman filter paper was used for filtrate collected water sample. Adwa digital pH meter (model AD8000) with glass electrode was used to measure pH of supporting electrolyte solution. 1000 ml volumetric flask and Plastic bottle (high density polyethylene bottle, HDPE) of 500 ml and 1000 ml were used for sampling. Candy stick (1 ml size) was used for preparation of modified carbon past electrode. Micro pipette was used for standard addition of stock solutions.

3.3 Electrolytic Cells and Electrodes

This work was performed using a three-electrode system with a one-compartment glass voltammetric cell, an Ag/AgCl reference electrode, platinum wire as an auxiliary electrode and carbon paste electrode (CPE) as working electrode.

Figure 3.2:- A Complete Cell Stands For Electro-Analytical Techniques (photo)

3.4. Preparation of Working Electrodes

Unmodified carbon paste (100 mg) was prepared by mixing 7 g graphite powder with 3.53 ml paraffin oil. The compositions of the paste were 75 % (w/w) graphite powder and 25 % (w/w) paraffin oil. The mixture was homogenized with mortar and pestle for 30 minutes and allowed to rest for 24 hours. The homogenized paste was packed in to the tip of a candy stick (3 mm diameter, 6.5 mm deep). A copper wire was inserted from the backside of the candy stick to provide electrical contact. Then the surface of the electrode was smoothed using a smooth white paper with a light manual pressure until a shiny surface is emerged.
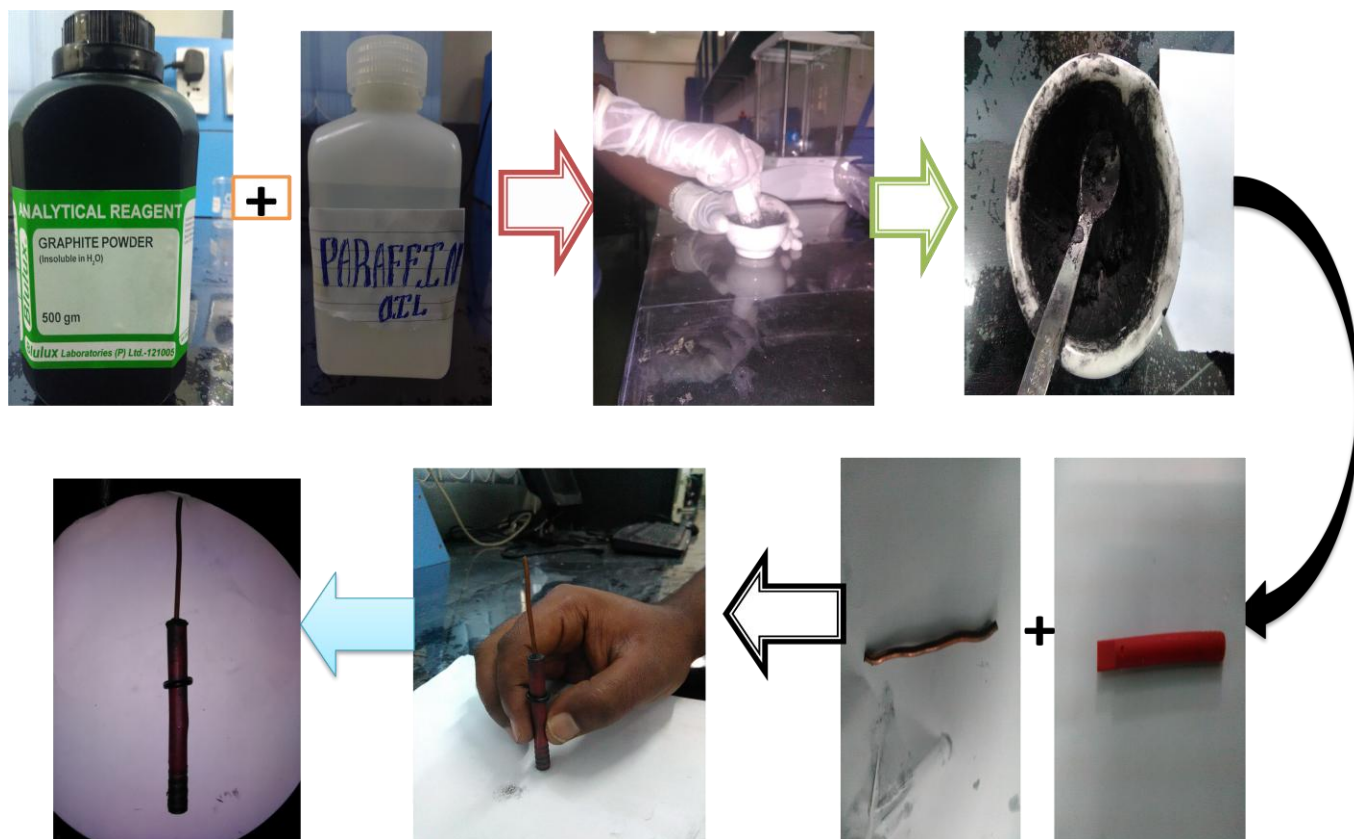
Figure 3.3: Carbon Paste Electrode Preparation Process

3.5 Preparation of Stock Solutions

3.5.1. Analyte Stock Solution

Lead (Pb^{2+}): 1.599 g of Pb(NO$_3$)$_2$ was dissolved in 80 ml of distilled water and finally the solution was dilute to the mark of 1000 ml volumetric flask. 1 ppm, 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm solutions were prepared by dilution.

Cadmium (Cd^{2+}): 2.744 g of Cd (NO$_3$)$_2$.4H$_2$O was dissolved in 80 ml of distilled water, and finally the solution was dilute to the mark of 1000 ml volumetric flask. 1 ppm, 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm were prepared by dilution.

The prepared stock solutions were containing 1000 ppm (mg/l) of the targeted metal ions. Standard solutions were prepared by series of dilutions of the stock solutions daily.

3.5.2   Electrolyte Stock Solution

Supporting electrolyte of 0.1 M of phosphate buffers ($NaH_2PO_4.2H_2O$ –Na_2HPO_4.) in the pH-2 was prepared from 0.1 M $NaH_2PO_4.2H_2O$ and 0.1 M Na_2HPO_4 in distilled water. The pH of the solutions were adjusted by adding drops of concentrated HCl and NaOH and pH value was adjusted from pH 2-11 with HCl and sodium hydroxide.

3.6 Description of the Study Area

Azezo is found in Amhara Regional State in north Gondar Zone. It is situated at $12^0 33$' (12.55^0) north to $37º25'32''$ (37.4256^0) longitude east. Altitude is 2,055 meters above sea level and is predominantly classified as Woina-Dega.

The study area is one of the industry zones. Among various industries in the study area of N/Gondar: Dashin brewery, Gondar plastic and ceramic fabric are major producer of heavy metals. Besides of this there are Garages and car wash. The area gets much of the flood water from Shinta River that accumulates around Angereb River. Around this study area there are ground waters that are used for drinking and house hold purposes. The rivers bring industrial wastes like heavy toxic metals from industry that they discharge their wastes to the river and some sinking down underground the earth and some are accumulates Angereb River.

Figure 3.4: Azezo Map Area Showing Sampling Sites (Google map)

3.7 Sampling and Sample Preparation

3.7.1 Sampling

3.7.1.1. Sample Collection:

The ground water samples were collected by following standard sample collection protocol and guidelines given [52, 53]. Special precautions are taken during the collection of samples. Before collecting the samples, the sample containers were soaked overnight in 2% nitric acid and washed with distilled water and dried in clean metal free area. At each sampling location, water samples were collected in two pre-cleaned containers for duplicate measurement. The bottles were rinsed three times with the ground water sample of the particular location and collected the final sample to avoid the contamination and 0.5 ml of Supra pure grade nitric acid was added to acidify the samples and also to prevent the loss of metals. All the collected ground water samples were preserving at 4 ^{o}C by using Lec refrigerator (refrigeration plc England). The details of sampling locations were summarized in table 3.1.

Table -3.1 DETAILS OF SAMPLING LOCATIONS:

LOCATION CODE	LOCATION NAME
GW-1	Azezo shinta kebele upper side of the factory.
GW-2	Azezo boyit kebele (below to the factory)

3.7.2 Sample Preparation

3.7.2.1. Sample Pre-Treatment

The collected water samples from different sample sites were filtered through a Whitman filter paper. The filtrates were acidified with concentrated nitric acid to bring the pH less than two; the acidification minimizes the adsorption of metals in to the walls of the container and to minimize changes of the physicochemical form of the metal [54].

3.7.3 Voltammetric Determination of Lead and Cadmium

To locate the oxidation and reduction for lead and cadmium, the cyclic voltammogram of 10 ppm lead and 10ppm cadmium solution were taken at various pH (1, 2, 3, 4, and 5). The potential windows were from -1.4 to 0.6 V and for lead 1, 2, 4, 6, 8 and 10 ppm of solution were prepared. The Pb and Cd were deposited by reduction on carbon paste electrode. The deposited Pb metal and cadmium metal were oxidized by scanning the potential from -1.4 to 0.6 V using square wave anodic stripping voltammetry. The voltammogram for samples and standard additions were recorded in similar manner.

The pH and other parameters were optimized for lead by taking 10 ppm of lead. The peak currents of metal in the sample, and after standard addition were recorded for calibration and quantification. The optimized parameter for lead was chosen for cadmium.

After optimization, 10 mL buffer and 10 mL real sample were transferred to an electrochemical cell and the resulting voltammogram was recorded.

4. RESULT AND DISCUSSION

4.1. Electrochemical Behavior of Lead and cadmium

4.1.1. Electrochemical Behavior of Lead

The electrochemical behavior of lead was studied using cyclic voltammetry in the potential window from -1.4 V to 0.6 V- at scan rate of 100 m V/s. The cyclic voltammogram of a 0.1 M phosphate buffer solution, figure 4.1-a, shows no detectable redox reaction takes place. A strong oxidation peak around a potential of -0.47 V was observed for a solution containing 10 ppm Pb^{2+} figure 4.1-b. But there is no well defined reduction peak.
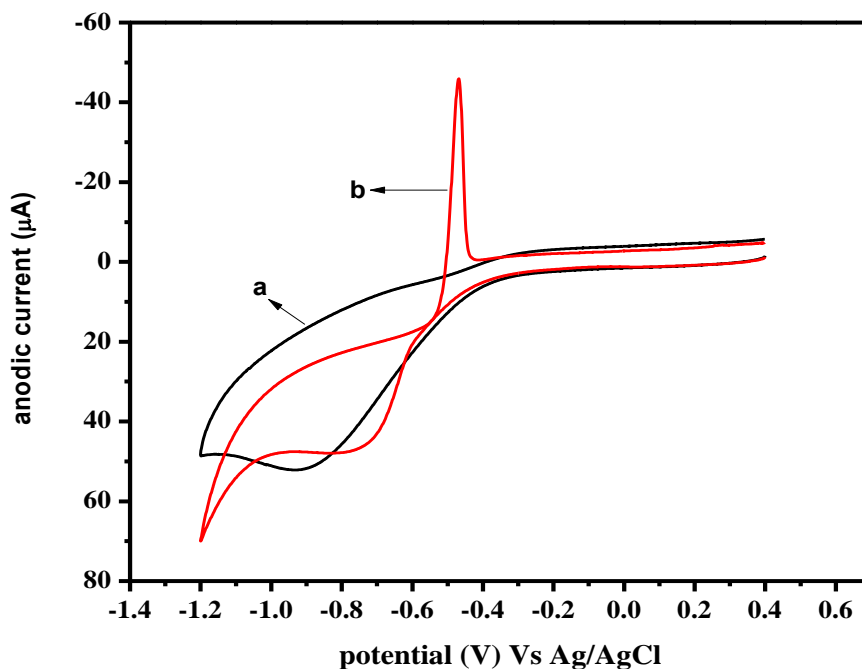

Figure 4.1: The cyclic voltammogram of (a) 0.1M phosphate buffer and (b) 10 ppm pb^{2+} at pH-2.

4.1.1.1. Effect of pH on Peak Current of Lead

To see the effect of pH on peak current, the cyclic voltammograms for 10 ppm lead solution was recorded at pH 1, 2, 3, 4, and 5. As can be seen from figure 4.2, varying the pH values of the supporting electrolyte would bring in different oxidation peak current responses of lead.
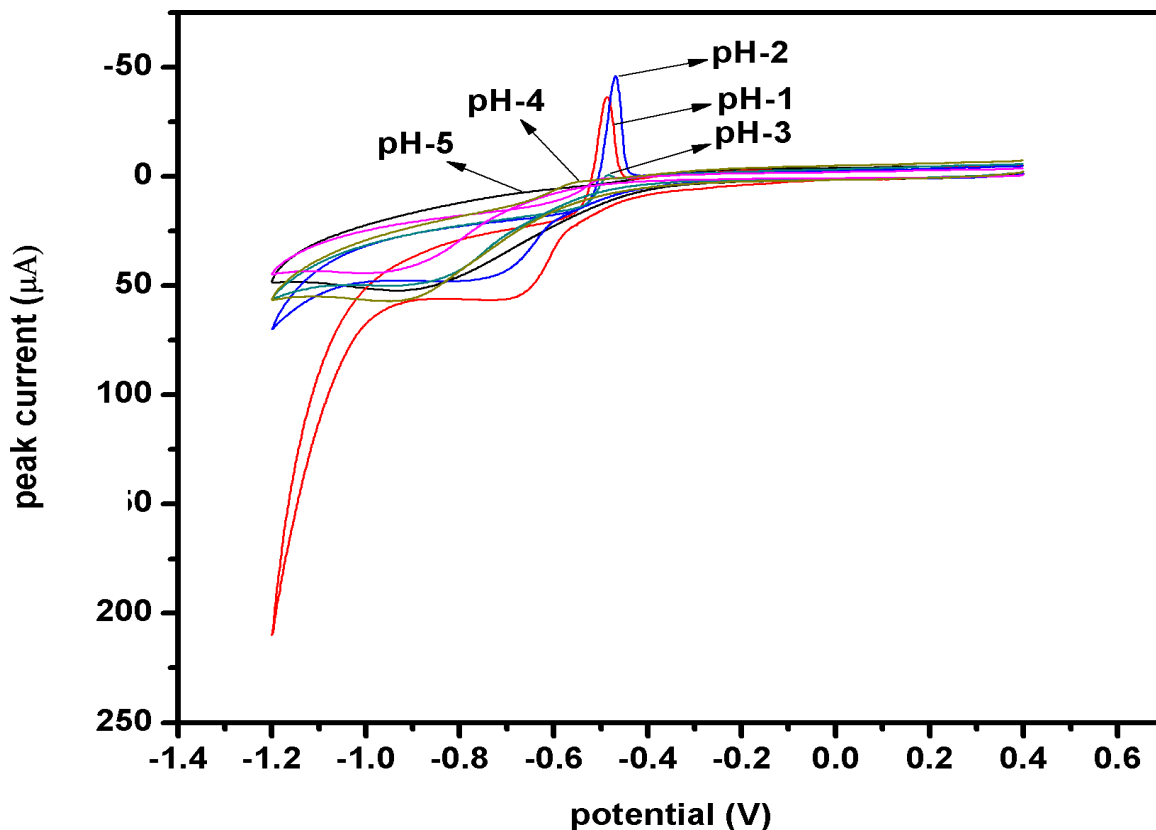
25

Figure 4.2: The Cyclic voltammogram of 10 ppm lead ion 0.1 M of phosphate buffer at pH of 1, 2, 3, 4 and 5.

Figure 4.3 shows the plot of oxidation peak current of the solution containing 10 ppm of Pb solution versus pH value of supporting electrolyte. It is observed from the figure that the oxidation peak current of lead metal increases sharply from pH value 1 to 2 and decreases when the pH value is further increased from 3 to 5. Hence pH-2 is used as the optimum value for this study.
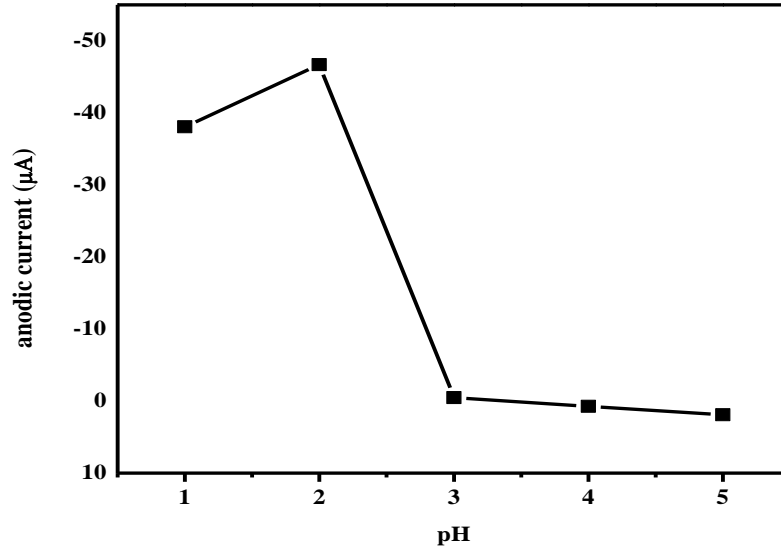
Figure 4.3: Plot of peak current Vs pH of 10 ppm Pb solution in 0.1 M phosphate buffer.

4.1.1.2. Effect of Scan Rate on Peak Current of Lead

The effect of scan rate on the cyclic voltammograms of lead in pH-2 of phosphate supporting electrolyte solution was studied. Fig. 4.4 shows the cyclic voltammograms of 10 ppm lead in pH-2 phosphate buffer solution. When the potential was scanned at different rate, under the same other experimental conditions, a linear relationship was observed between the peak current and the square root of the scan rate ($mV^{1/2}$). The peak current is proportional to flux of electroactive species towards the electrode. In a slow scan rate the diffusion layer will grow much farther from the electrode in comparison to fast scan and this makes flux to the electrode is smaller at slow scan rates than at faster rates. That is why peak current is directly proportional to scan rate.
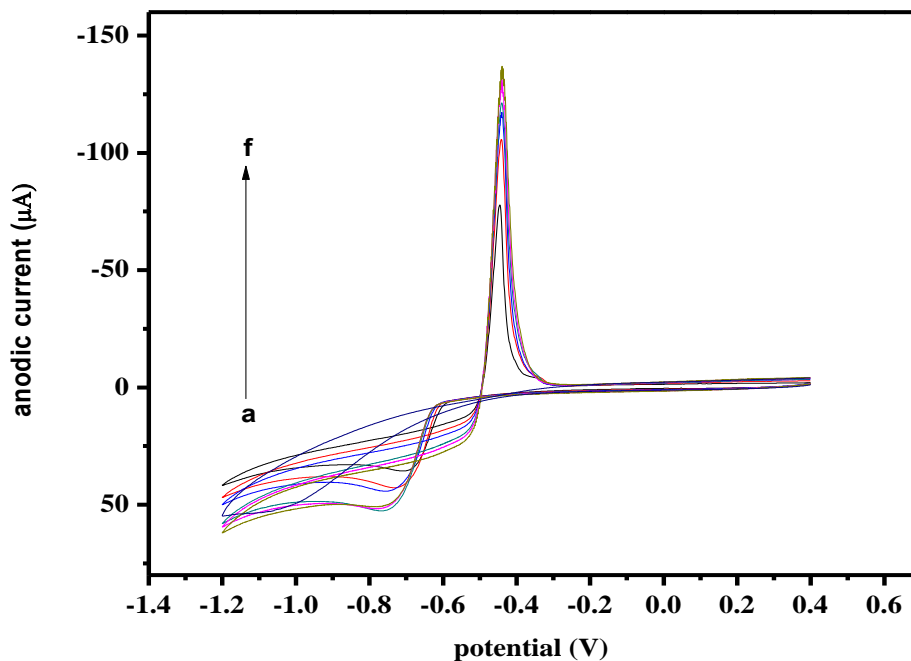
Figure 4.4: Cyclic voltammograms of carbon past electrode in pH-2 phosphate buffer solution containing 10 ppm Pb solution at various scan rates (a=25 mV/s, b=50 mV/s, c=75 mV/s, d=100 mV/s, e=125 mV/s, f=150 mV/s).

In order to investigate whether the oxidation process of lead metal at carbon past electrode is predominantly diffusion controlled the dependence of peak current on the scan rate and square root of scan rate was studied (fig. 4.5 and fig. 4.6 respectively). The peak current was more linearly dependent on the square root of scan rate (R^2=0.995) than on the scan rate (R^2=0.992) showing that the oxidation reaction of lead at carbon past electrode is predominantly diffusion controlled.
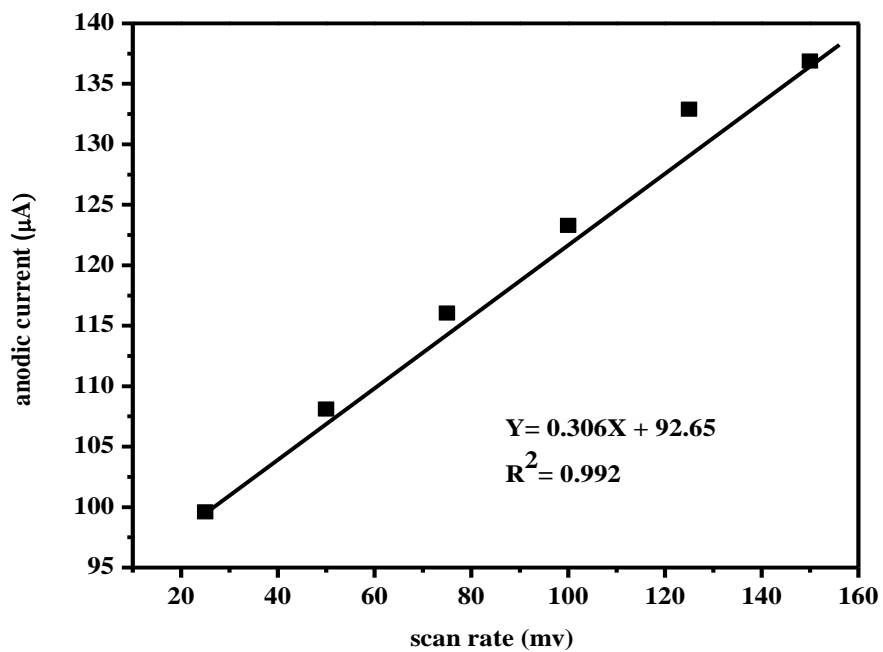
Figure 4.5: Plot of oxidative peak current 0f 10ppm lead solution in pH-2 phosphate buffer solution as a function of scan rate.
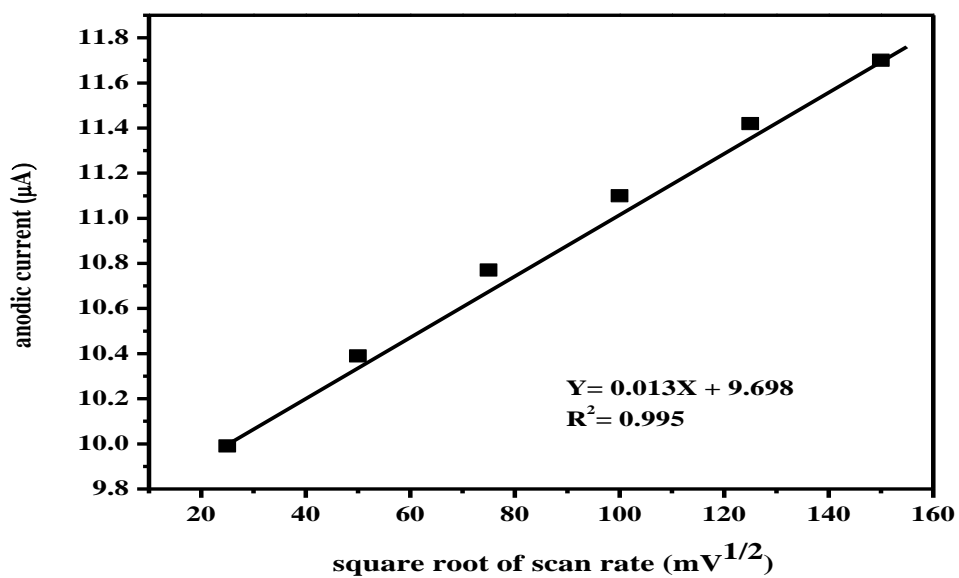

Figure 4.6: Plot of peak current versus square root of scan rate.

4.1.1.3. Effect of Scan Rate on Peak Current of Cadmium.

The effect of scan rate on the cyclic voltammograms of cadmium in pH-2 of phosphate supporting electrolyte solution was studied. Fig. 4.7 shows the cyclic voltammograms of 10ppm cadmium in pH-2 phosphate buffer solution. When the potential was scanned at different rate, under the same other experimental conditions, a linear relationship was observed between the peak current and the square root of the scan rate $(mV^{1/2})$. The peak current is proportional to flux of electroactive species towards the electrode. In a slow scan rate the diffusion layer will grow much farther from the electrode in comparison to fast scan and this makes flux to the electrode is smaller at slow scan rates than at faster rates. That is why peak current is directly proportional to scan rate.
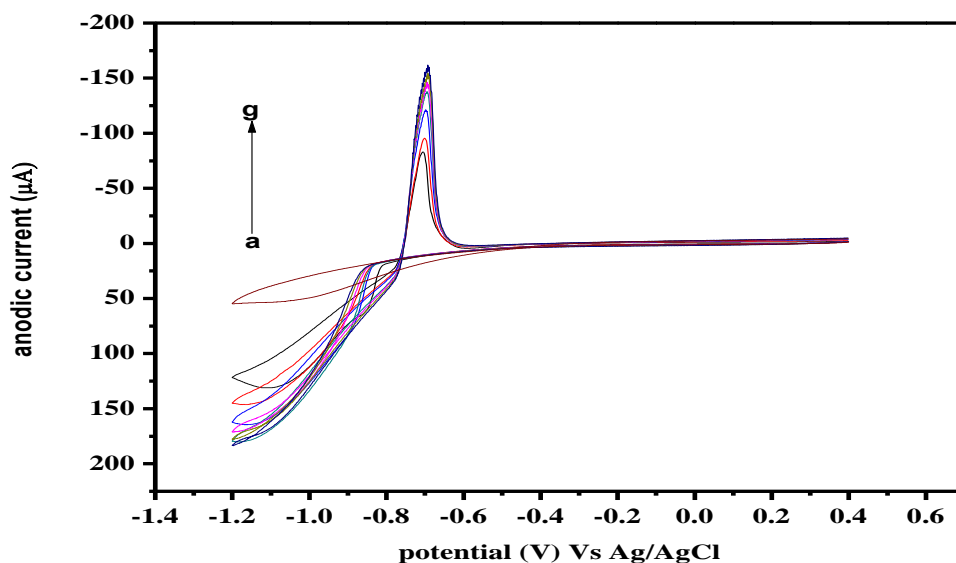
Figure 4.7: Cyclic voltammograms of carbon past electrode in pH-2 phosphate buffer solution containing 10ppm Cd solution at various scan rates (a=25 mV/s, b=50 mV/s, c=75 mV/s, d=100 mV/s, e=125 mV/s, f=150 mV/s, g=175 mV/s).

In order to investigate whether the oxidation process of Cd metal at carbon paste electrode is predominantly diffusion controlled, the dependence of peak current on the scan rate and square root of scan rate was studied(fig. 4.8 and fig. 4.9 respectively). The peak current was more

30

linearly dependent on the square root of scan rate ($R^2 = 0.993$) than on the scan rate ($R^2 = 0.990$) showing that the oxidation reaction of Cd metal at carbon past electrode is predominantly diffusion controlled.

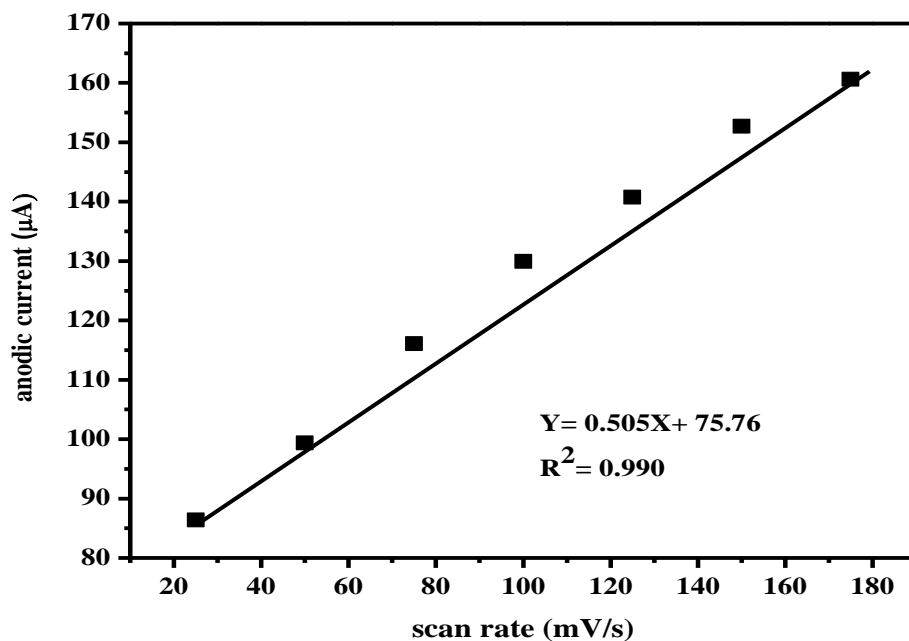$$Y = 0.505X + 75.76$$
$$R^2 = 0.990$$

Figure 4.8: Plot of oxidative peak current of 10 ppm Cd^{2+} in pH-2 phosphate buffer solution as a function of scan rate.

Figure 4.9 graph showing:
- y-axis: anodic current (μA), ranging from 9.0 to 13.0
- x-axis: square root of scan rate (mV$^{1/2}$), ranging from 20 to 180
- equation: y= 0.021x + 8.982
- R^2= 0.993
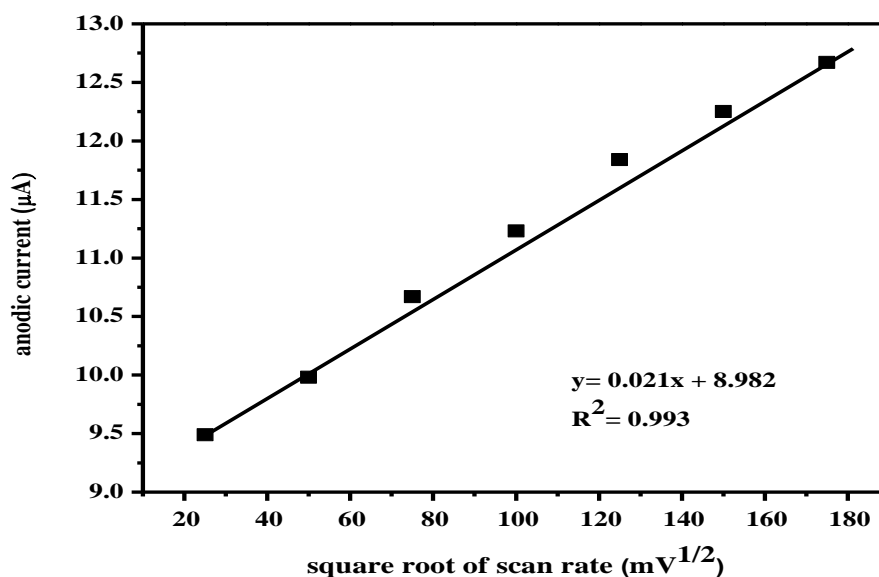
Figure 4.9: Plot of peak current versus square root of scan rate.

4.1.2 Square Wave Anodic Stripping Voltammetry

For the quantitative determination of lead and cadmium from N/Gondar two kebeles, namely shinta and boyit kebele, square wave anodic striping voltammetry was chosen as it is better in terms of peak intensity, effective discrimination against the charging background current, and very low detection limits (1×10^{-8} M) [50]. From figure 4.10 it is observed that the phosphate buffer gave no oxidation response whereas the anodic peak current was observed for 10 ppm Pb^{2+} and 10ppm Cd^{2+} solution in 0.1 M phosphate buffer at pH-2.

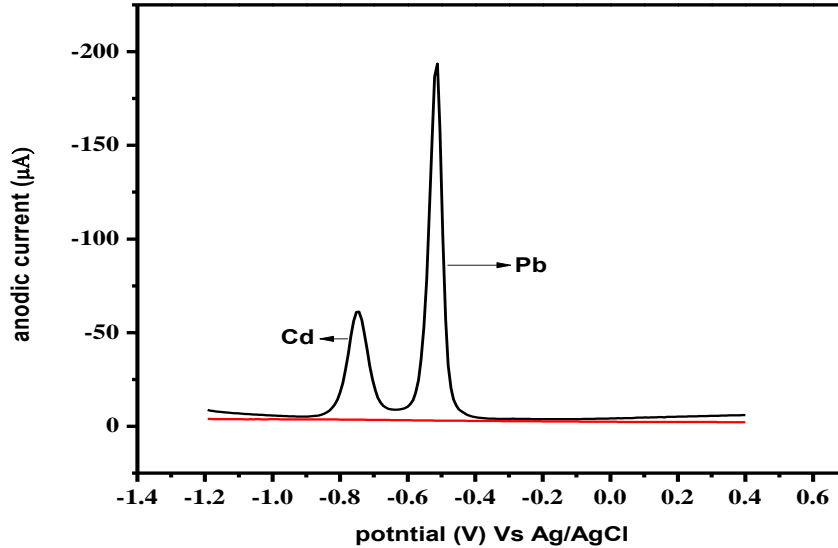**Figure 4.10:** square wave anodic stripping voltammogram of a) 0.1 M phosphate buffer and b) 10 ppm Pb^{2+} and 10 ppm Cd^{2+} solution in 0.1 phosphate buffers at pH-2.

The SWASV result shows a well-defined and symmetric anodic stripping peak current at peak potentials around −0.507 V and -0.744 V for lead and cadmium, respectively.

4.1.2.1 Optimization of Instrumental Parameters and Stripping Parameters

The effects of method parameters such as, accumulation potential, deposition time, step potential, amplitude and frequency on the peak current and peak potential of the 10 ppm lead ions were studied.

4.1.2.1.1 Effect of Frequency on peak current

To investigate the effect of frequency on peak current, SWAS voltammograms of 10 ppm Pb^{2+} at frequencies of 10 Hz, 15 Hz, 20 Hz, 25 Hz, 30 Hz, 35 Hz, 40 Hz, 45 Hz, and 50 Hz were recorded as shown in Figure 4.11.
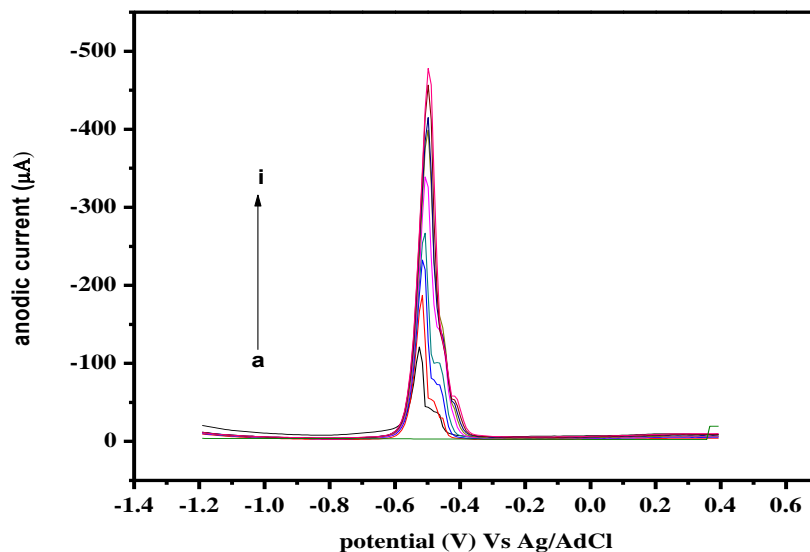
Figure 4.11: SWAS Voltammogram of 10 ppm Pb^{2+} in 0.1 M phosphate buffer at pH-2, deposition time 20 s, pulse amplitude 30 mV, and step potential of 9 mV and at various frequencies. a=10 Hz, b=15 Hz, c=20 Hz, d=25 Hz, e= 30 Hz, f= 35 Hz, g= 40 Hz, h= 45 Hz, and i= 50 Hz.

The effect of frequency on peak current can be shown in figure 4.11. From the figure it is observed that the peak current increases sharply as the frequency increases from 10 Hz to 30 Hz. After the frequency value of 30 Hz, the peak current increase with increasing frequency but with a different slope (the curve is leveled off) (Figure 4.12). So 30 Hz was chosen as the optimum value for the subsequent experiment.
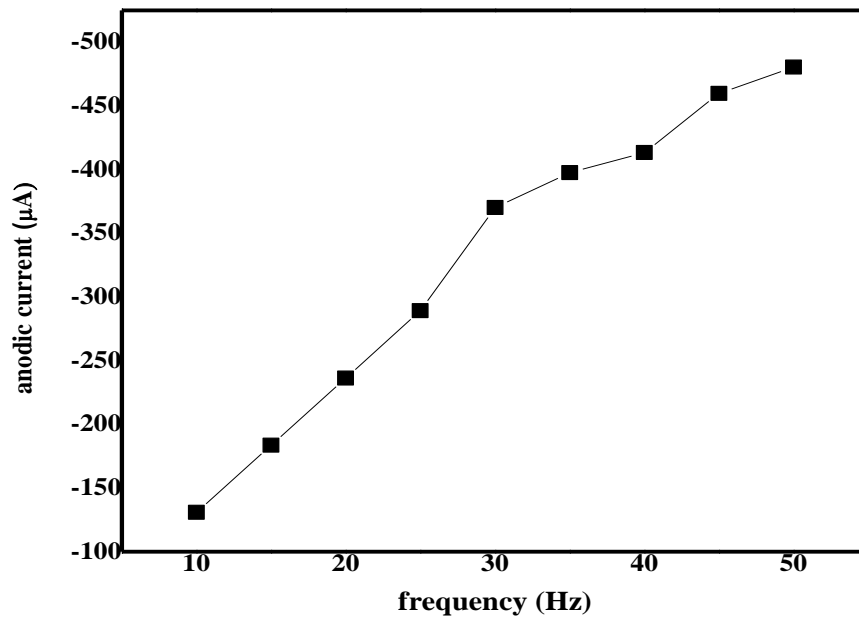
Figure 4.12: The plot of peak current as a function of wave frequency

4.1.2.1.2 Effect of Pulse Amplitude on Peak Current

The effect of pulse amplitude on peak current was investigated. As it is shown in Figure 4.13, the peak current is increased sharply as the pulse amplitude increases from 10 mV to 40 m V. The peak currents usually increase with increasing amplitude. However, the width of the peak also increases as the square wave amplitude grows larger and normally one refrains from increasing the square wave amplitude, because resolution may be degraded unacceptably
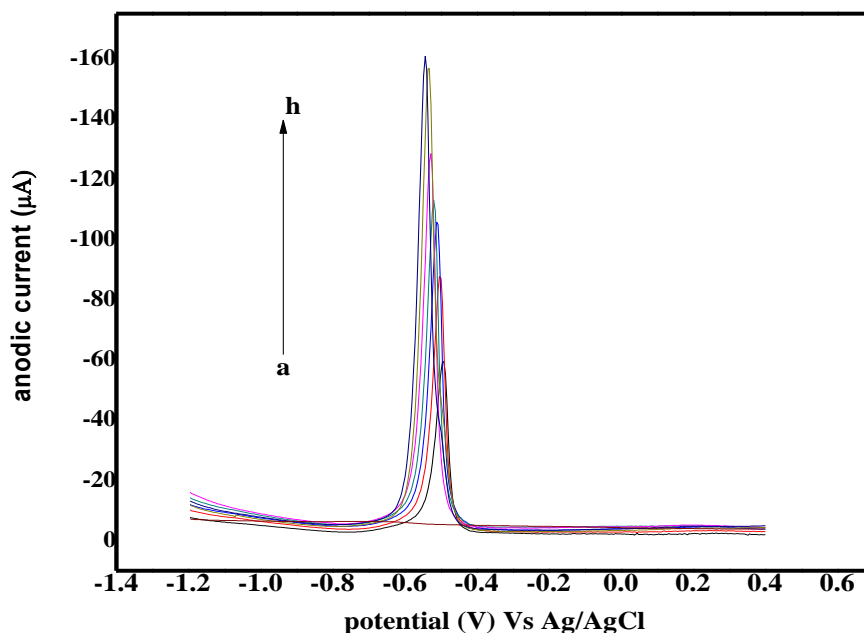
Figure 4.13: SWAS Voltammogram of 10 ppm Pb^{2+} at various pulse amplitudes of a=10 mV, b=15 mV, c=20 mV, d=25 mV, e=30mV, f=35mV, and g=40mV in 0.1 M phosphate buffer at pH-2, deposition time 20 s, frequency 30 Hz, and deposition potential -0.8V.

As it is shown in Figure 4.13, the value of the measured peak current increases sharply as the pulse amplitude increased from 10 mV to 40 mV. From the figure it is observed that the peak current increases sharply as the frequency increases from 10 Hz to 30 Hz. After the pulse amplitude value of 30 Hz, the peak current increase with increasing amplitude but with a different slope (Figure 4.14). An optimum value of 30mV was chosen for further studies and for real sample analysis. Greater values of the pulse amplitude were not employed, in order to avoid the decrease of resolution.
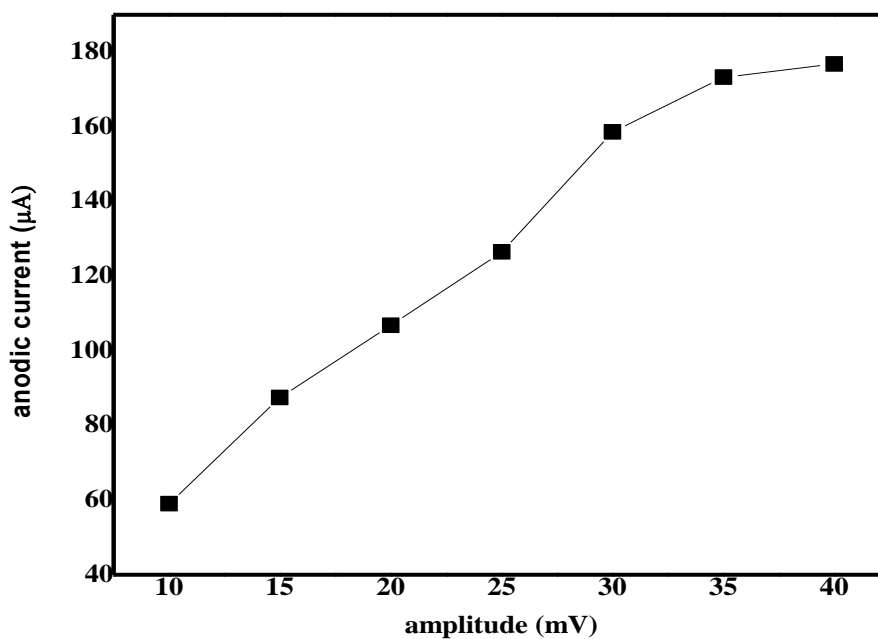
Figure 4.14: The Plot of Peak Current as a function of pulse amplitude

4.1.2.1.3 Effect of Step Potential on Peak Current

The effect of step potential on peak current was investigated. As it is shown in Figure 4.15, the peak current is increased sharply as the step potential increases from 3 mV to 9 m V.
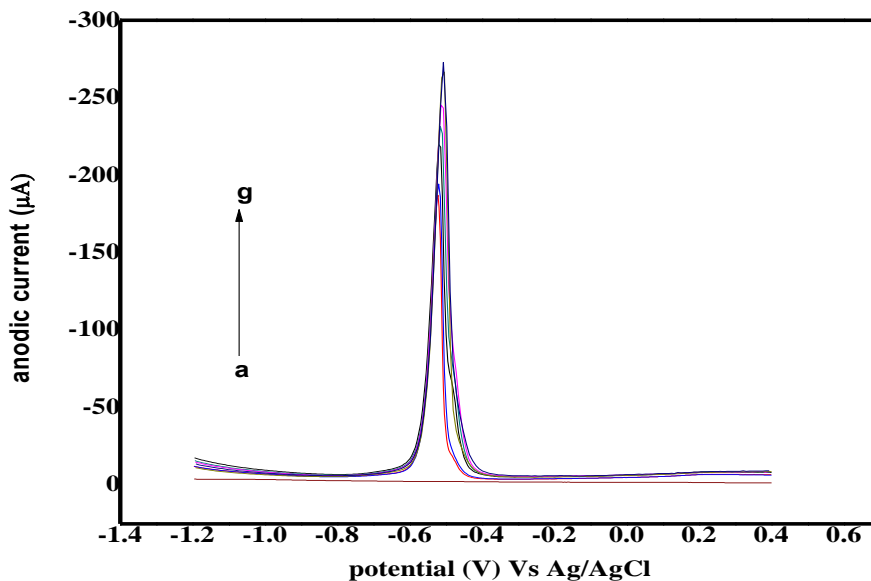
Figure 4.15: SWAS voltammogram for 10 ppm Pb^{2+} in 0.1 M phosphate buffer (pH-2) at deposition potential of -0.8 V, deposition time of 20 seconds, pulse amplitude of 30, frequency 30 Hz and at several step potentials of a=3 mV, b=4 mV, c=5 mV, d=6 mV, e=7 mV, f=8 mV and g=9 mV.

But the peak current increases with a different slope as shown in figure 4.16. Although the step potential increases with a different slop, but it looks the slope is smaller when the step potential increases from 8 to 9. Thus, the step potential 8 mV is chosen as the optimum value for the subsequent experiment.
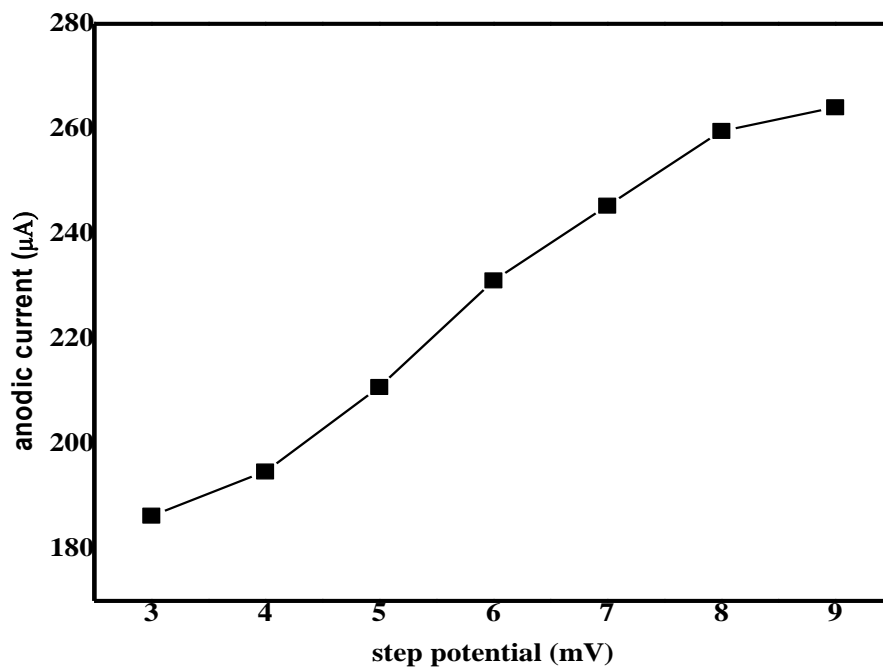
Figure 4.16: The Plot of peak current versus Step Potential.

4.1.2.1.4 The Effect of Deposition Time on Peak Current

Deposition time is very important in anodic stripping voltammetry. As deposition time increases, the amount of analyte deposited increases. If sensitivity is required, the deposition time should be increased. However, there would be inter metallic binding and the surface of the electrode is being covered with analyte as the deposition time increases [55]. Thus, there should be an optimum deposition time for the subsequent experiment.
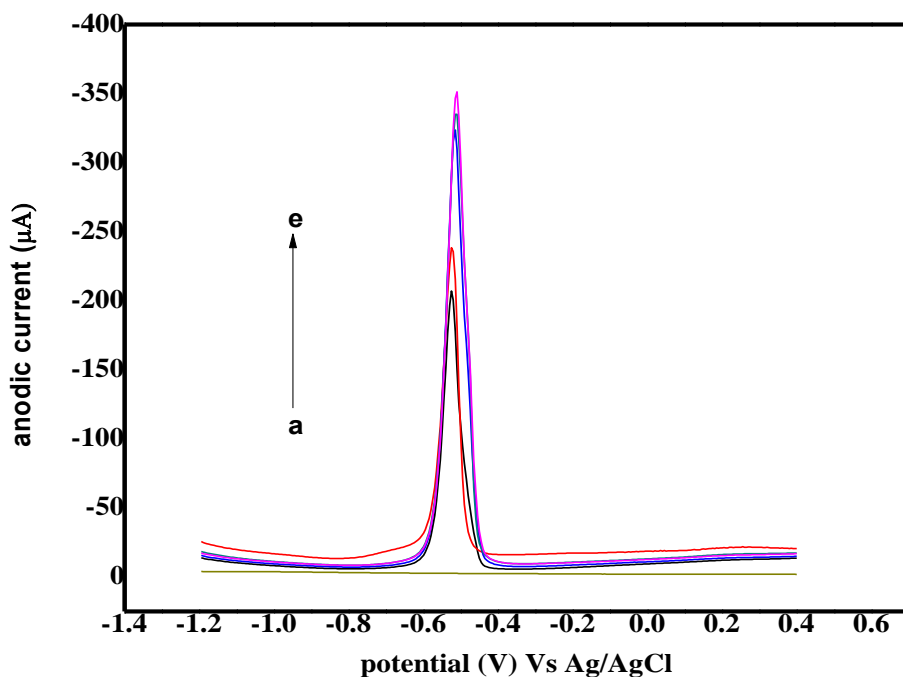
Figure 4.17: SWAS voltammogram for 10 ppm Pb^{2+} at various deposition times of a=10 s, b=15 s, c=20 s, d=25 s and e=30 s in 0.1 M phosphate buffer: at deposition potential of -0.8 V, pulse amplitude 30 mV, step potential 8 mV, and frequency 30 Hz.

As it is shown in Figure 4.17, the peak current increases sharply as the deposition time increased from 10 s to 30 s. But the peak current increases with a different slope. The curves are leveled as the time increases from 20 s to 30 s (Figure 4.18). Thus, deposition time of 20 s was chosen as the optimum value for this study.
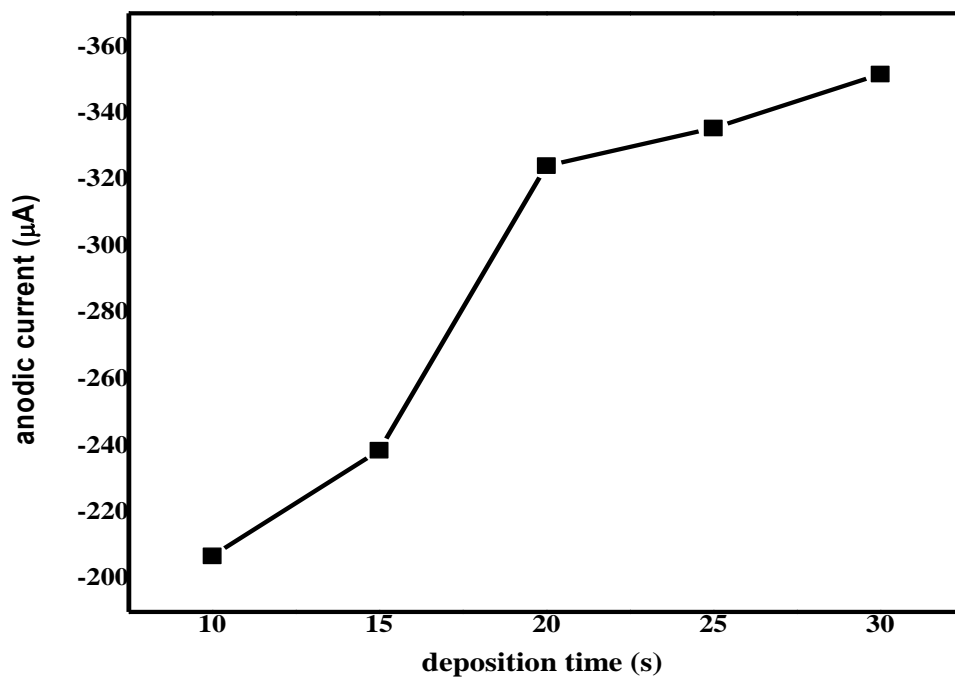
Figure 4.18: Peak current Vs deposition time for 10 ppm Pb (II) in 0.1 M phosphate buffer.

Table 4.1: Optimum Parameters for Analysis of Lead and Cadmium with SWASV in N/Gondar Azezo Shinta and Boyit Kebele Ground Water.

Parameter	Description
Working electrode	Carbon past electrode
Calibration	Standard addition method
Mode	SW
pH	2
Deposition potential	-0.8 V
Deposition time	20 s
Pulse amplitude	30 mV
Frequency	30 Hz
Step potential	8 mV

4.1.2.1.5 Effect of Varying Pb and Cd Concentration on Peak Current

Under the optimum parameters (pH=2, f=30 Hz, E_p= -0.8 V, deposition time=20 s, pulse amplitude=30 mV and step potential=8 mV), the calibration graph for determination of Pb and Cd were obtained in the concentration range 1.0-10 ppm. As shown in fig. 4.19, the anodic peak current is increased with concentration. The regression equation is represented by equation 8 and 9 with a correlation coefficient of 0.996 and 0.994 respectively as shown in fig 4.20: a and b respectively.

- **For lead** $I_p (\mu A) = 16.60[Pb^{2+}] + 25.89$ ---(8)
- **For cadmium** $I_p (\mu A) = 6.098[Cd^{2+}] + 7.251$ --- (9)
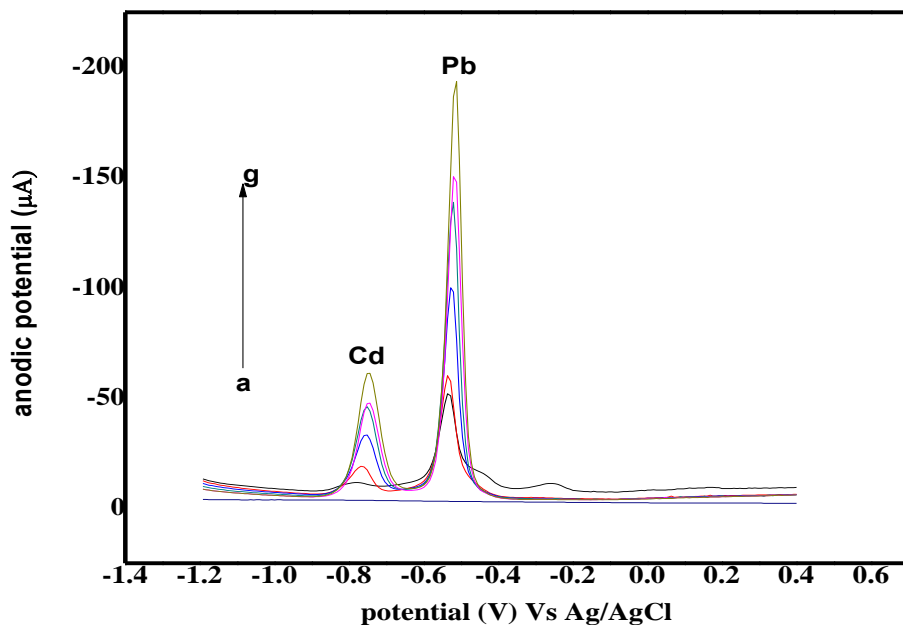
Figure 4.19: A SWAS voltammograms of   a= 0.1 M buffer b=1 ppm, c=2 ppm, d=4 ppm, e=6 ppm, f=8 ppm and g=10 ppm of Pb^{2+} and 10ppm of Cd^{2+} solution at optimum condition as in Table 4.1.

In figure 4.19: It is also observed that the stripping potential of Pb and Cd appeared to increase peak current as the concentration of Pb and Cd solution increased.

Calibration curves were prepared to determine the concentration of Pb and Cd in the sample solution. The calibration coefficient of Pb and Cd was determined by plotting peak current versus working standard solutions concentration.
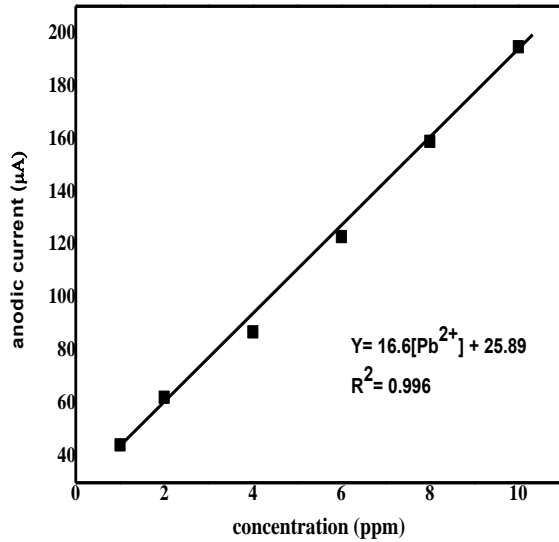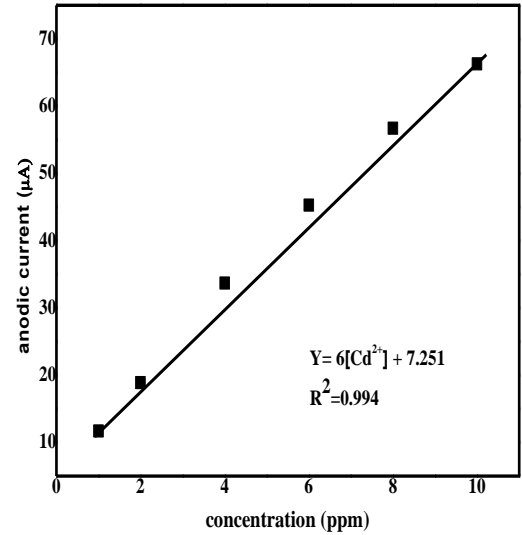
Figure 4.20: Calibration Plot of (a) Peak Current versus Concentration of Pb^{2+} and (b) peak current versus concentration of Cd^{2+}.

4.2 Determination of Concentration of Lead and Cadmium

The level of lead and cadmium in ground water collected from the two sites in N/Gondar azezo (shinta and boyit kebele) was investigated by SWASV at carbon past electrode in 0.1 M phosphate buffer of pH 2. The analysis was done at deposition potential of -0.8 V versus Ag/AgCl and a deposition time of 20 second. The concentration of lead and cadmium was calculated from the correlation coefficients of the linear current-concentration calibrated plots. Before determining the concentration, the electrochemical behavior of lead and cadmium would be highlighted and other parameters would be optimized. On this study the electrochemical parameters of lead was chosen as the electrochemical parameter of cadmium.

4.2.1 Application of the SWASV Method for Lead and Cadmium Determination

4.2.1.1 Method Validation

The repeatability of the measurement was calculated from six independent runs of lead and cadmium solution. LOD and LOQ of lead were obtained as 0.524 mg/l and 1.746 mg/l, respectively from the calibration graph as shown in Figure 4.20 (a). LOD and LOQ of cadmium were obtained as 0.698 mg/l and 2.327 mg/l respectively from the calibration graph as shown in Figure 4.20 (b).

4.2.1.2 Application of Real Sample Analysis

The applicability of CPE for determination of Pb and Cd was demonstrated by applying it for the determination of toxic heavy metal content in ground water sample. These samples were prepared and added to electro-chemical cell for analysis.

Figure 4.21 and 4.22 show voltammograms of ground water real samples taken from shinta (GW-1) and boyit (GW-2) kebele respectively. Fig 4.21 shows the voltammogram for Pb obtained from standard addition in ground water (one) sample. The shapes, baselines and positions of the peak potential and the increased in peak current are similar to the voltammogram of the standard lead and cadmium solution.

Figure 4.21: SWAS voltammograms of samples of shinta (Gw-1) (a)=10 ml real sample and 10 ml phosphate buffer , (b) b+1000 µL, (c) c+1000 µL and (d) d+1000 µL of 10ppm standard lead and cadmium solution under the optimized parameters.

The result shows there is no peak potential shift in the case of lead in GW-1 sample. The value of the oxidation potential was at -0.507V. However, at the oxidation potential of Cd, peak current was not detected GW-1 sample. This due to may be concentrations of cadmium in GW-1 was below the detection limit.

Fig 4.22 shows the voltammogram for Pb obtained from standard addition in GW-2 sample. The shapes, baselines and positions of the peak potential and the increased in peak current are similar to the voltammogram of the standard lead and cadmium solution.
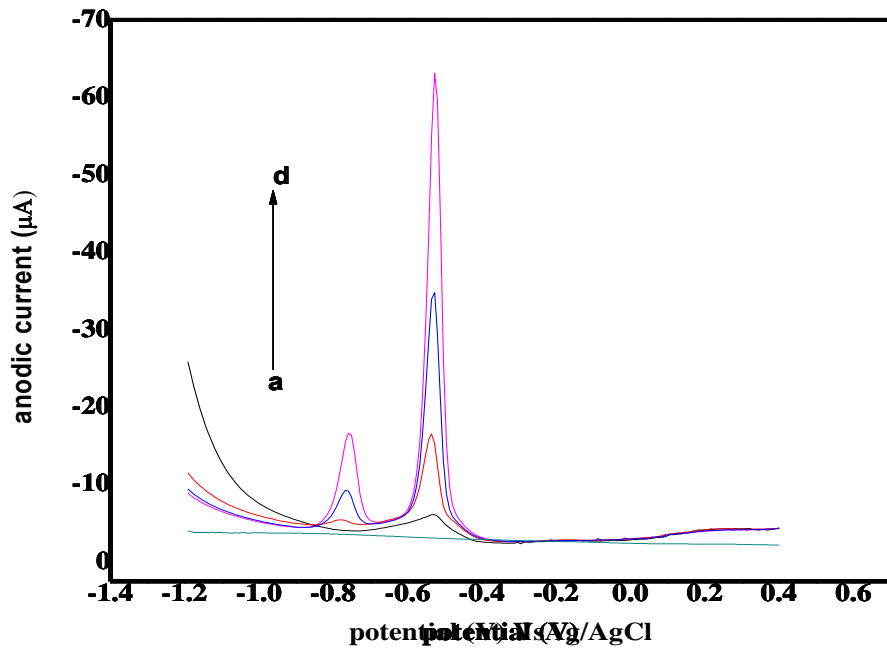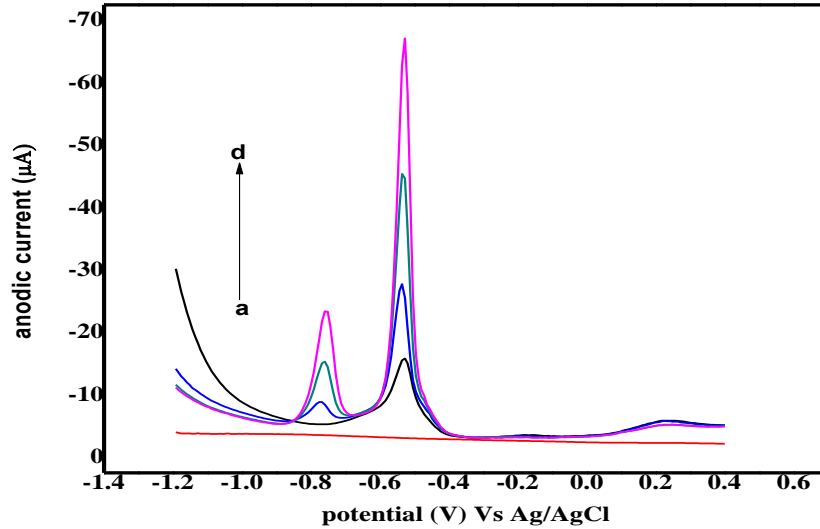
Figure 4.22: SWAS voltammograms of samples of boyit (close to the factory) (GW-2): (a) 10 ml real sample and 10 ml phosphate buffer , (b) a+1000 µl, (c) b+1000 µl and (d) c+1000 µl standard 1:1 mixed ratio of lead and cadmium solution under the optimized parameters.

The result shows there is no peak potential shift in the case of lead in GW-2 sample. The value of the oxidation potential was at -0.507V. However, at the oxidation potential of Cd, peak current was not detected GW-2 sample. This due to may be concentrations of cadmium in GW-2 was below the detection limit

4.2.1.3 Comparison the Concentration of Lead and Cadmium between GW-1 and GW-2.

The level of lead and cadmium in N/Gondar azezo kebele the two selected cites of GW sample were studied using square wave anodic stripping voltammetry at carbon past electrode in phosphate buffer at pH of 2. The concentrations of lead were 1.8 mg/l and 2.4 mg/l in GW-1 and GW-2 respectively. There was significant difference in concentration of lead among the two samples. GW-2 sample is highly polluted by Pb due to the presence of different pollutants including point source (include discharges from a sewage treatment plant, a factory, or a city storm drain) and non-point sources around GW-2 where located than GW-1. Thus, the quality of this water is not safe for domestic use than GW-1 (Figure: 4.23).
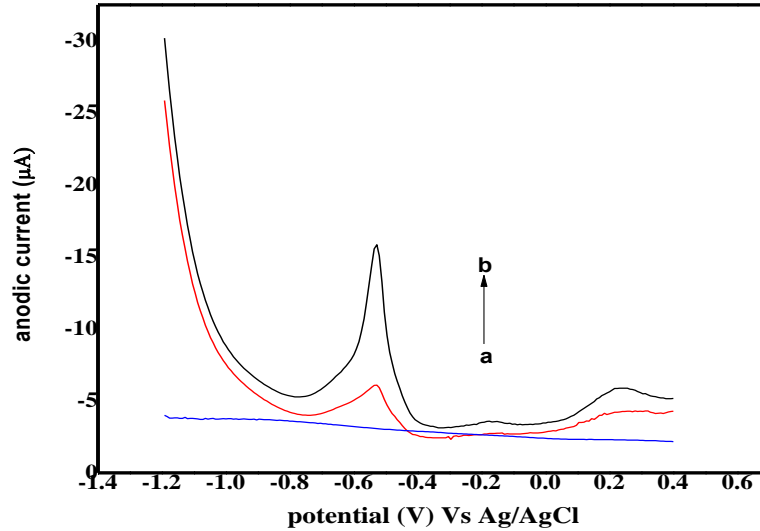
Figure 4.23: SWAS voltammograms of (a) samples of shinta Gw-1 and (b) boyit GW-2.

4.2.1.4 Degree of Recovery

The degree of recovery for each samples were determined from the above figures as shown in table: 4.1 below with an excellent recovery value of 93% and 95.6% respectively.

Table-4.1:- Determination of recovery for each sample.

No	Samples	Concentration Pb in the sample before addition of standard (mg/l)	Concentration Pb after addition of 0.9mg/l of 1:1 mixed ratio of Pb and Cd.(mg/l)	% recovery
1	G.W-1	1.8	2.64	93%
2	G.W-2	2.4	3.26	95.6%

Table 4.2: comparison of Pb and Cd concentration in ground water sample of this study compare with WHO.

Lead was detected appreciably in both ground water samples than maximum allowable concentration of WHO. But cadmium was not detected in both water samples.

Heavy metals (Pb and Cd)	WHO maximum allowable concentration (mg/l)	Found value of Pb and Cd ground water of the two selected area.(mg/l)	
		G.W-1	G.W-2
Lead (II)	0.010	1.8	2.4
Cadmium (Cd)	0.0050	ND	ND

5. Conclusion and Recommendation

5.1 Conclusion

In this work, working parameters were optimized to determine the amount of Pb, and Cd, in SWASV techniques using modified carbon paste electrode. Under working conditions the amount of Cd and Pb in ground water sample has been successfully determined. The effect of working parameters on the voltammetric response of Pb^{2+} and Cd^{2+} solution was also investigated and the results showed that the peak current is directly proportional to scan rate, wave frequency, amplitude, and step potential.

Based on the result obtained, the concentration of studied heavy metal Cd was not detected in the two selected ground water sample. The concentration of studied heavy metal Pb was detected in the ground water sample in the selected area (N/Gondar, azezo kebele namely shinta and boyit) and its value was determined as 1.8 mg/l shinta and 2.499 mg/l boyit. The concentration in both study sites was found above the safe limit of WHO. From this finding, we conclude that the two selected ground waters are highly polluted by Pb. So the quality of that ground water is not safe for domestic use.

5.2 Recommendations

Based on the outcome of the study, has recommended the following points.

1. Proper drainage and sewer systems should be constructed in the industry to ensure proper disposal of hazardous liquid waste, thereby preventing seepage into groundwater.
2. Industries should be adopted the strategy of reuse and recycling of materials such as used oil and brake fluids.
3. Peoples who they live in the research area do not use the polluted ground water for domestic use.

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