

Biogenic Silver nanoparticles Based Electrochemical Sensor for Selective Detection of Heavy Metal Ions (Pb^{2+} and Cd^{2+})



Dejene Tilahun Teklemariam

A Thesis Submitted to the Department of Applied Chemistry,

School of Applied Natural Science

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Applied Chemistry (in Analytical Chemistry)

Office of Graduate Studies

Adama Science and Technology University

November, 2023

Adama, Ethiopia

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Declaration

I hereby declare that this Master Thesis entitled “Biogenic Silver nanoparticles Based Electrochemical Sensor for Selective Detection of Heavy Metal Ions (Pb^{2+} and Cd^{2+})” is my original work. That is, has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All source of materials that are used for this thesis have been duly recognized by proper citations.

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I, the advisor of this thesis, hereby certify that I have read the revised version of the thesis entitled “Biogenic Silver nanoparticles Based Electrochemical Sensor for Selective Detection of Heavy Metal Ions (Pb^{2+} and Cd^{2+})” prepared under my guidance by Dejene Tilahun Teklemariam submitted in partial fulfillment of the requirements for the degree of Master of Science in Applied Chemistry (Specialization in Analytical Chemistry). Therefore, I recommend the submission of the revised version of the thesis to the department following the applicable procedures.

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Approval Page

I, the advisor of the thesis entitled “Biogenic Silver nanoparticles Based Electrochemical Sensor for Selective Detection of Heavy Metal Ions (Pb^{2+} and Cd^{2+})” and developed by Dejene Tilahun Teklemariam, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis

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LIST OF ABBREVIATION

Ag NPs	Silver nanoparticles
NPs	Nanoparticles
MNP	Metal nanoparticles
HMI	Heavy Metal Ion
ABS	Acetate Buffer solution
LOD	Limit of detection
XRD	X-Ray Diffraction
UV-Vis	Ultraviolet-Visible spectroscopy
FTIR	Fourier Transform Infrared spectroscopy
SEM	Scanning electron microscopy
DLS	Dynamic Light scattering
SWASV	Square wave anodic stripping Voltammetry
CV	Cyclic Voltammetry
CPE	Carbon paste electrodes
M-CPE	Modified Carbon paste electrodes
RSD	Relative standard deviation
HA	Hagenia abyssinica

Abstract

Heavy metal ions and other harmful elements currently pollute the environment. Among heavy metals, cadmium and lead ions are two of the most common contaminants that affect the environment in both natural and anthropogenic ways. Protection of the environment requires proper determination and quantification of these metal ions. Thus, developing a proper sensor with less cost is the focus of the present research studies. Electrochemical sensors have attracted great attention for the determination of these hazardous elements. Herein, a sensitive electrochemical sensor modified by using green synthesized silver nanoparticles from *Hagenia abyssinica* plant extract provided a new opportunity for enhancing the electrocatalytic performance of the fabricated sensor. The synthesized Ag NPs were characterized using UV–Vis, XRD, FTIR, DLS, and SEM techniques. The peak absorbance of the UV–Visible spectra was at 423 nm, confirming the formation of Ag NPs. SEM analysis showed the existence of small spherical nanoparticles with a size range of 10 to 20 nm (average 17 nm). XRD analysis showed that the Ag NPs were face-centered cubic (fcc) with crystallite sizes of 14 nm, 12 nm, and 16 nm for metal to plant extract ratios of 1:1, 1:3, and 3:1 NPs, respectively. FTIR analysis was used to confirm the existence of various functional groups responsible for reduction and stabilization during the biosynthesis process. DLS describes the degree of uniformity and homogeneity of the nanoparticles. Cyclic voltammetry and square wave anodic stripping voltammetry techniques were used to evaluate the electrochemical behavior of the two metals at the modified electrode relative to the unmodified electrode. Moreover, experimental variables such as modifier % ratio, pH of the supporting electrolyte, deposition time, and deposition potential have been optimized. Based on an optimal condition, fairly good calibration lines were obtained to detect these two ions with a detection limit (LOD) of 2.7 µg/L for Cd (II) and 1.3 µg/L for Pb (II). Furthermore, the repeatability, reproducibility, and stability of the present sensor were determined with satisfactory results, and the possible effects of inorganic ions were investigated but did not cause any significant interference. In addition, the proposed method was utilized in the simultaneous detection of Cd (II) and Pb (II) metal ions in real matrix samples, which gave recoveries of 96.2 to 103.7% for cadmium and 97.5 to 104.2% for lead.

Keywords: Heavy metal ions, Electrochemical sensor, Silver nanoparticles, Green synthesis, *Hagenia abyssinica* plant leaf extract

1. INTRODUCTION

1.1 Background of the Study

Currently, environmental pollution is considered a major threat worldwide, especially to aquatic ecosystems. With accelerated industrialization, increasing agricultural activities, and rapid urbanization, various toxic and poisonous substances can enter natural waterways, contaminate drinking water, and subsequently cause severe health problems (Ivanišević, 2023). Among them, heavy metal ions are micropollutants that represent a growing environmental problem and have affected human health and the environment. Major sources of these heavy metal ions are cosmetics and their byproducts, fertilizers, and other chemicals generated from industrial or household waste. Heavy metals, such as mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), and arsenic (As), are widely distributed in the natural environment and pose serious hazards to human health, as proven by many studies. Among heavy metal ions, lead and cadmium ions, which are two of the most common contaminants, have attracted strong interest globally due to their persistent and non-biodegradable characteristics, even at low concentrations, which leads to severe human health hazards such as renal, reproductive, and nervous dysfunctions, cancers, and DNA mutations (Munir et al., 2019). In the agricultural environment, Pb (II) and Cd (II) ions in soil or water are mainly derived from wastewater discharge, vehicle emissions, lead-acid batteries, fertilizers, mining, and industrial wastes (Wang et al., 2019). These two heavy metals in farmland soil are easily absorbed by crops and vegetables and can enter and become enriched in the human body through multiple absorptions, ingestion, and dermal contact. According to the World Health Organization and the Ministry of Health of Vietnam have set the limit values for lead and cadmium in drinking water at 10 and 3 $\mu\text{g L}^{-1}$ (Kalachev et al., 2023; WHO, 2011), respectively.

To assess the levels of Pb (II) and Cd (II) ions in environmental water and soil, an inexpensive and convenient analytical tool is needed for heavy metal ion determination. Nowadays, many methods have been exploited and applied in testing organizations during the past decades, including graphite furnace atomic absorption spectrometry (Valasques et al., 2020), flame atomic absorption spectrometry (Altunay et al., 2020), inductively coupled plasma emission mass spectrometry (ICP-MS) (Nawi et al., 2020), and inductively coupled plasma atomic emission spectroscopy (Alhussaini et al., 2022). Nevertheless, these methods are expensive, require trained personnel, are

time-consuming, and unsuitable for on-site analysis. Thus, it is important to develop a simple, rapid, and cost-effective method for Pb (II) and Cd (II) ion detection. On the other hand, electrochemical sensors play a prominent role in the metal sensing field due to their simplicity, selectivity, reduced cost, and high sensing performances, essentially when the electrode surface is modified to improve the sensitivity and selectivity of the sensors (Jebril, Cubillana-Aguilera, et al., 2021).

Furthermore, nanoparticles have been incorporated into electrochemical sensors for a superior enhancement of their response. Nanoparticles (NPs) have attracted great attention because of the incredible electrical, magnetic, thermal, and catalytic characteristics that are generated when their particle size is miniaturized. A large number of nanomaterials, including carbon nanostructures (e.g., graphite and CNTs), metal and metal oxides, quantum dots, silica NPs, and other NPs, have been investigated for their applications as electrochemical sensors (Dai et al., 2018). Recent progress in nanoscience and nanotechnology has provided new platforms for the synthesis and applications of green metallic nanoparticles. Among the metal nanoparticles, silver nanoparticles (Ag NPs) have functioned as appropriate materials for electrode surface modification due to their unique properties, such as excellent conductivity, reflectivity, high surface area-to-volume ratio, and their ability to make them promising platforms as catalysts (M. S. Shivakumar et al., 2019). AgNP can be synthesized using different physical and chemical methods. However, the high cost of production and toxicity issues associated with the above techniques opened the gate to a very cost-effective, reliable, and eco-friendly green synthesis method of nanoparticles using a plant extract that provides an improvement over the chemical methods and can be used for bulk synthesis (M. Shivakumar et al., 2020).

Recently, several researchers have reported green chemistry-based nanoparticle synthesis for heavy metal ion detection. However, there is limited research on silver nanoparticles using *Hagenia abyssinica* plant leaf extract as a capping or reducing agent. Although Ag NPs have been synthesized for electrochemical properties (Murthy et al., 2020), there is no study on the electrochemical sensing of heavy metal ion activities of silver nanoparticles. In the current investigation, *Hagenia abyssinica* is a member of the Rosaceae family and is a species of flowering plant native to central and eastern Africa, including Sudan and Ethiopia. It is used for the synthesis of silver nanoparticles since it contains a chemical composition that can be used as a reducing

and/or capping agent. Plant extracts contain a variety of phytochemicals, such as saponins, tannins, alkaloids, flavonoids, terpenoids, and phenolic compounds. In early periods, *Hagenia abyssinica* plant leaf extract was used for many medicinal purposes, such as tapeworm and liquid drunk, as a remedy for diarrhea and stomachache (Wolde et al., 2016).

So, in the present work, for the first time, we report the synthesis of Ag NPs exploiting *Hagenia abyssinica* plant leaf extract as a capping and reducing agent in a simple and faster process. The optical, structural, and morphology properties of these biosynthesized silver nanoparticles were characterized using different techniques such as UV/visible, XRD, FTIR, SEM, and DLS analysis, resulting in the silver nanoparticles having a smaller size, which would be interesting for electrochemical sensors. The electrochemical properties of biogenic Ag NPs were also evaluated using cyclic voltammetry and square wave anodic stripping voltammetry. Thus, this paper describes the green synthesis of silver nanoparticles using *Hagenia abyssinica* plant leaf extract and the application of a silver nanoparticle-modified carbon paste electrode for the simultaneous determination of Pb (II) and Cd (II) in wastewater.

1.2 Statement of the problem

At a global level, environmental pollution is one of the most serious problems due to its widespread and long-term harm. The rapid growth of urbanization and industrialization improves our quality of life. Many developments in the industry have brought plenty of new products and services. These advancements cause not only the production of useful technology but also the increased use of chemicals. Ecological contamination is responsible for the destruction of environmental systems and for sickness and disease in humans, plants, and animals. The three major types of environmental contamination are atmospheric, water, and soil pollution. Atmospheric and water contamination can lead to enormous disasters in a short time (Eddaif et al., 2019). Many processes involve chemicals, which are harmful to human health and the environment when they are released. Heavy metal ions such as Pb (II) and Cd (II) are toxins due to their harmful impact on human health even at very low concentrations. They can be released easily into the environment via human activities and the processing of natural resources (Wang et al., 2019).

Thus, early detection of these heavy metal ions is a vital task to protect the environment and avoid pollution. The detection of heavy metal ions remains an enormous problem due to measuring these

ions at very low concentrations, as well as the need for complex sampling procedures, specialists for measurement and evaluation, not using in-site detection, and the application of costly apparatuses. Therefore, it is important to develop a simple, rapid, and cost-effective method for Pb (II) and Cd (II) ion detection and thus minimize their impact on the environment. One of the most promising methods for the detection of heavy metal ions in wastewater is using an electrochemical sensor (Naseri et al., 2022). Recent studies have been devoted to the use of electrochemical sensors in the detection of Pb (II) and Cd (II) ions in wastewater because this method plays a prominent role in the metal sensing field due to its ease of use, selectivity, low cost, and high sensitivity. Moreover, high overpotential and low redox signals in electrochemical determination are major problems for the determination of food, drug, and water pollutant compounds with unmodified electrodes, creating a serious necessity for electrode modification (Karimi-Maleh et al., 2020).

To overcome this problem, nanomaterials with unique properties have been suggested in different fields, especially electrochemical sensors (Baghayeri et al., 2018). As a conductive material, Ag NPs can be used to fabricate modified sensors because silver nanoparticles have good electrical conductivity and are powerful mediators for the fabrication of sensitive electrochemical sensors (A. N. Ahmed et al., 2018). To date, different modifiers of electrochemical sensors have been used to detect Pb (II) and Cd (II) ions in wastewater. The search for modified electrodes with low cost, low limit of detection, high sensitivity, high stability, and easy accessibility as a choice for the detection of Pb (II) and Cd (II) ions in the wastewater process has motivated our group to perform the current study. Therefore, this research is intended to use silver nanoparticles that have been synthesized by employing the green method using *Hagenia abyssinica* leaf extract to develop electrochemical sensors by using these nanoparticles as modifiers of carbon paste electrodes for the detection of Pb (II) and Cd (II) ions in wastewater.

1.3 Objective of the Study

1.3.1 General Objective

The general objective of this study is to synthesize and characterize silver nanoparticles by using *Hagenia abyssinica* medicinal plant leaf extract based electrochemical sensors for selective detection of heavy metal ions (Cd (II) and Pb (II)).

1.3.2 Specific Objective

The specific objectives of these studies are as follows:

- To synthesize biogenic silver nanoparticles by using *Hagenia abyssinica* plant leaf extract
- To characterize the synthesized Ag NPs by using UV-Visible, FTIR, XRD, SEM, and DLS
- To prepare and study the electrochemical behaviors of biogenic AgNP and modified carbon paste electrodes by using CV and SWASV.
- To optimize the experimental parameters, such as the modifier ratio, supporting electrolyte pH, deposition time, and deposition potential.
- To evaluate the analytical performance of AgNP-modified carbon paste electrodes for the determination of Cd (II) and Pb (II) in standard solutions.
- To study the detection of Cd (II) and Pb (II) in wastewater using a biogenic Ag NP-modified carbon paste electrode.

1.4 Significance of the Study

Many studies are being conducted to discover new electrochemical sensors for the detection of heavy metals. The greatest advantage of this study is that silver nanoparticles were synthesized by a green process from the *Hagenia abyssinica* plant leaf extraction method, which is eco-friendly, and the modifier electrode from biogenic Ag NPs could be an alternative electrode for monitoring heavy metal ions such as cadmium and lead in wastewater samples. This thesis can provide a hint for the use of locally available materials together with NPs for the construction of electrochemical sensors. The study will help the community learn about the toxic nature of heavy metal ions and the importance of controlling heavy metals in wastewater as well as in other samples.

1.5 Scope of the Study

This research work is limited to the green synthesis of silver nanoparticles using *Hagenia abyssinica* plant leaf extract and characterization of the nanoparticles using XRD, FTIR, DLS, SEM, and UV–Visible techniques and the application of a silver nanoparticle modified carbon paste electrode (Ag NPs/CPE) for the simultaneous determination of Cd (II) and Pb (II) in wastewater. The electrochemical properties of the green synthesis of silver nanoparticles modified carbon paste electrode were evaluated using cyclic voltammetry and square wave anodic stripping voltammetry.

2. LITERATURE REVIEW

2.1 Nanoparticles

Nanoparticles are particles that range between 1-100 nm. Reducing the particle size of the materials results in unique and improved properties, such as surface-to-volume ratio, and physical, chemical, optical, and electronic properties. The peerless properties of nanoparticles are liable to gain multifunctional properties and lead to their widespread application as catalysts, electrical conductors, sensors, antioxidants, and antimicrobial agents (Turunc et al., 2021). Nanoparticle can be divided into metal-based, metal oxide-based, and carbon-based NPs. Metal-based NPs (MNPs), especially those based on noble metals, have drawn more attention because of their optical, electrical, and sensing characteristics. MNPs can be synthesized via several pathways, such as electrochemical techniques, laser ablation, gamma-radiation, photochemical techniques, and chemical reduction. They are considered excellent substances for constructing electrochemical sensors (Ali et al., 2021). Currently, the development of NP-based electrochemical sensor devices has drawn great attention in the field of industrial, environmental, clinical, and food analysis owing to their attractive performance: fast response, convenient operation, high sensitivity, and selectivity. Electrochemical sensors offer the possibility of miniaturization and the potential for the development of portable hand-held devices for real time monitoring. Recently, extensive studies have been performed to explore the electrochemical behavior of biosynthesized MNPs and their potential in sensor design (Dodevska et al., 2022).

2.2 Metal Nanoparticles

Metal nanoparticles are well known for their unique physical, chemical, and biological properties, which depend on their size, shape, and surface charge. The morphology and dispersity of metal nanoparticles depend on the mode of their synthesis. Mostly, the synthesis of nanoparticles is based on physical and chemical methods; however, the current studies in this field have raised concerns regarding the possible risks and the related effects of nanoparticles on the environment and humans. Due to the growing application of nanoparticles in almost every field of science and technology, researchers have emphasized the biological synthesis of metal nanoparticles (Rai et al., 2021).

2.3 Silver Nanoparticles

Among the different metals studied to date, silver nanoparticles (Ag NPs) are one of the most engineered nanoparticles used in several commercial areas, including medical devices, healthcare products, cleaning agents, food storage, packing, and textile coatings (Ahluwalia et al., 2018). They are also used for environmental applications because of their potential antimicrobial activity against bacteria, fungi, algae, and plant extracts. In recent studies, it is well known that metals at the nanometer scale may offer many advantages in the electrochemical field due to their high surface energy and conductivity, which help in catalyzing electrochemical reactions and enhancing charge transfer at the electrode surface. Moreover, silver nanoparticles have been proposed and applied as electrode modifiers because of their large effective surface area, excellent conducting capability, fast mass and charge transport, and effective electrocatalytic characteristics (Chelly et al., 2021).

2.4 Methods for Synthesizing Silver Nanoparticles

The most commonly used approaches for nanoparticle synthesis are the top-down and bottom-up approaches. (1) The "top-down" approach, involves restructuring a bulk material to create a nanomaterial. These methods are physical techniques wherein materials are milled, cut, and shaped using tools. (2) The "bottom-up" approach, which implies the construction of a nanomaterial from basic building blocks, where atoms or molecules form larger particles by self-assembly, is a chemical or biological method that is considered the best to prepare nanoparticles (Filipa & Ang, 2020).

In recent years, nanoparticles synthesis has been one of the most fascinating areas of scientific research, and there is an increasing focus on manufacturing nanoparticles in environmentally acceptable ways (Raj et al., 2021). The synthesis method of Ag NPs, like most nanomaterials, is mainly divided into three methods: physical, chemical, and biological.



Figure 1: Synthesis of silver nanoparticles

2.5 Biogenic (Green) Synthesis of Silver Nanoparticles

Nanoparticle synthesis by biological methods is a growing area of nanotechnology (Roy & Barik, 2010). The biological synthesis of NPs is the simplest, nontoxic, and yet most eco-friendly method for producing high-quality NPs. As a more affordable and sustainable alternative to chemical and physical processes, green synthesis of metallic nanoparticles has been proposed. Due to its numerous applications in biotechnology, biomedicine, and other industries, silver nanoparticles have drawn the interest of researchers in recent years. Nano silver is used as an antibacterial agent in textiles, home water purification systems, medical equipment, cosmetics, electronics, and household appliances due to its chemical stability, excellent conductivity, and catalytic nature (Pannerselvam et al., 2020). Additionally, Ag NPs synthesized in a single step, such as biological synthesis, have a higher degree of stability, diversity, and adequate dimensions (Lee & Jun, 2019). Biological route synthesis requires living organisms such as bacteria (Saravanan et al., 2018), fungi (Feroze et al., 2020), algae (Arya et al., 2019), and plants (R. H. Ahmed & Mustafa, 2020). In addition, Ag NPs have also been synthesized using bio-organic compounds such as amino acids, enzymes, and sugar (Talekar et al., 2016). Among these methods, plants are being widely explored for the fabrication of Ag NPs because of some advantages, such as non-involvement of the complex process of maintenance of microorganism culture, shorter reaction times and ease of scaling up for large scale synthesise.

2.5.1 Bacteria assisted synthesis of silver nanoparticles

Silver nanoparticles produced by microorganisms can be classified into two distinct categories, either intracellularly or extracellularly, depending on the location where they are produced. Ag NPs generally be produced by bacterial bio reduction process in which the reduction of the AgNO_3 precursor from Ag^+ into Ag^0 forms Ag NPs by nicotinamide adenine dinucleotide (NADH)-dependent enzyme (A Pavlatou, 2020). To synthesize nanoparticles, bacterial species have been considered potential candidates due to their inherent ability to reduce heavy metals, as the cell wall of the bacteria is responsible for the reduction because of the presence of various important functional groups. Examples of bacterial species that may help in the green synthesis of silver nanoparticles are *Escherichia coli*, *Klebsiella pneumonia*, *Actinobacteria* sp., *Bacillus cereus*, *Lactobacillus* spp, and *Pseudomonas aeruginosa* (Arif & Uddin, 2021).

2.5.2 Fungi assisted synthesis of silver nanoparticles

Fungi are well known for their ability to decompose organic matter. Fungi can synthesize Ag NPs intra or extracellularly depending on the location of the synthesized Ag NPs. Some metal ions induce specific proteins, which can hydrolyze the ions (Naganthran et al., 2022). Fungi reduce Ag^+ ions to Ag^0 forming Ag NPs. NADH and NADH-dependent nitrate reductase are involved.

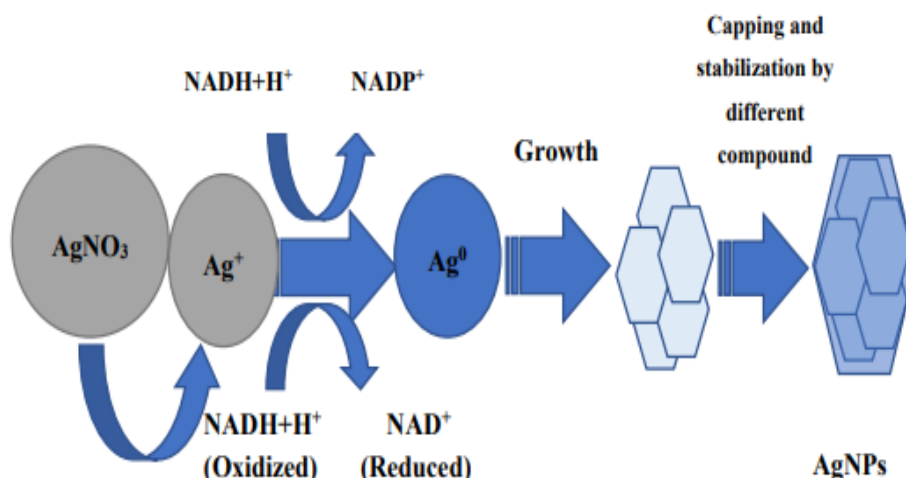


Figure 2: The supposed mechanism of silver nanoparticles biosynthesis.

Fungi are fancied because they secrete many proteins and enzymes, which directly accelerate and increase the synthesis of Ag NPs. Due to their ability to tolerate and bioaccumulate metals, fungi have attracted more attention in the biological production of Ag NPs. Biosynthesis involving fungi is usually free from toxic chemicals (Mughal et al., 2021).

2.5.3 Algae assisted synthesis of silver nanoparticles

Algae are the earliest and most abundant photosynthetic organisms on Earth. Additionally, algae are abundant in resources such as pigments, peptides, proteins, and secondary metabolites, which act as nano-bio factories. Three steps are required for Ag NP synthesis using algae: (i.) heating or boiling water or organic solvent and algal extract for a specified duration, (ii.) preparing a metal precursor solution, and (iii) incubating the precursor with algal extract under controlled conditions with continuous stirring. The color change of the AgNO₃ algal extract mixture was then monitored to determine whether Ag NPs were formed (Naganthran et al., 2022).

2.5.4 Plant assisted synthesis of silver nanoparticles

In recent years, the use of plant extracts for the preparation of metallic nanoparticles has been proposed as an easy and convenient alternative to chemical and physical methods. The plant extracts that induce Ag NP formation contain reducing agents, such as the metabolites of phenolic compounds, flavones, alkaloids, and sterols (Abdulsahib, 2021). Compared with microorganisms, plant extracts are inexpensive, easily available, and suitable for industrial use because they do not require purification or the use of cultures. Meanwhile, microbes require aseptic conditions and high maintenance. The time required for the formation of Ag NPs is faster for plant extracts than for microorganisms (Nur et al., 2020). Different parts of the plant, including fruits, roots, flowers, leaves, peels, etc., have been successfully utilized for the green synthesis of Ag NPs. In the last few years, many studies have been conducted on the green synthesis of bioactive Ag NPs using different parts of plants, such as fruits, seeds, roots, flowers, stems, leaves, and peels. For instance, the leaf extract of *Clerodendrum viscosum* was used for the facile, rapid, and eco-friendly synthesis of bioactive Ag NPs (Nahar et al., 2020). They also investigated the antimicrobial efficacy of biosynthesized Ag NPs against various pathogenic bacteria. The seeds and roots of *Durio zibethinus* and *Rheum palmatum*, respectively, were used for green synthesis of Ag NPs

(Burduşel et al., 2018). Peel extracts of different vegetables, such as *Lagenaria siceraria*, *Luffa cylindrica*, *Solanum Lycopersicon*, *Solanum melongena* and *Cucumis sativus*, were investigated for the synthesis of bioactive Ag NPs (Sharma et al., 2016). Various parameters, such as the extract salt ratio, incubation time, incubation temperature, and pH, also greatly affect the easy, rapid, high, and stable synthesis of Ag NPs using plant extracts (Huq, 2020). The probable mechanism of plant-mediated synthesis of Ag NPs is the chemistry of reduction and oxidation. It has been proposed that the plant extract contains vitamins, amino acids, proteins, enzymes, organic acids, flavonoids, terpenoids, alkaloids, polyphenols, and polysaccharides, which have significant roles in the reduction of silver salts and serve as capping and stabilizing agents (Sukweenadhi et al., 2021).

2.6 Application of Biogenic Silver Nanoparticles in Electrochemical Sensors

2.6.1 Biogenic Ag NP-Based Electrochemical Sensors

Electrochemical sensors are an important technique to analyze any target material quantitatively and qualitatively with good selectivity and sensitivity. The sensors are portable and have good sensitivity and selectivity. It does not require any prolonged procedure, skilled power, or pretreatment for the mediator. The fundamental concept in the detection of analytes by electrochemical sensors involves the measurement of electric current generated by chemical reactions in the electrochemical system. The reactions that occur at the interface of the surface of an electrode between the recognition element and the target/binding analyte generate an electrical double layer, and thus, this potential is measured after transforming these chemical reactions into this measurable electrochemical signal by a recognition element and a transducer of the sensor (Ananda Murthy et al., 2022).

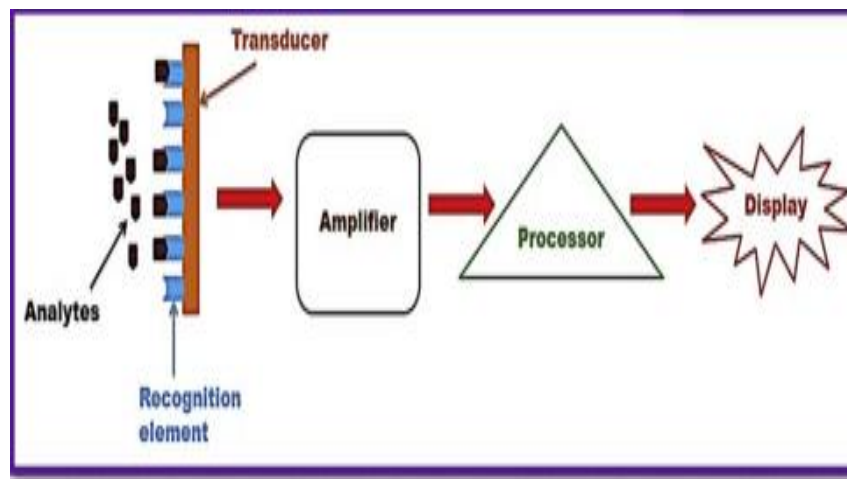


Figure 3: Basic Principle of Electrochemical Sensor

Generally, electrochemical sensing systems are based on four main components: a transducer, a capture probe, a reporter probe, and the signal transduction method. A transducer (electrode) is an element that converts chemical reactions into measurable electrical signals. Various factors can affect the transduction efficacy, such as the electrode material, kinetics of the redox reaction at the electrode surface, and electrolytic conditions. Redox-active species could be oxidized by donating electrons to the electrode or reduced by receiving electrons from the electrode surface. The oxidized or reduced species are constantly shuttled between the electrode surface and the bulk solution, forming a double layer that behaves like a parallel plate capacitor. A capture probe is an element that can recognize and bind to targeted analytes. It is usually immobilized directly on the electrode surface, enhancing its selectivity toward the targeted analytes. A reporter probe is an element that generates a signal in response to analytes. Capture probes such as aptamers and peptides can also be used as reporter probes. Signal transduction methods, which monitor changes in current or potential resulting from analyte-electrode interactions, include voltammetric, amperometry, and chronoamperometry methods (Zahran et al., 2021).

The performance of all electrochemical sensors is strongly influenced by the working electrodes. In general, the redox reaction of the electroactive species at the bare electrodes (metal electrodes, glassy carbon electrodes, screen-printed, carbon paste electrodes, and inkjet-printed electrodes) is often difficult due to the slower kinetics of the electrochemical reactions for a few compounds and

overpotential requirements. To improve the sensing mechanism, bare electrodes are usually modified with nanomaterials that exhibit excellent electrical conductivity and high catalytic activity (Tajik et al., 2021). Recently, NPs have been incorporated into electrochemical sensors to optimize the electrode material by increasing the surface area, improving the immobilization efficiency, consolidating molecular recognition, and enhancing the transduction signal (Zahran et al., 2021). Potential materials for electrode modification should permit access to NPs that possess strong adsorption ability, high conductivity, large surface-to-volume ratio, high surface reaction activity, and increased electron, and mass transfer rates. Many nanomaterials, including carbon nanostructures (e.g., graphite and CNTs), metal and metal oxides, quantum dots, silica NPs, and other NPs, have been investigated for their applications as electrochemical sensors. The surface modification of electrodes with metallic NPs has been employed extensively in the development of novel electrochemical sensors. Among the metal nanoparticles, Ag NPs are commonly used for the surface modification of electrodes. Because, silver nanoparticles have good electrical conductivity, and physicochemical properties, they supply excellent electron transfer rates with low detection limits (A. N. Ahmed et al., 2018).

A current trend in the sensor field is directed toward solving analytical problems by developing low-cost, miniaturized, and portable devices that can be operated in the field. Electrochemical techniques, used to achieve simple and sensitive analysis of particular interest because of their fast response and low detection limit (LOD). To create an electrochemical sensor, the working electrode is either glassy carbon or screen-printed. Reference electrodes (Ag/AgCl) must be used to maintain a stable potential, and counter electrodes (Au/Pt) will be used to connect to the electrolyte and provide current to the working electrode (Jayaprakash & Kannappan, 2022a).

2.6.2 Biogenic Silver Nanoparticles for Electrode Modification

Enormous effects have been required to build a sustainable sensor with high sensitivity and selectivity. To overcome this dilemma, the utilization of bio-synthesized nanomaterials is a promising tool to build biocompatible low-cost sensors that are prepared from natural sources. In this context, the main purpose of biosynthesized NPs is to develop highly sensitive, nontoxic sustainable sensors (Jayaprakash & Kannappan, 2022b). Ag NPs could be incorporated into electrodes through different in-situ and ex-situ approaches. The in-situ approach depends on the

electrochemical deposition of Ag NPs at electrode surfaces through the electrochemical reduction of Ag^+ ions with subsequent nucleation, aggregation, and coalescence of metallic particles. Electrochemical deposition is considered the most frequently used method for electrode modification (Jiang et al., 2020). The ex-situ approaches include drop casting, spin coating, sticking, transfer sticking, and carbon paste modification. Notably, gold, glassy carbon, graphite, and carbon paste electrodes were mainly used for electrode modification with Ag NPs. The efficiency of Ag NP adsorption at the electrode surface was monitored through the detection of the oxidation peak of the Ag NPs (Zahran et al., 2020).

2.6.3 Working Principles of Electrochemical Sensing Techniques

In general, three electrode systems are employed for selective voltammetric and amperometric detection of environmental pollutants, which include a working electrode (WE) where oxidation or reduction (OR) of the electroactive species (analyte) takes place, a reference electrode (RE) that provides a constant potential, and a counter electrode (CE) that is important for a complete circuit for the charge transfer process (Figure 4). The counter electrode is usually a platinum wire, and the reference electrode is either a standard calomel electrode (SCE) or a saturated (sat.) Ag/AgCl electrode (Terán-Alcocer et al., 2021). The electrodes are immersed in an aqueous primary electrolyte solution to improve ionic conductivity and reduce migration during the mass transfer of one or more targeted species. The most often used electrochemical device, voltammetric sensors, are explained in more detail below.

The working principle of voltammetry is based on the variance of the time-dependent excitation potential (linear, in pulses, or in squares), and the current output is correlated with the concentration of the analyte in Figure 4. In voltammetry, the measured current is composed of the faradic current and the charging current (also known as the non-faradic component). The faradaic current results from electron transfer between the analyte and the electrode surface and is directly proportional to the concentration of the target species. The charging current is not an analytical signal; it is the result of the perturbations in the electrode potential that lead to the charging or discharging of the electrical double layer (Karthik et al., 2022).

Cyclic voltammetry (CV) is one of the most important and widely used voltammetric techniques, where the current output is the result of a linear potential change (in the form of a triangular wave) within a given potential window. The peak current for a reversible system with diffusion control is described by the Randles–Ševčík equation (Equation (1)) (Paixão, 2020).

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2} \quad 1$$

where I_p stands for the peak current (A), n is the number of electrons exchanged in the reaction, A is the electroactive area of the electrode (cm^2), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), C is the concentration of the electroactive molecule in the electrolyte (mol dm^{-3}), and v is the scan rate (V s^{-1}). In this equation, the constant of 2.69×10^5 has units of $\text{C mol}^{-1} \text{V}^{-1/2}$.

Another technique in which the current is determined by a linearly varying electrode potential, this time in one direction, i.e., ideal for studying irreversible redox reactions, is linear sweep voltammetry (LSV). The other way to apply the potential is to use a pulse method a series of pulses with a linear baseline (differential pulse voltammetry, DPV) or a square pulse amplitude applied to a stair-step waveform (square wave voltammetry). The common denominator of stripping techniques is the preconcentration or removal of the analyte on and off the working electrode probe by controlling the applied voltage stress for highly sensitive quantification of the target molecule. Due to the analyte preconcentration, a much lower limit of detection (LOD) is achieved compared to other electroanalytical methods. The deposition step can be done in three different ways: (i) by applying a negative voltage in anodic stripping voltammetry (ASV), (ii) by applying a positive voltage in cathodic stripping voltammetry (CSV), and (iii) by adsorption of the analyte in adsorptive stripping voltammetry (Ad SV).

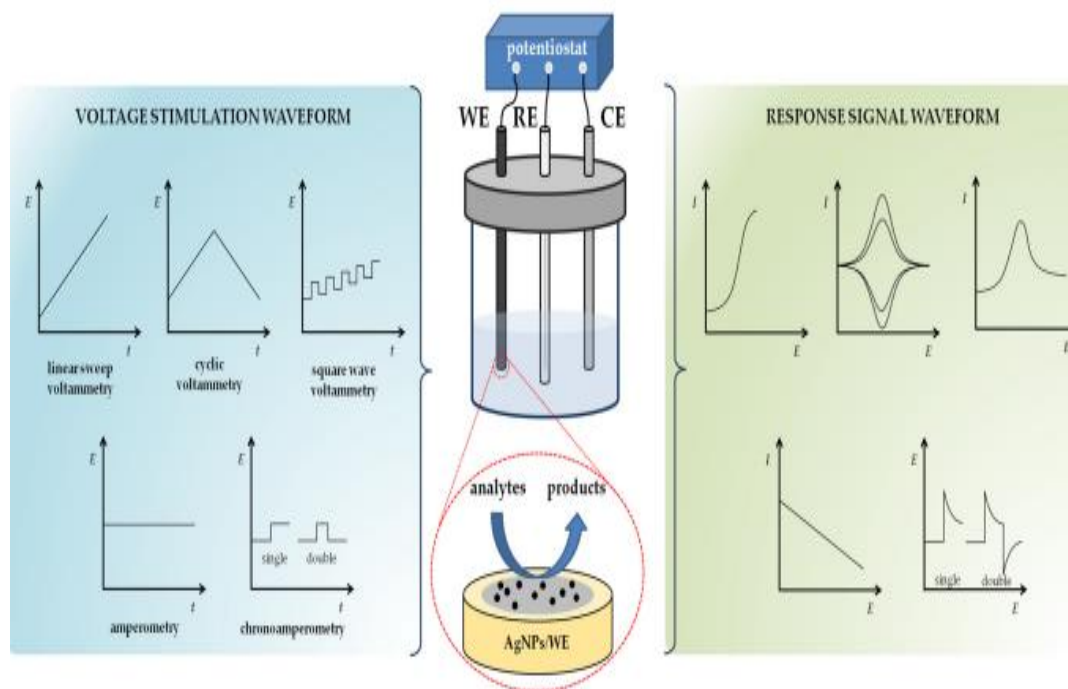


Figure 4. Schematic representation of voltammetric and amperometric techniques used for the detection of emerging water pollutants. In the scheme, E stands for potential, I for current, and t for time.

2.6.4 Electrochemical Sensors for Detection of Heavy Metal Ions

Heavy metal ions (HMI) are a group of naturally occurring metals and metalloids whose density is five times greater than that of water and are toxic even in trace amounts. Among them, mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr), and arsenic (As) are biologically non-essential elements and are classified as priority metal pollutants. On the other hand, copper (Cu) is an important component of various enzymes in humans and aquatic organisms, but has toxic effects at high concentrations. Extensive anthropogenic activities (industrial and domestic use of raw materials and metal-containing products) have resulted in widespread environmental pollution. The major problem with HMs in the environment is that they are not subject to biodegradation (Liu et al., 2019), But rather bioaccumulate in different tissues by complexing with various protein functional groups. Therefore, the release of hazardous metal species into environmental waters

from industrial or municipal waste has become a global concern. With the implementation of the Water Framework Directive (WFD) for water quality standards, the EU made the first move to reduce the harmful effects of HMs on the contamination of natural water resources (Ferrari et al., 2020). New thresholds for heavy metal contamination in tap water have been legislated for 2020, while the Drinking Water Directive (DWD) was established in 1998 to regulate the quality of water for human consumption. Therefore, the development of novel and highly sensitive sensing platforms for on-site quantification of hazardous metal ions contaminants in drinking and environmental water matrices is of extreme importance.

Among the electroanalytical detection methods for HMIs, anodic stripping voltammetry is the most used. In brief, the stripping technique involves two basic processes: (i) a deposition step, i.e., the accumulation of the analyte at the electrode surface (Equation (2)), and (ii) a stripping step, i.e., the reoxidation of the concentrated analyte in the electrode vicinity (Equation (3)). When the measurement conditions are constant, the obtained values of the oxidation peak currents are proportional to the concentrations of the analyte.



2.7 Parameters that Affect the Detection of Heavy Metal Ions

2.7.1 pH Value of the Electrolyte

It was found that HMIs have the largest stripping peak currents in certain solutions, such as acetate, phosphate-buffered saline (PBS), Tris-HCl, and Britton–Robinson (B-R) buffer solution, at suitable pH and concentration levels. When the pH values were too high, the HMI tended to hydrolyze, resulting in the reduction of the accumulating ions. The decrease in the currents at low pH values is probably because the protons and metal ions compete to bind with the donating atoms on the surface of the electrode (Yuanyuan et al., 2017). Because HMIs easily hydrolyze at a higher pH level, this pH range was chosen as the optimal acidity level for the analysis.

2.7.2 Deposition Potential.

The deposition potential is generally optimized due to its impact on the reduction rate. In addition, a more positive deposition potential can lead to an unstable reduction reaction, affecting the reproducibility of stripping analysis. A more negative deposition potential may lead to hydrogen evolution and reduction of other heavy-metal ions, by which interferences may be introduced.

2.7.3 Deposition Time.

In a certain range of deposition times, the stripping current of heavy metals is linearly correlated with deposition time. A larger deposition time can lead to saturation of the working electrode due to the small effective area of the working electrodes, which affects the linear detection range in heavy-metal analysis. A short deposition time leads to a decrease in sensitivity and current response in stripping analysis (Yuanyuan et al., 2017).

2.7.4 Scanning Rate.

Generally, the stripping peak current is linearly correlated with the scanning rate, while a faster scanning rate may introduce larger background noise and charging current.

3. MATERIALS AND METHODS

3.1 Chemicals and Apparatus

All chemicals used in this work were of analytical grade and were not further processed. Silver nitrate (99.98%, BDH), graphite powder (< 100 99.0%, Blulux), paraffin oil (370–500 mPas viscosity) (BDH), Cd (NO₃) 4H₂O (99.5%, BDH), Pb (NO₃)₂ (99.5%, BDH), HNO₃ (65%, UNICHEM), HCl (37%, Blulux), H₂O₂ (30%, Blulux), glacial acetic acid (99.5%, Blulux), sodium acetate (98%, Blulux), ethanol (≥ 97%), sodium hydroxide (97%, Blulux), potassium ferricyanide (II) trihydrate (ACS 98.5–102.0%), ethanol (≥ 97%), sulfate, chloride, and nitrate salts of reagent grade ions from (Merck and Sigma-Aldrich) were used for the optimization and interference study, and double distilled water was used.

The Ivium Technologies electrochemical workstation (Eindhoven, Netherlands) is a cutting-edge piece of equipment. The Nimbus analytical electronic balance, manufactured by Hoven Labs in Korea, is another essential tool. Additionally, we utilized a magnetic stirrer, centrifuge from Remuigyog Bomba in India, mortar and pestle, pH meter from Adwa in Hungary, UV-Vis spectrophotometer (Jasco V-770 spectrophotometer) from Japan, X-ray diffractometer (Shimadzu Corporation; XRD-7000 X-ray diffractometer), FT-IR spectrometer (Thermo Scientific Nicolet iS50) from the USA, SEM (JCM-6000 plus BENCH TOP SEM) from Shimadzu Corporation in Japan, dynamic light scattering from Malvern Panalytical in the UK, and a hot plate from Daihan Scientific in Korea.

3.2 Sampling and Preparation

The plant *Hagenia abyssinica* was collected in southeastern Ethiopia in the Oromia regional state in the East Arsi zone (Qarsa town), 235 km from Addis Ababa. Fresh leaves of *Hagenia abyssinica* were washed several times with running tap water and then with distilled water to remove dust particles. Then, they were allowed to dry in the shade at room temperature for 15 days to remove moisture from the leaves. The dried leaves were crushed with an electric grinder to produce a fine powder. Finally, the dried and ground samples were stored for further processing. Figure below



Figure 5: Steps involved in the collection of *Hagenia abyssinica* plant leaves

3.3 Preparation of the Plant Leaf Extract

For the extraction of the plant leaf fraction, 20 g of powdered leaves of *Hagenia abyssinica* were placed in a 500 mL conical flask containing 400 mL of deionized water. The flask was later covered with aluminum foil to prevent exposure to light. The mixture was then shaken with a mechanical shaker for 30 minutes, heated on a magnetic stirrer at 50 °C for 1 hour, and then cooled to room temperature overnight. Then, the prepared solution was filtered twice with Whatman No.1 filter paper to obtain a clear extract solution. The filtrate was stored at 4 °C for future experiments (Melkamu & Bitew, 2021).

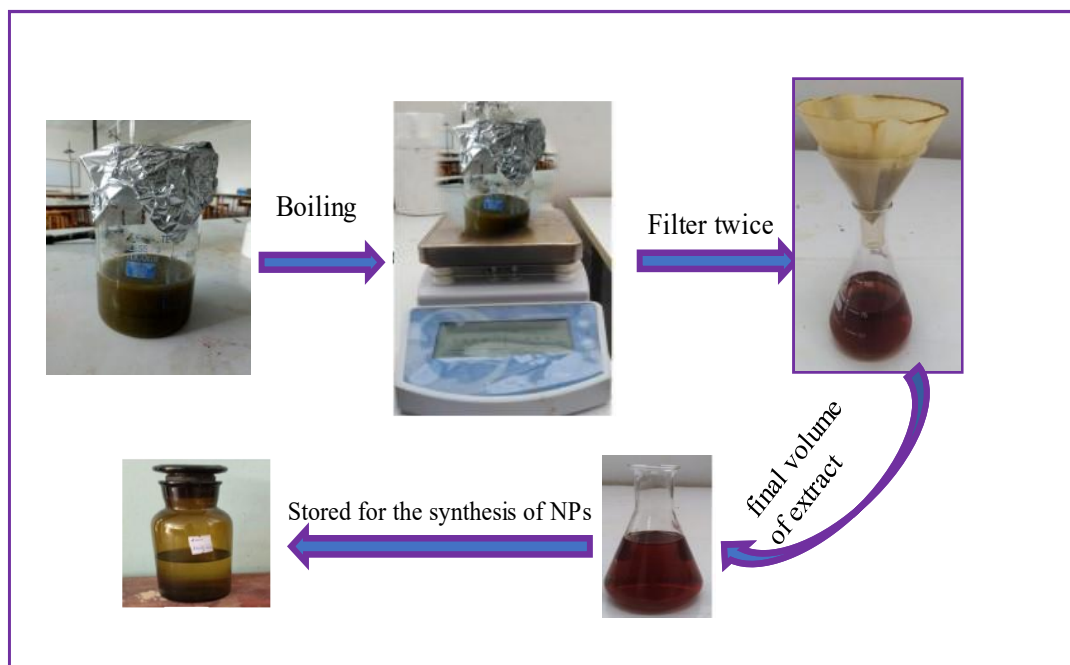


Figure 6: Steps involved in the preparation of *Hagenia abyssinica* plant leaf extract

3.4 Green Synthesis of Silver Nanoparticles Using *Hagenia abyssinica* Leaf Extract

In a typical experiment, biogenic silver nanoparticles were synthesized by mixing a solution of *Hagenia abyssinica* leaf extract with 0.15 M AgNO_3 . The extract was added to the silver nitrate precursor solution in three different ratios by volume. For a 1:1 ratio of 100 mL of silver nitrate and 100 mL of leaf extract, a 1:3 ratio of 50 mL of silver nitrate and 150 mL of leaf extract, and a 3:1 ratio of 150 mL of silver nitrate and 50 mL of leaf extract, Then, we added leaf extract slowly dropwise with constant stirring on a hot plate for 10 minutes at 40 °C, and all samples were continuously stirred magnetically for 2 hours without temperature. The appearance of a reddish-brown color visually indicates the formation of silver nanoparticles. The solution was left overnight, and the precipitate was separated by centrifugation at 10000 rpm for 20 minutes, followed by washing with deionized water and ethanol more than once. Then, the collected nanoparticles were further dried by using a hot air oven for 1 hour at 80 °C and ground to a fine powder for further analysis (Jebril et al., 2020).

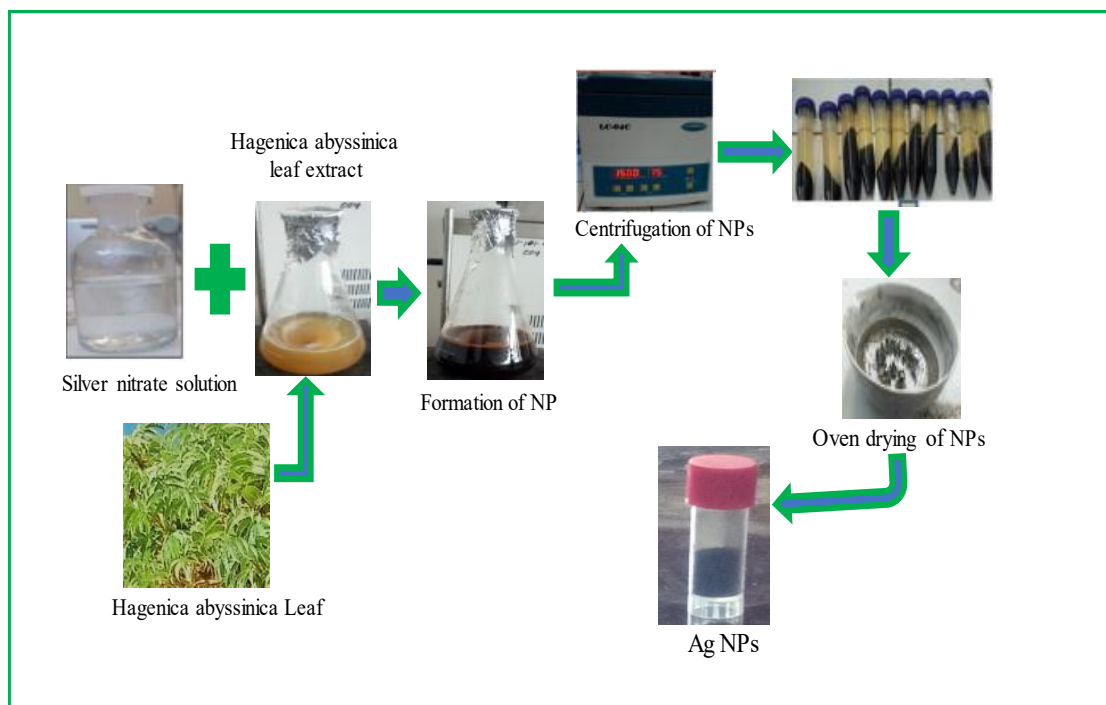


Figure 7: Schematic diagram of the synthesis procedure for green-Ag NPs

3.5 Preparation of the Carbon Paste Electrode

In this study, an unmodified carbon paste electrode was prepared by mixing 1.0 g of graphite powder and 0.357 g of paraffin oil (in a ratio of 70:25% w/w) and homogenizing thoroughly with a mortar and pestle for 30 minutes. The paste was then left for another 24 hours. Finally, the carbon paste was crammed into an electrode made from a 1 mL plastic syringe, on the opposite side of which a copper wire was inserted to establish electrical contact. The surface of the prepared carbon paste electrode was smoothed on clean paper before use. A thin layer of the surface was removed and replaced by a fresh paste whenever regeneration of the electrode was needed. Keeping the amount of graphite powder and paraffin oil constant (1.0 and 0.357 g, respectively), five modified carbon paste electrodes were prepared by varying the mass of Ag NPs added (5, 10, 15, 20, and 30 mg of biogenic Ag NPs). Then, five mixtures of graphite powder, paraffin oil, and varied amounts of Ag NPs were homogenized for 30 minutes and left for an additional 24 hours. Finally, five carbon paste electrodes modified with various amounts of Ag NPs were prepared (Amare et al., 2020).

3.6 Characterization Technique

The formation of synthesized Ag NPs was confirmed using UV-visible spectroscopy. Their optical properties were measured using a UV-Vis spectrophotometer (Jasco V-770 Spectrophotometer; Japan) at Addis Ababa Science and Technology University under the central laboratory department in the wavelength range of 200–800 nm with a 1nm resolution.

By utilizing an innovative X-ray diffractometer (Shimadzu Corporation (Japan); XRD-700 X-ray diffractometer) at the Adama Science and Technology University Material Science Department, XRD analysis was also conducted to demonstrate the crystalline character of the biologically produced Ag NPs. Using Cu K ($= 1.5406 \text{ \AA}^0$) radiation and an accelerated voltage of 40 KV, the X-ray diffraction patterns were captured in the range of 2θ from 10 to 80 at a scan rate of 20/min.

FTIR analysis was performed via Fourier transform infrared spectroscopy (Thermo Scientific Nicolet iS50, USA) at Addis Ababa Science and Technology University under the Chemical Engineering Department. The infrared spectra were derived from the produced Ag NPs in the range of $4000\text{--}400 \text{ cm}^{-1}$ at 16 cm^{-1} resolution and assigned peak numbers. An FTIR spectrometer was used to determine the organic functional groups linked to the surface of silver nanoparticles responsible for the reduction, stabilization, and capping agents.

SEM analysis of the biosynthesized Ag NPs was carried out using SEM (JCM-6000 plus BENCH TOP SEM, Shimadzu Corporation, Japan) at Korea University, which reveals information about the external morphology of the biosynthesized silver nanoparticle sample with direct visualization, and dynamic light scattering method was employed for the particle size analysis of the synthesized Ag NPs using Malvern Zetasizer nanosized (Malvern Panalytical, UK) in the size range of 0.1–10.000 nm.

3.7 Electrochemical Measurements

Voltametric experiments such as cyclic voltammetry (CV) and square wave anode stripping voltammetry (SWASV) were carried out using Ivium Technologies Eindhoven, Netherlands, connected to a personal computer at Adama Science and Technology University under the Applied Chemistry Department. Electrochemical experiments were performed employing a conventional

three electrode system with CPE or Ag NPs/CPE as the working electrode, a platinum coil as an auxiliary electrode, and Ag/AgCl as a reference electrode in a 0.1 M acetate buffer solution. The potential range utilized during these studies ranges between -0.1 V and 0 V.

All voltammetric measurements were performed using the following steps:

(a) Preconcentration step: In this step, the first acetate buffer solution (0.1 M, pH 5.0) was transferred into the voltammetric cell, and a known amount of Cd (II) and Pb (II) were spiked into it. The unmodified and modified carbon paste electrodes were then immersed into the cell, and Cd (II) and Pb (II) were accumulated on the surface of the electrodes by applying a potential of -1.1 V versus Ag/AgCl for a preselected period. At the end of the preconcentration time, a 10 second rest allowed the solution to become quiescent.

(b) Stripping step: cyclic or square wave voltammograms were recorded in the positive potential direction from -1.0 to 0 V versus Ag/AgCl. The pulse amplitude, frequency, and step potential were 10 mV, 10 Hz, and 6 mV, respectively. After each measurement, the electrode was renewed and pretreated by scanning (4–5 runs) in a 0.1 M acetate buffer solution. A fresh supporting electrolyte solution was used in each set of experiments to avoid the potential buildup of Cd (II) and Pb (II) in the electrochemical cell. Moreover, all electrochemical measurements were made at room temperature (24 ± 2 °C), and various optimization studies were carried out with Ag NPs and CPE. The cell was a one-compartment cell with an internal volume of 50 ml.

3.8. Cd (II) and Pb (II) Determination in Real Samples

To examine the practical utility of the biogenic Ag NP/CPE for the simultaneous sensing of Cd (II) and Pb (II), wastewater samples were used. The samples were collected from around Mojo town, which discharges wastewater from the leather industry into Lake Mojo. The water samples were filtered before the analysis to remove suspended particles. Moreover, the sample needs to be digested because it may contain organic matter that interferes with my work. Therefore, digestion was prepared following a procedure reported with slight modifications (Mekuria et al., 2021). 100 mL of water sample was placed into a 250 mL Erlenmeyer flask, to which a mixture of 30 mL of 65% HNO₃, 15 mL of 37% HCl, and 1.24 mL of 30% H₂O₂ was added. After that, the sample was digested for 1 hour using a hot plate at 95 °C until the brown gas was completely removed. The

flask was removed from the hot plate following the formation of a limpid solution and allowed to cool to room temperature. Then, the solution was transferred into a 100 mL volumetric flask by filtering with Whatman No. 1 filter paper, which was then diluted to the mark with distilled water. The pH of the samples was adjusted to pH 5 with 0.1 M acetate buffer prior to determination, and the optimal conditions were used for heavy metal ions detection in these experiments. The water samples were also spiked with a known concentration of standard solutions of Cd (II) and Pb (II) for the recovery study.

4. RESULTS AND DISCUSSION

4.1 Characterization of Synthesized Silver Nanoparticles

4.1.1 UV-Visible Spectroscopy Analysis

UV–Visible analysis was employed to validate the synthesized AgNP formation through surface plasmon resonance (SPR). Here, Ag NPs were synthesized using *Hagenia abyssinica* leaf extracts. Plant biomaterials were used as reducers, stabilizers, and cappers. After 10 min, and after adding the leaf extracts to the AgNO₃ solution, a modification of the obtained mixture, which changes from yellow to brown color, was observed, because of surface plasmon vibrations; this index indicates the production of Ag NPs. The active molecules present in the leaf extracts reduce Ag⁺ to Ag⁰. The NPs then generate clusters by the Ag atoms, and the biomolecules present in the mixture are responsible for their stabilization (Jebril, Fdhila, et al., 2021). Figure 9 presents the UV-Vis spectra in the range of 300–800 nm for the AgNO₃ aqueous solution, crude leaf extract, and the dark brown-colored mixture of the two. While no peaks were observed for either the precursor solution (curve a) or crude leaf extract (curve b) at the expected wavelength range of silver nanoparticles, a well-shaped peak centered at approximately λ_{max} 423 nm (curve c) for the mixture of the precursor solution and plant extract confirmed the synthesis of small silver nanoparticles. This absorption spectrum was obtained from the Ag NPs due to the surface plasmon resonance of valence electrons in atomic silver between the conduction and valence bands.

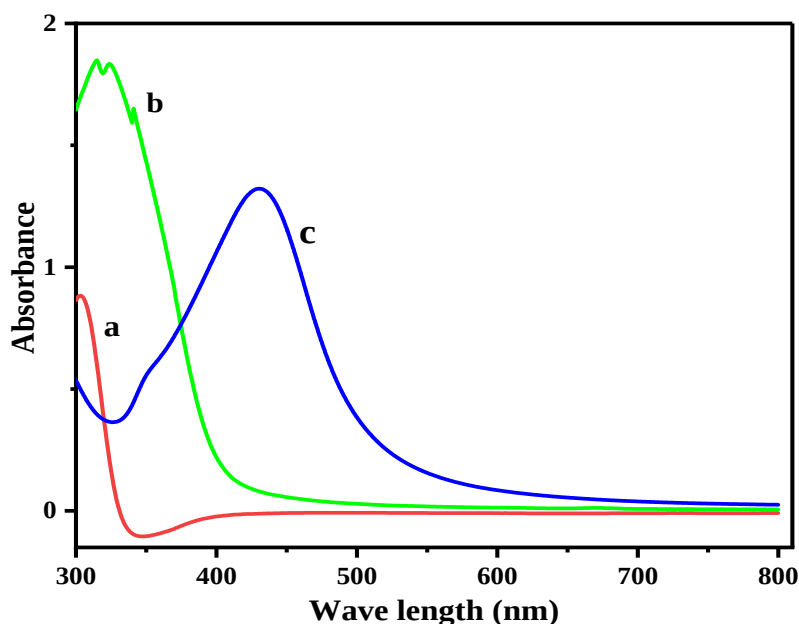


Figure 8: UV-Visible spectra of (a) AgNO₃ aqueous solution, (b) crude extract of *Hagenia abyssinica* leaf, and (c) Biosynthesized of Ag NPs.

Optical Band Gap Study

The optical properties have been observed by obtaining the absorption spectra from UV-Visible spectroscopic in the range wavelength from 300-800 nm. The absorption co-efficient related to the optical band gap has been calculated by using Tauc's plot method as follows:

$$\alpha = \left(\frac{k}{h\nu} \right) (h\nu - E_g)^n \quad 4$$

where α is a constant, $h\nu$ is the photon energy, h is Planck's constant and n is a number that describes electronic transition between valance and conduction bands, and E_g the energy band gap. The band gap energy of the green synthesized silver nanoparticle by using *Hagenia abyssinica* plant leaf extract was analyzed by using Tauc's plot method by extrapolating the linear portion of the UV-Visible curve which is shown in Figure 9-11. These band gap results show that the energy band gap of the Ag NP (1:1), Ag NP (1:3), and Ag NP (3:1) nanoparticles are 2.54 eV, 2.60 eV, and 2.49 eV respectively. Among the three nanoparticle ratios of Ag NPs, 1:3 volume ratios have

larger band gap energy and this indicates that the energy bandgap of AgNP is associated with particle size. The smaller particle size contains fewer number of atoms and reduces the potential attraction between the conduction electrons and metal ion of the particles. Due to this conduction band energy increases for the smaller particles. But for larger particles size contains larger number of atoms, thus increasing the attraction between conduction electrons and metal ions and therefore reduction the conduction band energy of the metal nanoparticles. In general, the particles with the large value of band gap energy can be further used in advance optoelectronic devices, batteries and sensors as a semi-conductive material. The value of band gap is much similar to earlier reported literature and this value could be due to quantum confinement effect (Das et al., 2016).

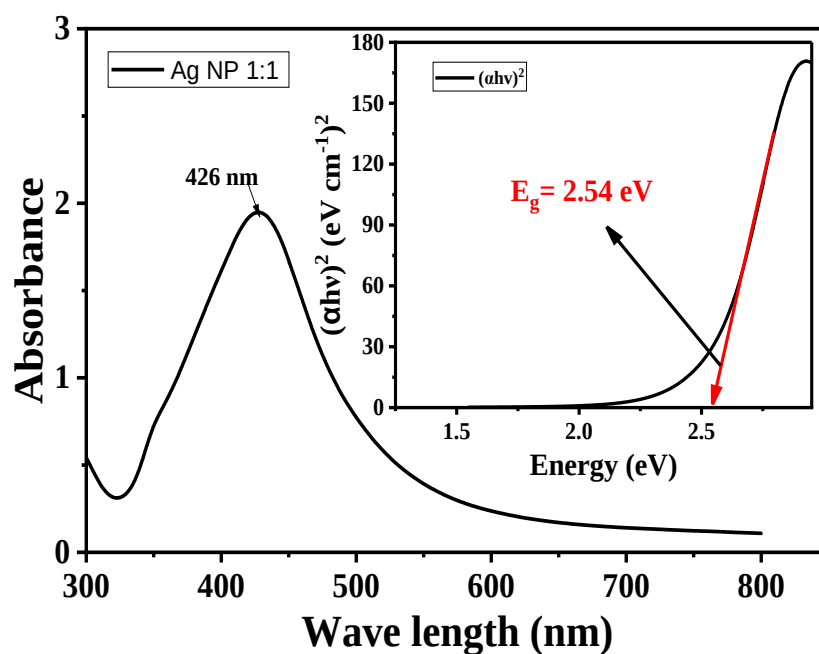


Figure 9: UV-Visible spectra of green-synthesized Ag NPs (1:1) and its corresponding band gap energy

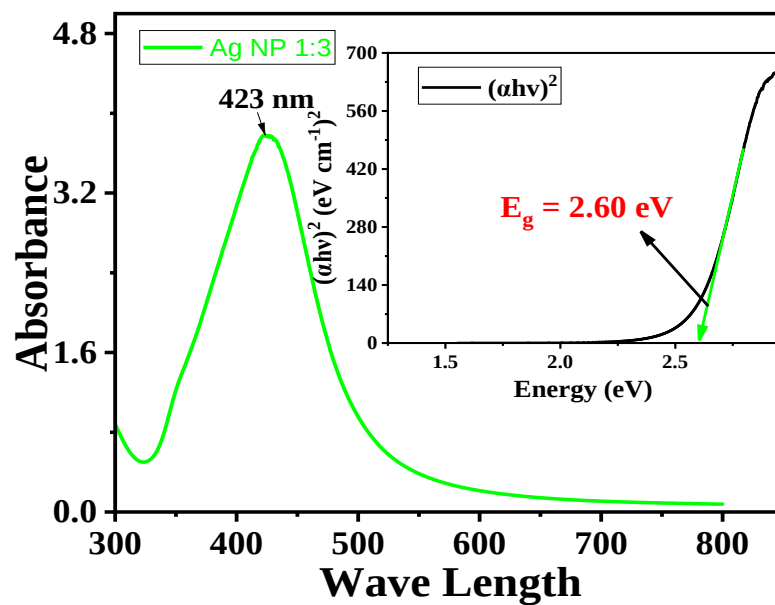


Figure 10: UV-Visible spectra of green-synthesized Ag NPs (1:3) and its corresponding band gap energy

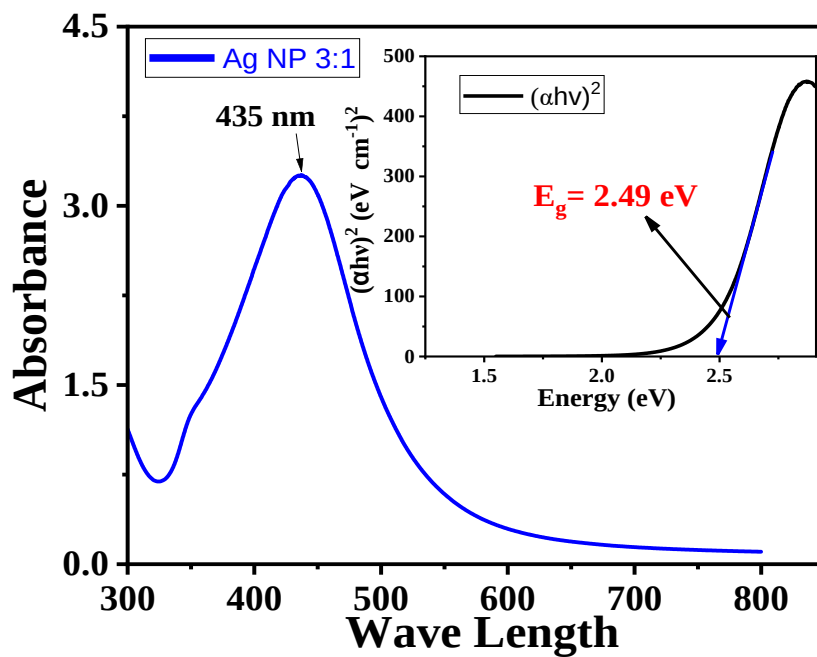


Figure 11: UV-Visible spectra of green-synthesized Ag NPs (3:1) and its corresponding band gap energy.

4.1.2 X-ray Diffraction (XRD) Analysis

XRD is a powerful characterization technique for both qualitative and quantitative analyses of nanoparticles. XRD analyses were used to confirm the formation of nanoparticles and determine their crystal structure. In addition, this technique has been used to calculate the crystalline nanoparticle size and measure the degree of crystallinity (Alharbi et al., 2022). The phase purity and crystallinity of the synthesized silver nanoparticles can be identified by XRD analysis. Three samples were synthesized with three metals to plant extract ratios: (1:1), (1:3), and (3:1). The XRD patterns of these samples show similarity in the peak position and intensity distribution, as shown in Figure 12. The diffraction peak was observed for (1:1 ratio of Ag NPs) in (curve a) at $2\theta = 38.12^\circ$, 44.03° , 64.41° , and 77.41° , which corresponds to the crystal plane of (111), (200), (220), and (311). Again, as shown in (curve b), the 1:3 ratio diffraction peaks were found at 2θ values of approximately 38.14° , 44.23° , 64.49° , and 77.41° , which could be assigned to the crystal planes of (111), (200), (220), and (311). Similarly, for the 3:1 ratio in curve c, diffraction peaks were observed at 2θ values of 38.15° , 64.41° , and 77.41° , which correspond to a crystal plane of (111), (200), (220), and (311), respectively.

The diffraction patterns of Ag NPs were found to be in good agreement with Joint Committee on Powder Diffraction Standards (JCPDS) card number 004-0783, which confirms the formation of pure Ag NPs without the formation of any secondary phase. This implies that the green synthesized AgNP possessed higher crystallinity, and no XRD detectable impurities were observed in this sample, which confirms the purity of the Ag NPs. The diffraction peaks (111), (200), (220), and (311) represent face-centered cubic silver, while the sharpness of these peaks indicates the formation of nanosized particles (Alharbi et al., 2022).

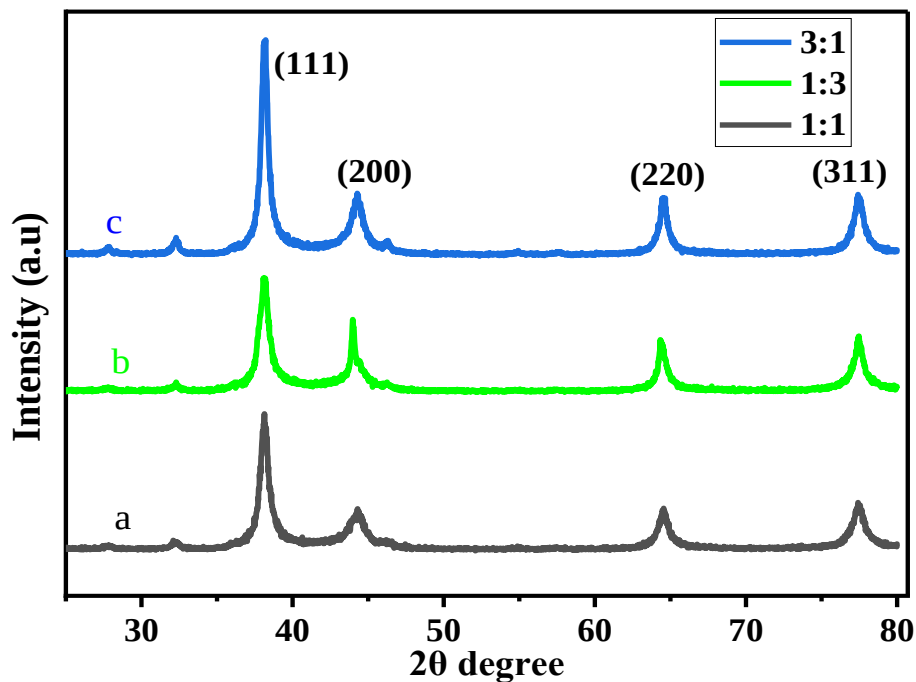


Figure 12: XRD patterns of green synthesized Ag NP using: (a) 1:1, (b) 1:3, and (c) 3:1 mass ratio of AgNO₃ aqueous solution to plant extract.

The crystal size of the green synthesized silver nanoparticles was calculated by using the Debye-Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad 5$$

where D is the estimated crystal size in nanometer (nm) from XRD patterns, θ is the Bragg angle in radians, λ is the wavelength of the X-ray source used ($\text{CuK}\alpha = 1.5406 \text{ \AA}$), β is the angular width at the half maximum of the diffraction peak in radians and K is the shape factor or Scherrer constant (0.9) of Debye-Scherrer's equation. As a result, the crystal sizes of the green synthesized silver nanoparticles corresponding to the highest intensity peaks (1:1), (1:3), and (3:1) were calculated and found to be 14 nm, 12 nm, and 16 nm, respectively. The results showed that the plant extract was responsible for the reduction or capping of the nanoparticles. It was also observed that the size of the NPs decreased with increasing amounts of the plant extract. It has been reported that the electrocatalytic activity of nanoparticles is highly dependent on their size and morphology. In

addition, the presence of smaller nanoparticles could be more beneficial for sensor development than larger nanoparticles (Jebril, Fdhila, et al., 2021). Here, Ag NPs in a 1:3 ratio of plant leaf extract to AgNO₃ solution are smaller in size than the other NPs.

Table 1: XRD data of synthesized Ag NPs.

Sample name	Peak position (2θ)	FWHM (deg)	Crystal size (D) (nm)	Average (D) (nm)
Ag NPs 1:1	38.12	0.77600	10.46843795	14
	44.03	0.57860	14.81005597	
	64.41	0.62360	15.05578083	
	77.41	0.67110	15.16924551	
Ag NPs 1:3	38.14	0.66960	12.55314614	12
	44.23	1.08000	7.939965605	
	64.49	0.71500	13.13694753	
	77.41	0.77170	13.19175931	
Ag NPs 3:1	38.15	0.54500	15.42356013	16
	64.51	0.56000	16.77491413	
	77.41	0.66930	15.21004133	

4.1.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier transform infrared spectroscopy analysis can assist in identifying biomolecules responsible for reducing Ag^+ ions and stabilizing the synthesized Ag NPs. To check the capped biomolecules with Ag NPs, an FTIR study was performed to confirm the functional groups that are responsible for reduction, stabilization, and capping agents, and it was compared with the FTIR spectrum of leaf extract alone. FTIR absorption spectra of green synthesized Ag NPs and *Hagenia abyssinica* leaf extract were studied in the range of 400 - 4000 cm^{-1} , as presented in Figure 13. FTIR analysis was performed for both plant leaf extract and green-synthesized Ag NPs. Figure 13 (curve a) shows the FT-IR spectrum of *Hagenia abyssinica* leaf extract. The broad band at approximately 3294 cm^{-1} is due to the N–H stretching vibration of the NH_2 group and the O–H group of the overlapping stretching vibration attributed to water and phenolic compounds present in the plant extract. The stretching mode of the carbonyl group ($\text{C}=\text{O}$) and N–H bending primary amides was observed at 1634 cm^{-1} , suggesting the presence of carboxylic, aldehydes, esters, or ketone-containing compounds arising from flavonoids and tannins.

The FTIR band of the synthesized Ag NPs in Figure 13 (curve b) showed a change in the position and intensity of the peaks. The displacement at 3435 cm^{-1} may be related to hydrogen bond breakage, which plays a role in reducing silver ions into silver nanoparticles. The similarity of the spectral pattern for plant leaf extract and the synthesized nanoparticles may be evidence for the existence of the identified phytochemicals in the synthesized Ag NPs. In addition, the FTIR spectrum of biogenic-Ag NPs shows peaks corresponding to the weak intensity and broad band centered at 629 cm^{-1} , which is possibly due to the interaction of Ag with protein molecules in the extract.

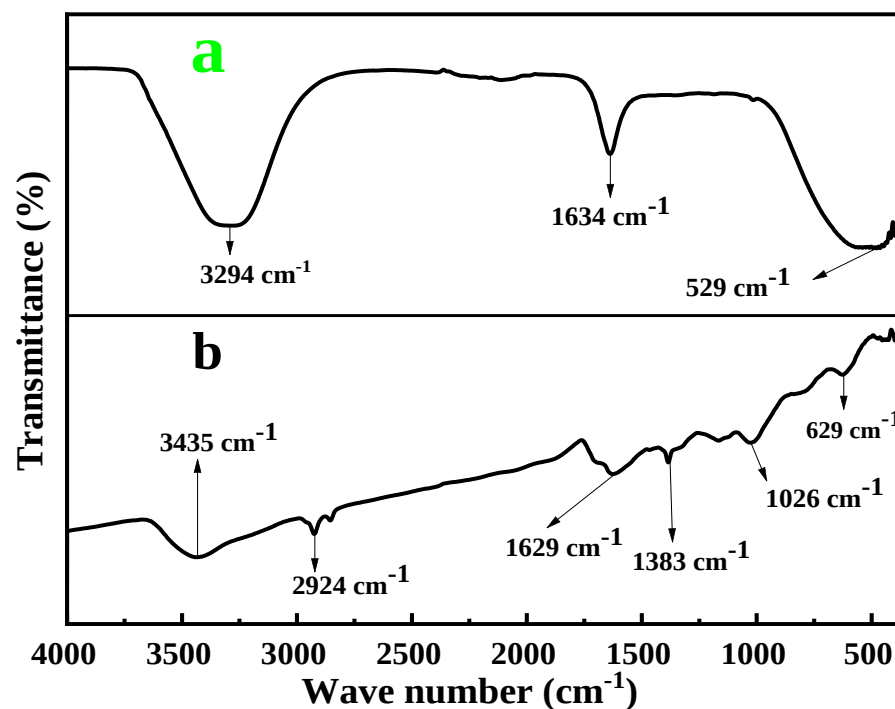


Figure 13: FTIR spectra of (a) *Hagenia abyssinica* leaf extract and (b) synthesized Ag NPs.

4.1.4 Scanning Electron Microscopy (SEM) Analysis

Among the various electron microscopy techniques, SEM can determine the surface morphology of nanoparticles, such as their shape, size, and size distribution (Alharbi et al., 2022). The results of the SEM analysis are presented in Figure 14 below. In this study, SEM analysis was utilized to identify the morphology and size of stabilized biogenic Ag NPs at several magnifications (1.00 kx, 10.00 kx, 50.00 kx, and 30.00 kx) in Fig. 14 (A–D), and the results showed that Ag NPs have spherical shapes with different sizes ranging from 10 to 20 nm. The average particle size was measured to be approximately 17 nm. The particle size distribution was calculated from a histogram, considering 200 particles, from which, the average biogenic AgNP size was measured using ImageJ software. In general, the results suggested that *Hagenia abyssinica* leaf extract plays roles as a reductant and capping agent to synthesize and scatter Ag NPs.

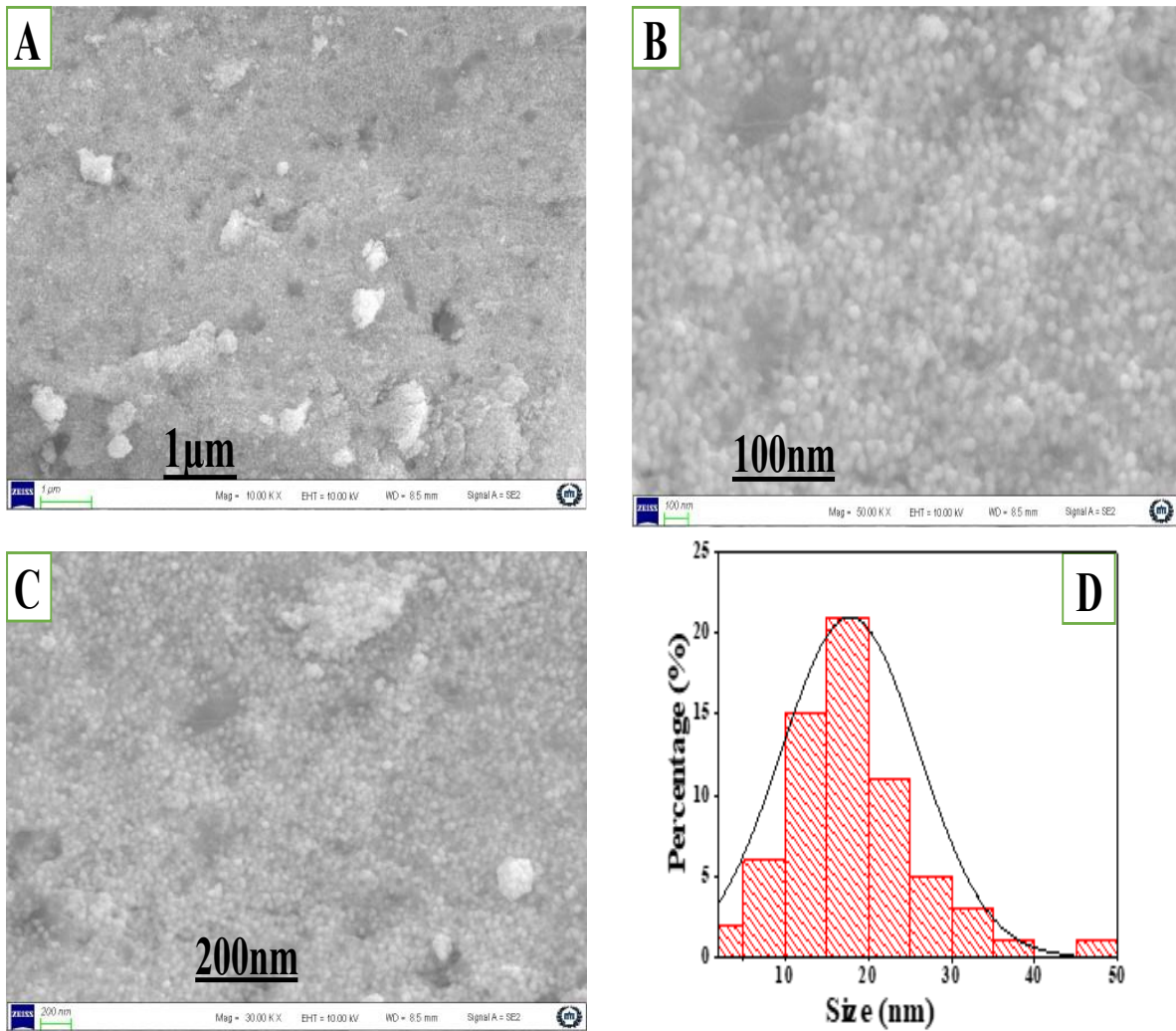


Figure 14: (A-C) SEM image of Ag NPs synthesized using *Hagenia abyssinica* leaf extract at different magnifications: (A) 10.00 kx, (B) 50.00 kx, (C) 30.00 kx, and (D) their corresponding size distribution histogram

4.1.5 Dynamic Light Scattering (DLS) Measurement Analysis

The dynamic light scattering technique determines the hydrodynamics of nanoparticle size and is measured in an aqueous suspension containing a metallic core, ions, and biological biomolecules attached to the surface of NPs (Alwhibi et al., 2021). In this study, the DLS measurements of the average size of biogenic Ag-NPs are depicted in Figure 15. The average particle size of the formed biogenic Ag NPs was approximately 23.56 nm, while the single peak below and the polydispersity index value of 1.000 derived from dynamic light scattering described the degree of uniformity and homogeneity of the nanoparticles.

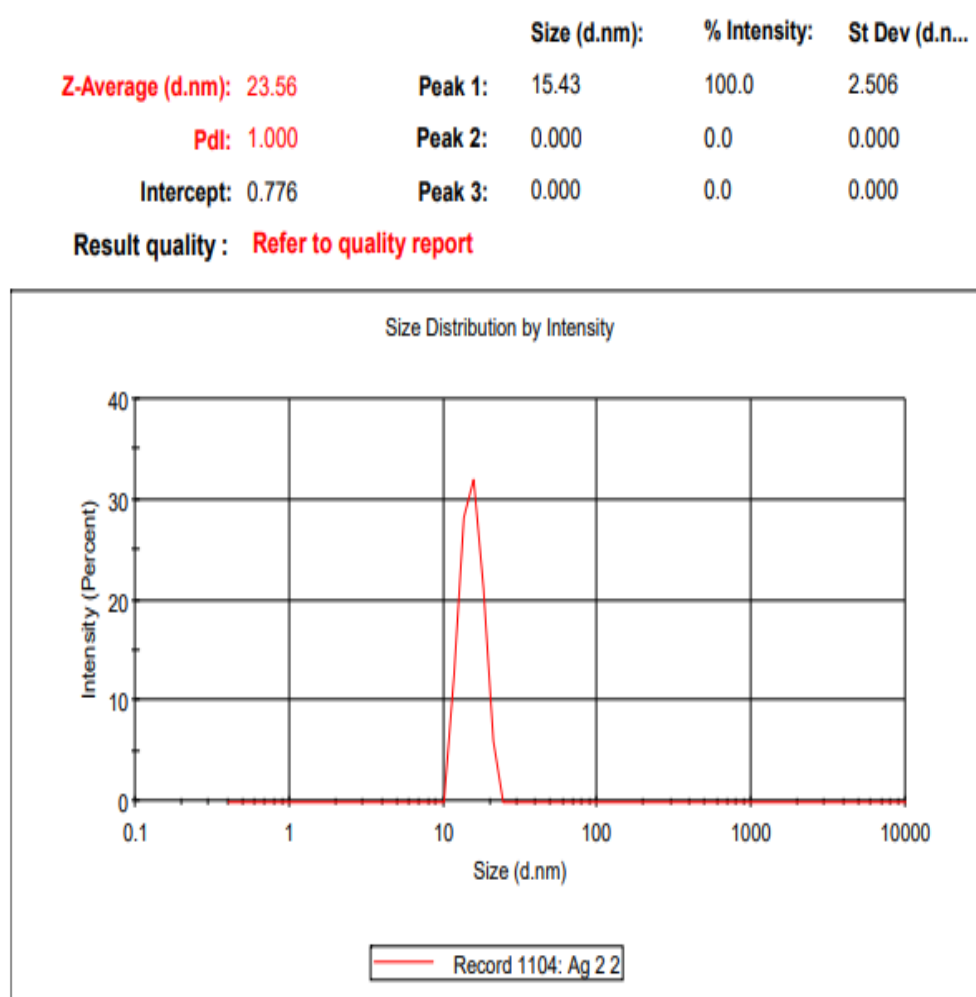


Figure 15: DLS measurement of the average size of biogenic synthesized Ag NPs.

4.2 Electrochemical Characterization of Ag NPs/CPE

It should be noted that both bare and modified electrodes were evaluated by cyclic voltammetry (CV) in a 0.1 M KCl solution containing a redox probe 1 mM [Fe (CN)₆]^{3-/4-} solution to evaluate the Ag NP/CPE functions. Fig. 16 displays the CV voltammogram of [Fe (CN)₆]^{3-/4-} redox at the bare CPE (curve a) and Ag NP/CPE (curve b) modified electrodes. The bare CPE exhibited an irreversible electrochemical response for the redox reaction of [Fe (CN)₆]^{3-/4-} coupled with a peak-to-peak (ΔE_p) separation of 0.35 V. Moreover, the irreversible redox current response ($\Delta E_p = 0.48$ V) was intensely augmented by modifying the CPE with Ag NPs in comparison with the bare modified electrode. Such a condition might be due to the accelerated transfer of electrons and larger surface areas of the Ag NPs/CPE, resulting in greater current responses. In addition, the peak-to-peak potential separation of the Ag NP modified electrode (curve b) increased ($\Delta E_p = 0.48$ V), and the peak current (7.40 μ A) increased significantly in comparison with the response current obtained at the bare CPE (4.48 μ A). Therefore, the increased current in the Ag NP modified electrode was attributable to the high conductivity, good antifouling property, fast electron transfer rate, and high electrochemical activity of the Ag NPs present at the surface of the electrode, which remarkably augmented the electrode function toward analyte oxidation. This conclusion is also supported by the results of the electrodes' active area. The electrochemically active area (A) of the electrodes was calculated according to the Randles-Sevcik equation below.

$$I_p = 2.691 \times 10^5 \times n^{3/2} \times A \times D^{1/2} \times C \times v^{1/2}$$

where I_p is the peak current (μ A); n is the number of electrons exchanged ($n=1$); A is the surface area of the electrochemically active electrode (cm^2); D is the diffusion coefficient of the pair [Fe (CN)₆]^{3-/4-} in solution ($6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$); C is the concentration of [Fe (CN)₆]^{3-/4-} (1 mM); v is the potential sweep rate (V s^{-1}). The calculation reveals that the surface area of biogenic Ag NPs/CPE is (0.21 cm^2), much larger than that of CPE (0.013 cm^2). These results explained why the CPE modified by biosynthesized Ag NP give increased electrochemical response compared to using the bare CPE or just modifying each individual component.

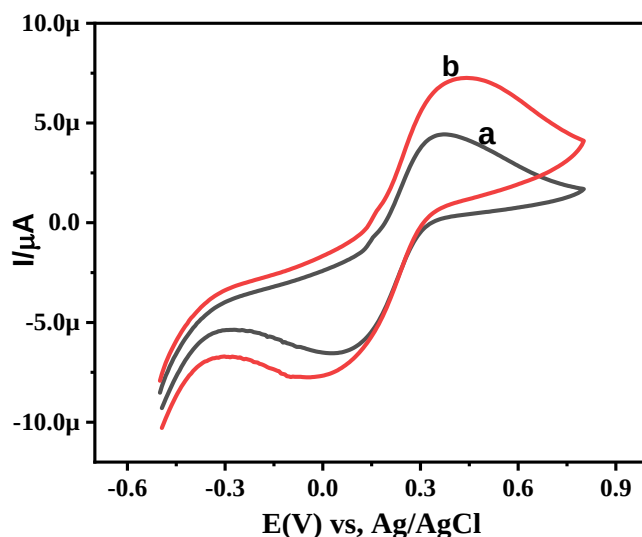


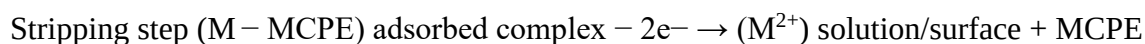
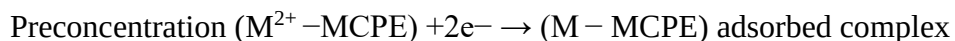
Figure 16: Cyclic voltammograms of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (1 mM in 0.1 M KCl): (a) CPE and (b) Ag NPs/CPE. Scan rate: 50 mV/s.

4.2.1 Electrochemical Behavior of Cd (II) and Pb (II) at the CPE and M-CPE

In this study, the electrochemical behavior of two distinct electrodes, the bare/CPE and the modified AgNP/CPE, for detecting Cd (II) and Pb (II) was investigated. Fig.17 shows the cyclic voltammograms of Cd (II) and Pb (II) at unmodified and modified electrodes in ABS (0.1 M, pH 5.0) in the potential range -1.0 V and 0 V versus Ag/AgCl electrode. As seen in the figure, no redox peaks were observed within the investigated potential range for the unmodified CPE (not shown) and Ag NP-CPE (cycle b, blank line) in the absence of Cd (II) and Pb (II) ions. In the presence of Cd (II) and Pb (II) ions, unmodified CPE (cycle a red line) shows a medium anodic peak at -0.68 V and -0.44 V and a cathodic peak at a potential of -0.80 V and -0.66 V, while the modified electrode (cycle c, green line) exhibits a strong anodic peak current at -0.66 V and -0.40 V and a cathodic peak at -0.79 V and -0.59 V. In comparison with the unmodified CPE, the peak intensity enhancement and peak shift at the Ag NP/CPE are due to the complex formation of Cd (II) and Pb (II) ions with the Ag NPs. The anodic peak currents of Cd (II) and Pb (II) at the Ag NP-modified electrode are substantially larger and sharper than the corresponding cathodic peak currents. Hence, the anodic peaks of Cd (II) and Pb (II) were systematically studied by square wave anodic stripping voltammetry for analytical application.

Figure 18 below shows square wave anodic stripping voltammograms for simultaneously determining 33.1 $\mu\text{g/L}$ Cd (II) and Pb (II) using the above-mentioned electrodes under the optimized conditions. Therefore, the anodic peak currents of Pb (II) and Cd (II) were measured at -0.69 V and -0.49 V for the bare electrodes and - 0.70 V and -0.51 V for the Ag NP/CPE, respectively. Moreover, compared to the unmodified CPE, the current for the Ag NP/CPE (31.14 μA and 44.19 μA) was higher than the current for Cd (II) and Pb (II) oxidation at the bare CPE (7.41 μA and 10.66 μA). The excellent conductivity provided by Ag NPs was accompanied by an increase in surface area, resulting in greater current responses. Therefore, the Ag NP/CPE was selected for the simultaneous determination of Cd (II) and Pb (II).

According to the observed results and similar studies reported in the previous literature (Hashemi et al., 2019; Hermouche et al., 2021), the proposed mechanism for the reduction and oxidation of Cd (II) and Pb (II) on the modified carbon paste electrode (M-CPE) surface can take place in two reaction steps as follows:



Where M = [Cd (II) and Pb (II)] and MCPE = modified carbon paste electrode.

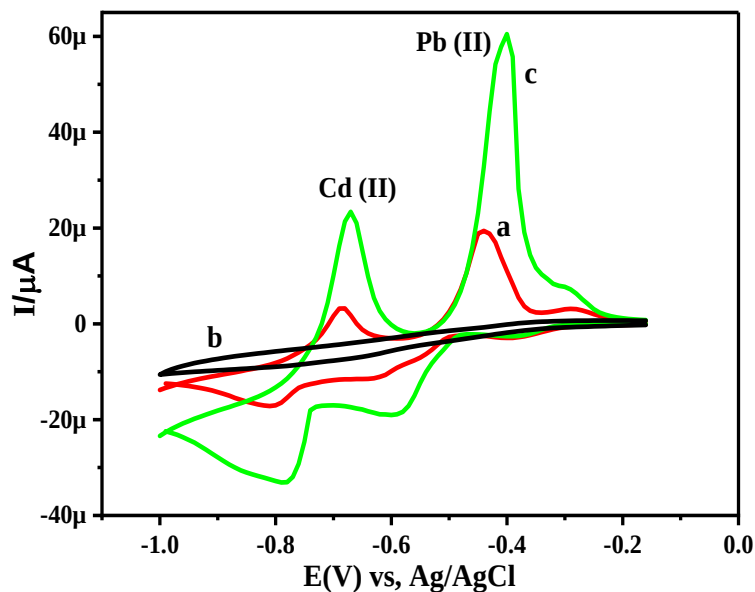


Figure 17: Cyclic voltammograms of (a) unmodified CPE with 33.1 μM Cd (II) and Pb (II) accumulation, (b) Ag NP modified CPE without Cd (II) and Pb (II) accumulation, and (c) Ag NP modified CPE with 33.1 μM Cd (II) and Pb (II) accumulation from 0.1M acetate buffer solution (pH 5) with accumulation potential of -1.1 V, accumulation time 120 s, scanned from -1.0 to 0 V, and scan rate at 0.1 V/s

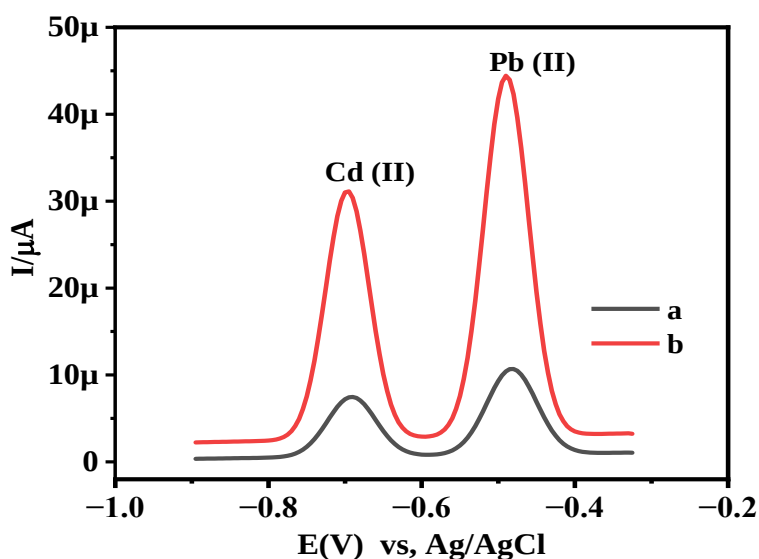


Figure 18: Square wave voltammograms of 33.1 μM Cd (II) and Pb (II) in 0.1 M acetate buffer solution (pH 5) at the (a) unmodified carbon paste electrode and (b) Ag NP- modified carbon paste electrode. Accumulation time: 120 s; accumulation potential -1.1 V and potential from -1.0 to 0 V with pulse amplitude 10 mV, frequency 10 Hz, and step potential 6 mV

4.2.2 Effect of Scan Rate on the Peak Potential and Peak Current

The scan rate variation is a bias to determine the nature of the process involved at the surface electrode/solution interface and to deduce several kinetics parameters related to this process. The cyclic voltammogram was recorded in 33.1 $\mu\text{g/L}$ Cd (II) and Pb (II) in acetate buffer solution (pH 5) at the Ag NP/CPE. The scan rate varied in the range of 20 and 175 mV s^{-1} (Fig. 19). In this study, to investigate the reversibility of the redox reaction each metal undergoes at the modified carbon paste electrode, the effect of the scan rate on the respective peak potential values was examined. As shown in Figure 19, both the oxidation and reduction peaks for each metal showed potential shifts with scan rate, confirming the irreversibility of the redox couples. In addition, when the scan rate increases, the peak potential of Cd (II) and Pb (II) slightly shifts toward a more positive potential. This indicates that the electrode reaction is a typical surface controlled irreversible process. An electrochemical reaction requires a specific lapse of time to ensure the diffusion of the active species and the transfer of charge at the electrode surface, so in the case of an increase in scan rate, one can limit the time interval of the electrochemical reaction, which results in an "observed shift" toward more + potentials (for anodic peaks) or - potentials (for cathodic peaks). This shift is mainly due to the "delay" of the electrochemical reaction due to the shortness of the allocated time compared to a lower scan rate that allows more time for the reaction to occur (Elgrishi et al., 2018).

Moreover, the kinetics of the redox process were investigated by comparing the correlation coefficient values (R^2) for the dependence of the peak current on the scan rate and square root of the scan rate. The observed higher correlation of the peak current with the square root of scan rate than the correlation of the peak current on scan rate (R^2) in Figure 20 revealed that the oxidation reaction of both metals at the Ag NP/CPE electrode was controlled by mass transfer, although charge transfer also contributed significantly.

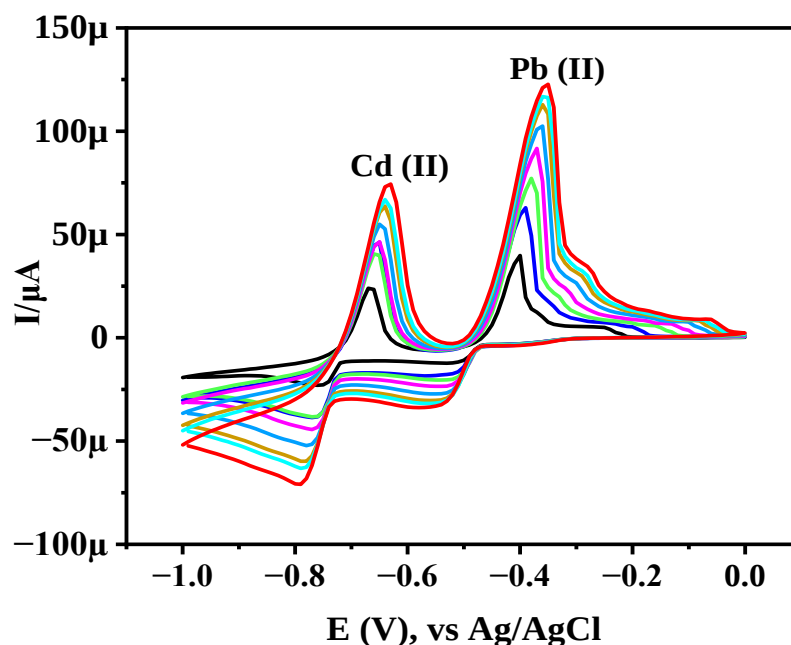


Figure 19. Cyclic voltammograms of the Ag NPs/CPE in a pH 5 acetate buffer solution containing a mixture of 33.1 µg/L Cd (II) and Pb (II) at various scan rates (a-h: 20, 40, 60, 80, 100, 125, 150, 175 mVs⁻¹, respectively).

Figure 20 below illustrates a linear plot of the current intensity (I (pa, pc)) versus the scan rate square root ($v^{1/2}$) characterized by linear regression equations and correlation coefficients given in Table 2, according to Randles Sevcik this linearity reveals that a diffusion process controls the redox kinetics of the metallic ions on the modified carbon electrode surface.

Table 2: Linear regression of scan rate (V) and square root of scan rate ($V^{1/2}$) variation.

Analyte	$I = f(V)$	$I = f(V^{1/2})$
Cd (II)	$I_{pa} = 0.31(V) + 23.93$ ($R^2 = 0.946$)	$I_{pa} = 5.24 (V^{1/2}) + 3.74$ ($R^2 = 0.972$)
	$I_{pc} = -0.17(V) - 10.74$ ($R^2 = 0.997$)	$I_{pc} = -3.22 (V^{1/2}) + 2.29$ ($R^2 = 0.986$)
Pb (II)	$I_{pa} = 0.54(V) + 39.08$ ($R^2 = 0.921$)	$I_{pa} = 10.14 (V^{1/2}) - 3.58$ ($R^2 = 0.981$)
	$I_{pc} = -0.13(V) - 6.80$ ($R^2 = 0.977$)	$I_{pc} = -2.52 (V^{1/2}) + 4.58$ ($R^2 = 0.993$)

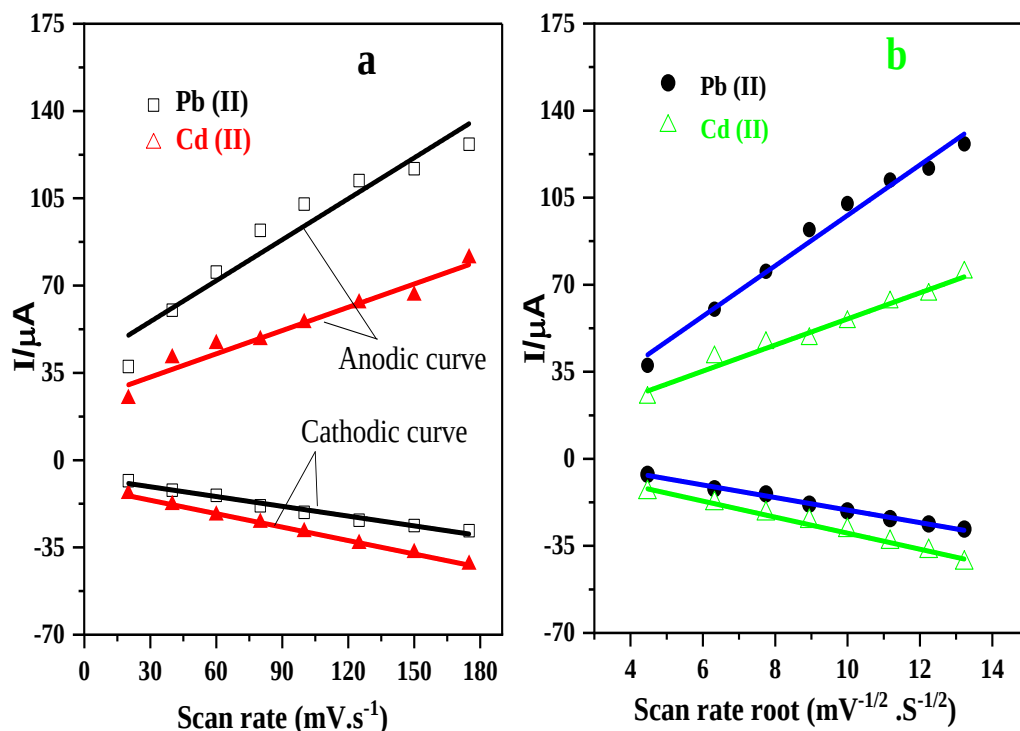


Figure 20: Calibration plot for the redox peak current of Cd (II) and Pb (II) versus (A) scan rate and (B) square root of scan rate

4.3 Optimization of Experimental Conditions

In this work, an optimization study by square wave anode stripping voltammetry (SWASV) was established to determine the optimal parameters promoting the maximum detection of Cd (II) and Pb (II) at the Ag NP/CPE surface. Square waves are more sensitive and more powerful for discriminating faradaic from non-faradaic than cyclic voltammetry. Using the SWASV method, the silver nanoparticles loading, pH of the supporting electrolyte, deposition potential, and deposition time were optimized with the default method parameters.

4.3.1 Effect of the Electrode Composition

The composition of the electrode material can affect the peak response of Cd (II) and Pb (II). The effect of the Ag NP content within the carbon paste electrode on the voltammetric response was studied by square wave anodic stripping voltammetry. In this work, five different electrodes were prepared from 5, 10, 15, 20, and 30 mg weight-to-weight ratio Ag NP containing carbon pastes

were investigated for their voltammetric signals under identical conditions. As shown in Figure 21 (a), the highest peak current was obtained for the electrode when the Ag NP content was- 15 mg. Electrodes with either lower or higher modifier composition gave a smaller peak current of Cd (II) and Pb (II). The decrease in the current responses at higher composition (> 15 mg of Ag Np) might be attribute to the decrease in the conductive carbon particles in the carbon paste. The decrease in the current responses at the modifier content < 15 mg of Ag NPs may be due to the lower extent of complexation because of the smaller coverage of the modifier on the electrode surface. Hence, the electrode modified with 15 mg of Ag NPs was used for all subsequent experiments.

4.3.2 Effect of Supporting Electrolyte pH

The effect of supporting electrolyte pH on the voltammetric peak current of Cd (II) and Pb (II) was studied in the pH range of 3 to 6.5 in acetate buffer solution. As shown in Figure 21 (b), the current response was strongly pH dependent, and the highest stripping peak current was found at pH 5.0 (ABS). Below and above pH 5.0, the peak currents decreased. At excessively low pH values (< 5.0), the decrease in the peak current of Cd (II) and Pb (II) can be attributed to the increase in the proton concentration. Proton can compete with Cd (II) and Pb (II) for binding to the donating atoms of the modifier, the ligand at the surface of the electrode. Furthermore, at pH values below 5.0, the modifier, the ligand, can slowly dissolve in the solution and lose its ability to immobilize Cd (II) and Pb (II) ions. The decrease in the anodic peak current at a higher pH of the buffer solution ($\text{pH} > 5.0$) may be due to cation hydrolysis. Thus, pH 5 was used as the optimum pH for subsequent experiments.

4.3.3 Effect of Deposition Potential

In the accumulation step, the amount of voltage applied on the working electrode has a significant role in the accumulation of Cd (II) and Pb (II) ions and hence results in a difference in the response of voltammetric peak currents. In this study, the deposition potential was varied between -0.90 V and -1.30 V. As shown in Figure 21 (c), the peak responses increased with negative accumulation potential up to -1.1 V, and the highest peak current was obtained at this potential. Above and below this potential, the peak current decreases. However, further negative accumulation potential after -1.1 V could not obviously increase the peak currents; at more negative potential values,

impurities could be easily reduced. Furthermore, hydrogen evolution can decrease the peak current intensities at such negative potentials. Hydrogen bubbles might damage the metal deposition at the electrode surface and lead to a decrease in current signals at very negative potentials (Salih et al., 2017). At more positive potentials, a decrease in the anodic peak current can be attributed to the fact that the target metal ions could hardly be reduced due to inefficient reduction potential. Therefore, -1.1V was chosen as the optimum accumulation potential for all subsequent measurements.

4.3.4 Effect of Accumulation Time

The effect of accumulation time on the response of the stripping peak current of Cd (II) and Pb (II) ions was investigated in the range of 0-180 s. in Figure 21 (d) below. The accumulation time has a significant influence on the detection sensitivity of Cd (II) and Pb (II) ions. As shown in the Figure 21 (d), the peak current increased rapidly at first, and then gradually increased with more accumulation time. A slight increase in peak current intensity at the higher accumulation times might be due to the saturation of the electrode surface with loaded target ions and/or the attainment of steady-state equilibrium of adsorption/complex formation. Thus, to obtain a linear relationship between the Cd (II) and Pb (II) ion concentration and peak current, a relatively short accumulation time must be employed to avoid the saturation effect. Considering the sensitivity and resolutions of adjacent peaks, the accumulation time is optimized at 120 seconds in the experiments performed in the study.

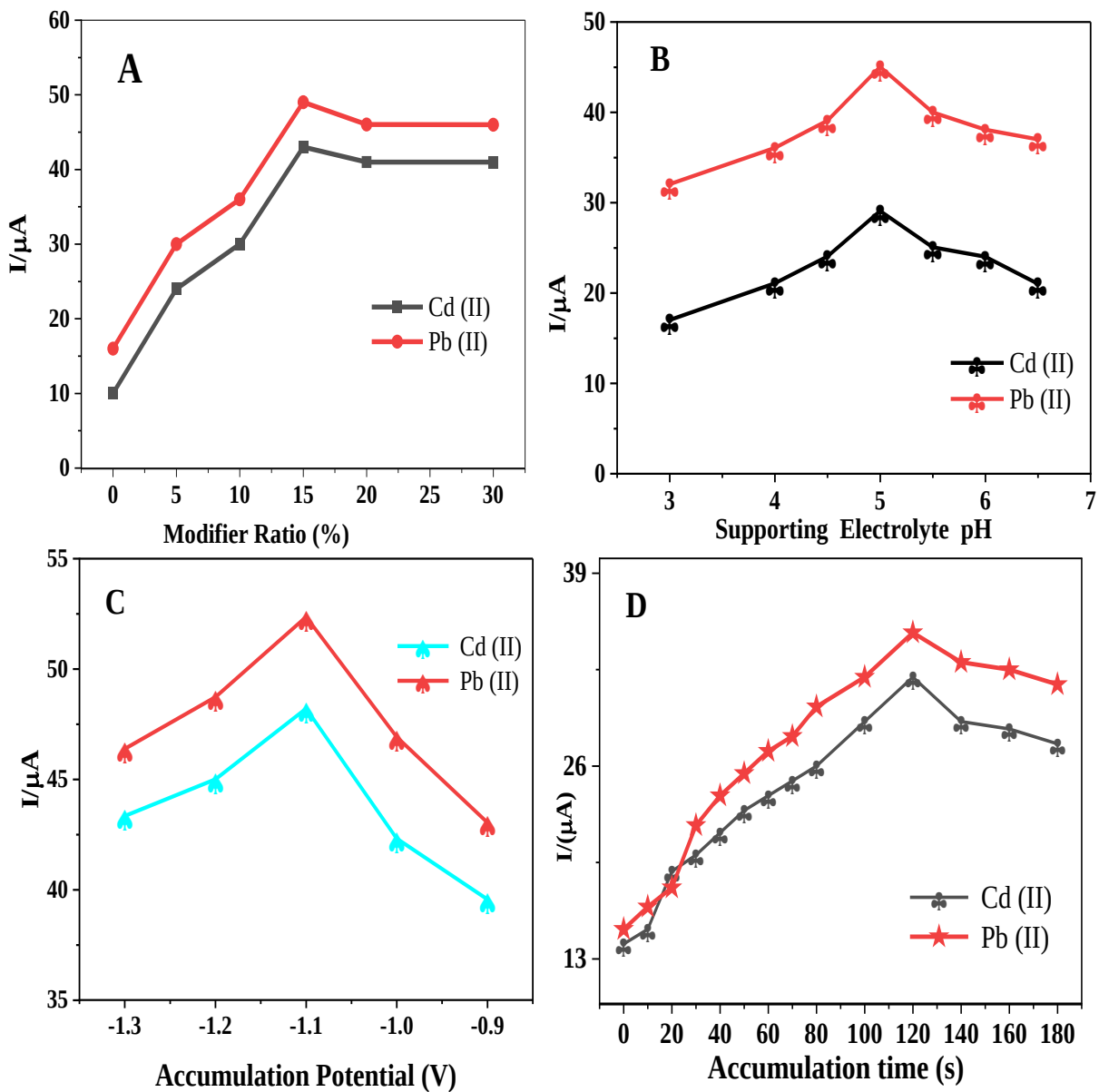


Figure 21: Influence of experimental parameters (A) modifier ratio (%), (B) supporting electrolyte pH, (C) accumulation potential, and (D) accumulation time on the response of the Ag NPs/CPE in the presence of 33.1 $\mu g/L$ Cd (II) and Pb (II).

4.4 Validation of the Electrode

4.4.1 Linear Range and Limit of Detection

After optimization of the experimental parameters, the determination of Cd (II) and Pb (II) was conducted at Ag NP-modified CPE using the square wave anodic stripping voltametric (SWASV) method. To determine the relationship between anodic peak currents and Cd (II) and Pb (II) concentrations, square wave voltammograms were recorded in acetate buffer solution (ABS) at pH 5.0. The dependence of the SWASV peak current on the concentrations of the two analytes was evaluated under three different conditions: the concentration of both varied in parallel, the concentration of Pb (II) varied while keeping Cd (II) constant, and Cd (II) varied while keeping Pb (II) constant to see the effect of the presence of one analyte on the determination of the other.

As shown in Figure 22, the sensor's sensitivity, and linear range for Cd (II) and Pb (II) were evaluated in the current work. With increasing ion concentrations, the response of the signals was enhanced. Both Cd (II) and Pb (II) stripping peak currents increased proportionally with increasing concentrations of Cd (II) and Pb (II) ions. The calibration curves of Cd (II) and Pb (II) were linear from 0.8 $\mu\text{g/L}$ to 52.9 $\mu\text{g/L}$, respectively. The linear equations were evaluated as $I/\mu\text{A} = 1.0061[\text{Cd}]/\mu\text{g/L} + 7.3086$ and $I/\mu\text{A} = 1.3838 [\text{Pb}]/\mu\text{g/L} + 13.011$ for Cd (II) and Pb (II), with correlation coefficients (R^2) of 0.9992 and 0.9996, respectively. The detection limits were recorded to be 2.7 $\mu\text{g/L}$ for Cd (II) and 1.3 $\mu\text{g/L}$ for Pb (II)

At a fixed concentration of Cd (II) of 6.6 $\mu\text{g/L}$, with increasing Pb (II) content, the peak currents of Pb (II) rose quickly, whereas the Cd (II) currents remained relatively constant (Fig. 23). Moreover, Pb (II) peak currents were linear with concentrations between 0.8 $\mu\text{g/L}$ and 52.9 $\mu\text{g/L}$, and the computed regression line was defined as: $I/(\mu\text{A}) = 0.7517 [\text{Pb}]/(\mu\text{g/L}) + 8.2172$ with an acceptable correction coefficient of $R^2 = 0.9997$ (Figure 23). Furthermore, we performed Cd (II) determination by enhancing the Cd (II) concentration and fixing Pb (II) at 6.6 $\mu\text{g/L}$. As shown in Figure 24, the SWASV responses experienced a linear enhancement with increasing Cd (II) concentration in the range between 0.8 $\mu\text{g/L}$ and 52.9 $\mu\text{g/L}$, whereas the Pb (II) responses were functionally constant. Finally, the relative calibration plot and correlation coefficient in Fig.24 were $I/(\mu\text{A}) = 0.6969[\text{Cd}]/(\mu\text{g/L}) + 9.4951$ with an acceptable correction coefficient of $R^2 = 0.9993$.

Notably, the introduced technique exhibited a beneficial linear range and reasonable LOD. In addition, an analytical function comparison of a few electrochemical determinations published by earlier articles was conducted. According to Table 3, the designed sensor had a greater linear range and lower LOD in comparison to some previous studies.

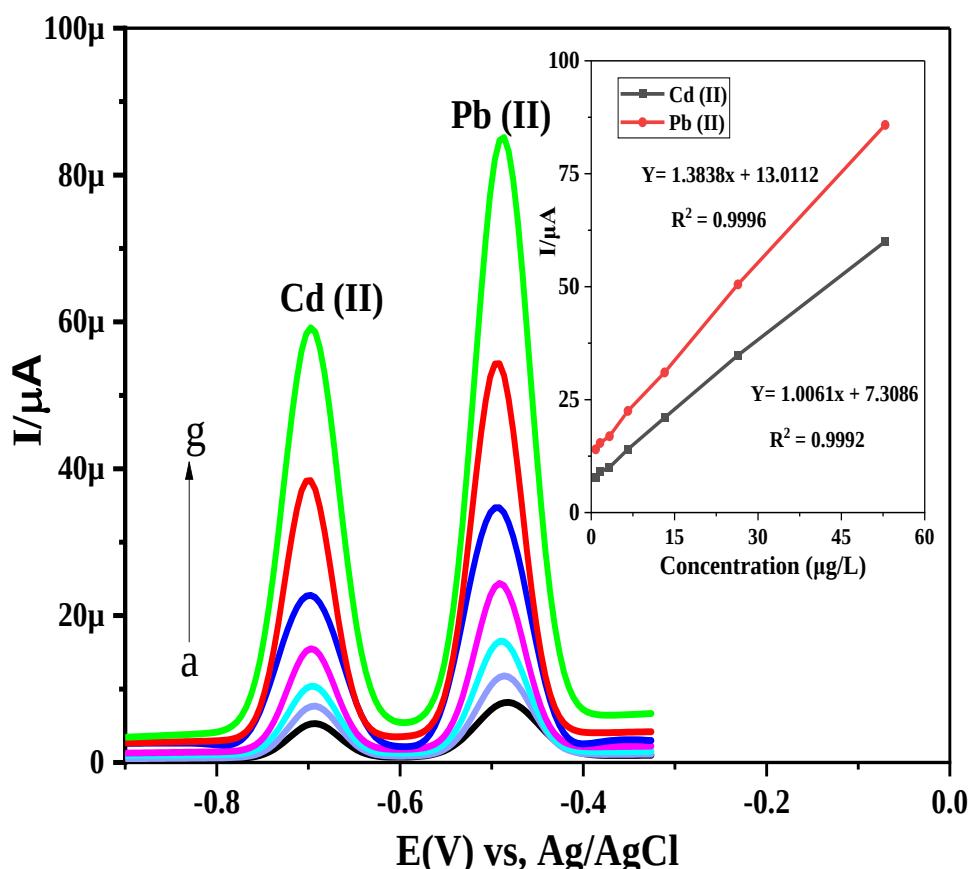


Figure 22: SWASVs of the Ag NP/CPE at pH 5.0 containing different equimolar mixtures of Cd (II) and Pb (II) (a- g: 0.8, 1.6, 3.3, 6.6, 13.2, 26.4, and 52.9 $\mu g/L$, respectively) at $E_{acc} = -1.1$ and $t_{acc} = 120$ s and the corresponding calibration curve of Pb (II) and Cd (II).

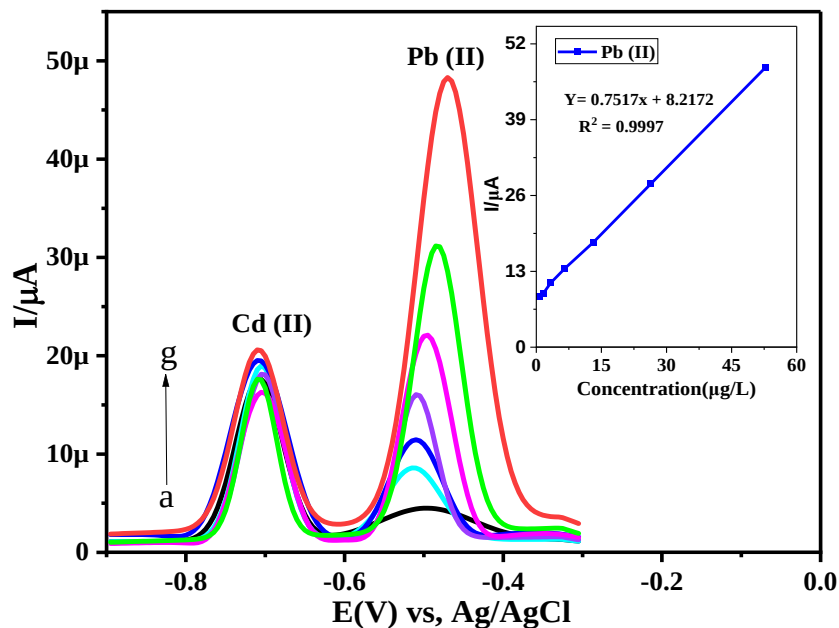


Figure 23. SWASVs Ag NPs/CPE in pH 5.0 ABS containing 6.6 $\mu\text{g/L}$ Cd (II) and various concentrations of Pb (II) (a – g: 0.8, 1.6, 3.3, 6.6, 13.2, 26.4, and 52.9 $\mu\text{g/L}$, respectively) at $E_{\text{acc}} = -1.1$ V and $t_{\text{acc}} = 120$ s, and corresponding calibration curve of Pb (II) ions.

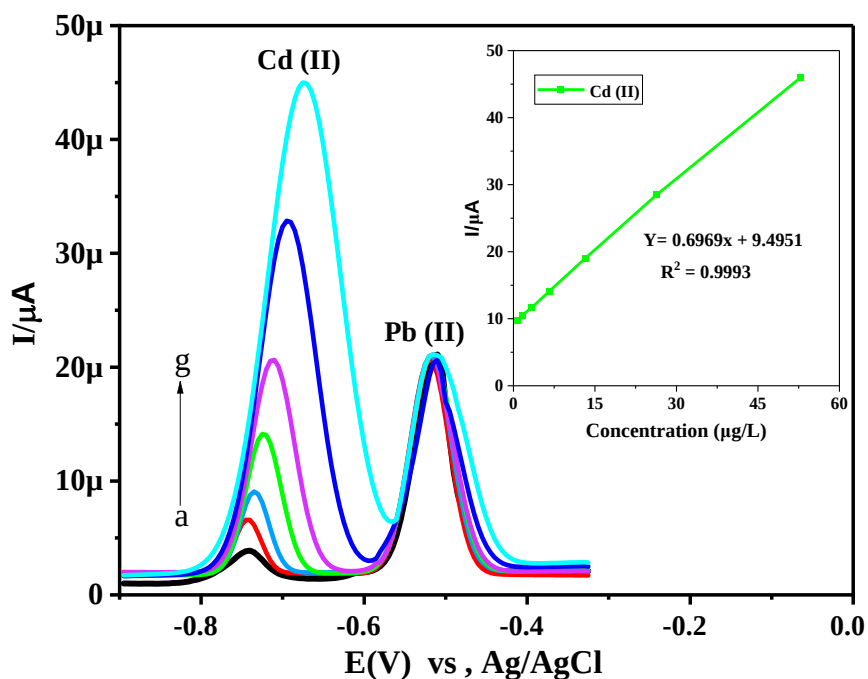


Figure 24: SWASVs of the Ag NPs/CPE in pH 5.0 ABS containing 6.6 $\mu\text{g/L}$ Pb (II) and variable concentration of Cd (II) (a - g: 0.8, 1.6, 3.3, 6.6, 13.2, 26.4, and 52.9 $\mu\text{g/L}$, respectively) at $E_{\text{acc}} = -1.1$ V and $t_{\text{acc}} = 120$ s and the corresponding calibration curve of Cd (II).

Table 3: Comparison of the proposed sensor for determination of Cd (II) and Pb (II) with others.

Electrode	Technique	Linear range (µg/L)	LOD (µg/L)	Reference
MWCNTs/CPE	SWASV	Cd (II), 58.4 - 646.2 Pb (II), 58.4 - 646.2	8.4 6.6	(Tarley et al., 2009)
E. crassipes/CPE	SWASV	Cd (II), 10 - 5000 Pb (II), 10 - 5000	4.9 2.1	(Jackfama et al., 2019a)
Ag-NPs-SPCNFE	DPASV	Cd (II), 9.5 - 39.7 Pb (II), 8.9 - 100.4	2.8 2.7	(Bastos-Arrieta et al., 2018)
GC/GQDs-NF	SWASV	Cd (II), 20 - 200 Pb (II), 20 - 200	11.3 8.49	(Pizarro et al., 2020)
Gr/PANI/PS/SPE	SWASV	Cd (II), 10 -500 Pb (II), 10 - 500	4.43 3.3	(Promphet et al., 2015)
HA/Ag NP/CPE	CV & SWASV	Cd (II), 0.8 - 52.9 Pb (II), 0.8 - 52.9	2.7 1.3	This study

4.4.2 Examination of Repeatability, Reproducibility, and Stability

In this stage, the repeatability of the proposed electrode was investigated by performing six repeated determinations of 6.6 µg/L Pb (II) and Cd (II) using the same electrode under identical conditions, as shown in Figure 25 below. Moreover, the relative standard deviation (RSD) for the response of six repeated measurements was found to be 3.2% and 3.4% for Pb (II) and Cd (II) ions, respectively. Such a significant repeatability confirmed non-poisonousness of the modified electrode by the redox products and its' capability to experience the repeated utilization. For achieving biogenic Ag NPs /CPE reproducibility, six Ag NP /CPEs have been built individually and analyzed in the aqueous solution consisting of Pb (II) and Cd (II) (6.6 µg/L). In addition, RSD-value of the anodic peak currents equaled 3.3% and 3.8% for Pb (II) and Cd (II) respectively, that demonstrated the good reproducibility of the modified Carbon paste electrodes. Furthermore, the stability of the proposed electrode was determined by recording the peak currents of 6.6 µg/L Pb (II) and Cd (II) over a period of 30 days (in the first week, one measurement per day, and then once a week). The maximum deviation for the peak current response after 30 days was found to be 3.9 % and 4.4% for Pb (II) and Cd (II), representing a reasonable stability of biogenic Ag

NPs/CPE based on the optimum conditions. Therefore, the high stability and reproducibility indicate that the proposed modified electrode has good suitability for real sample analysis.

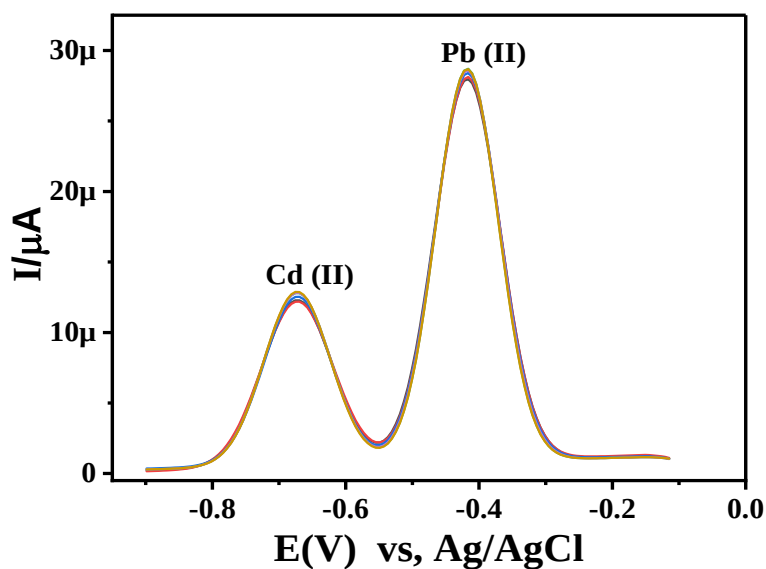


Figure 25: SWASV voltammograms for six successive determinations of 6.6 µg/L Cd (II) and Pb

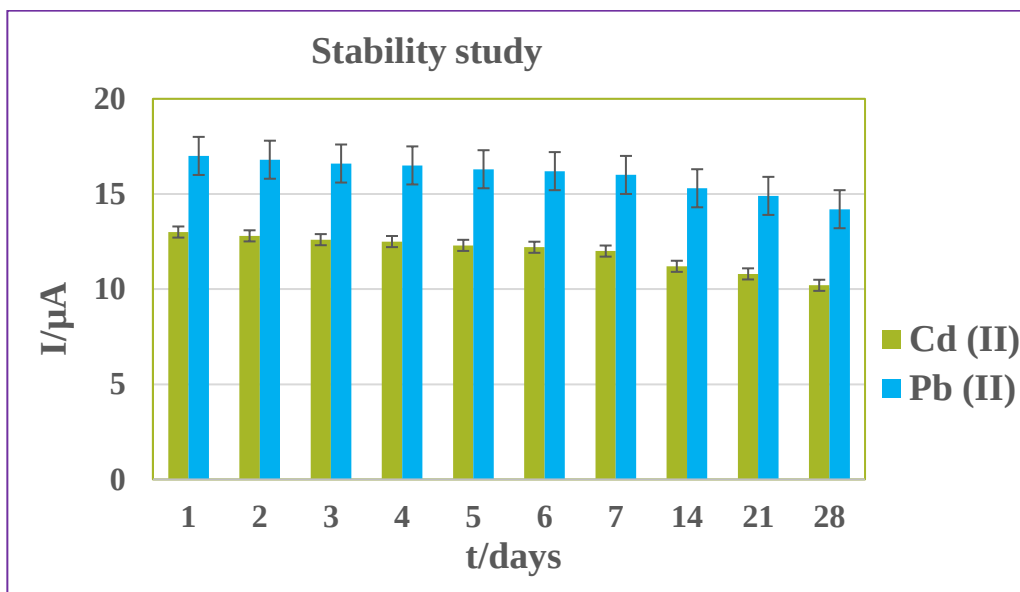


Figure 26: The stability of Ag NPs/CPE for 6.6 µg/L Cd (II) and Pb (II) over a period of 30 days.

4.4.3 Interference Studies

The interference effect of various co-existing ions on the analyte solution was studied by adding different inorganic ions into the preconcentration medium containing 6.6 µg/L Pb (II) and Cd (II). These foreign ions can compete with analyte for the binding sites of the modified carbon paste electrode, or even under the experimental conditions, some can be electrochemically active and, as a result, change the peak current intensity. This experiment was performed under the optimum conditions for the determination of Cd (II) and Pb (II) ions. Interference is considered when the presence of a foreign ion in a preconcentration medium changes the peak current intensity at the peak potentials of Cd (II) and Pb (II). The interference tolerance limit was considered as the concentration of foreign ions, which creates a $\pm 5\%$ relative error in the intensity of the Cd (II) and Pb (II) peaks (Jackfama et al., 2019b). Furthermore, we verified by SWASV and under the same optimal conditions the influence of certain ions, such as Ca^{2+} , Mg^{2+} , Mn^{2+} , Co^{3+} , Fe^{2+} , Zn^{2+} , and Ni^{2+} in the presence of 6.6 µg/L target ions. As shown in Figure 26, the percentage deviations of the current intensity background relative to the studied analytes are less than 5%, which is tolerable. Meaning that interference does not occur up to 100-fold for Ca^{2+} , Mg^{2+} , Mn^{2+} , and Co^{3+} , 30-fold for Fe^{2+} , and Zn^{2+} , and 20-fold for Ni^{2+} . This difference in interfering folds is allotted to intermetallic competition between these interfering and the target ions toward functional groups of the Ag NP-CPE surface.

4.5 Real Sample Analysis

Determining the presence of Cd (II) and Pb (II) in wastewater is an important task to investigate environmental and occupational exposure. Heavy metal ions are considered more dangerous for humans and other living organisms, because they cause many diseases. For this reason, it should be removed from all environments. In this research work, a biogenic Ag NP/CPE sensor was produced for heavy metal ion detection at the lowest levels by using a standard addition method. To obtain information on the utility of the introduced sensor, three various concentrations were utilized to spike the wastewater sample. Then, the samples were transferred to the electrochemical cell, and the SWASV method was used for direct analysis. According to the analyses (Table 4), recovery ranged between 97.1 to 103.3 % for cadmium and 99.86 to 104.6 % for lead ions in the

triplicate experiments. Therefore, good recovery range indicated the acceptable accuracy and reproducibility of the designed sensor.

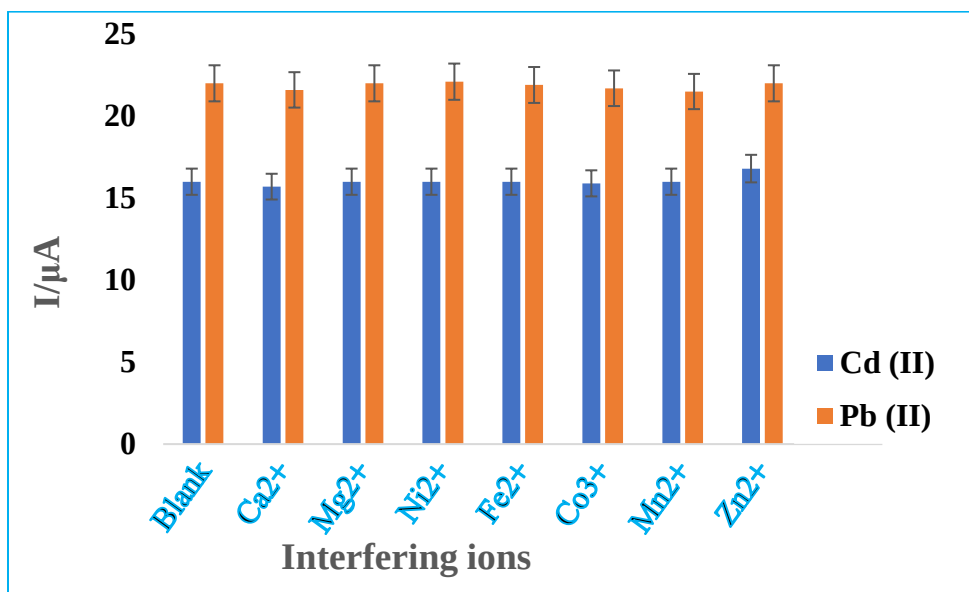


Figure 27: Selectivity of Ag NPs/CPE for simultaneous detection of Cd (II) and Pb (II).

Table 4: Determination of Cd (II) and Pb (II) in wastewater samples using Ag NPs (n=3)

Sample	Pb (II) Spiked (μg/L)	Pb (II) found (μg/L)	Recovery (%) Pb (II)	Cd (II) spiked (μg/L)	Cd (II) found (μg/L)	Recovery (%) Cd (II)
Waste water	0	NF	-	0	NF	-
	4.0	3.9	97.5	4.0	3.85	96.2
	6.0	6.25	104.2	6.0	6.1	101.6
	8.0	7.99	99.87	8.0	8.2	103.7

NF: Not found

$$\text{Recovery}(\%) = \frac{\text{Found}}{\text{Added}} * 100$$

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

Knowing that heavy metal ions are endocrine disruptors that give rise to various emerging diseases, such as breast and prostate cancers as well as neurodegenerative diseases, their detection at trace levels with a sustainable and real-time approach has become a major issue. Herein, we have demonstrated that the synthesis of Ag NPs is possible by a simple, low cost, eco-friendly, and rapid biological route using *Hagenia abyssinica* leaf extract at room temperature. The synthesized nanoparticles and hence modified electrode were characterized using UV–Vis, XRD, FT-IR, SEM, DLS, and cyclic voltammetric techniques, resulting in the silver nanoparticles synthesized from *Hagenia abyssinica* leaf extract having a smaller size of approximately 17 nm, which would be interesting for electrochemical sensor activity. The biosynthesized Ag NPs were used as catalysts in electroanalysis and were pasted onto the surface of carbon paste electrodes to build a novel AgNP/CPE-modified nano sensor. This sensor was employed for determination of Cd (II) and Pb (II) ions, obtaining excellent figures of merits concerning: high sensitivity, low LOD of 2.7 µg/L for Cd (II) and 1.3 µg/L for Pb (II), good stability with a lifetime of approximately 1 month and a good selectivity toward other inorganic ions with a deviation less than 5%, as well as repeatable of the modified electrode relative standard deviation (RSD) was found to be 3.2% and 3.4% for Pb (II) and Cd (II) ions, and reproducible results with an RSD of 3.3% and 3.8% for Pb (II) and Cd (II) ions, respectively, thanks to the green Ag NPs as cost-effective nanomaterials. In addition, our proposed nano sensor has been employed successfully for Pb (II) and Cd (II) ion determination in wastewater samples, showing a good recovery percentage value between 96.2 and 103.7% for cadmium and 97.5 and 104.2% for lead ions. We think that our results provide an exciting perspective for sustainable large scale nano sensor production by carbon paste electrode surface engineering using green nanoparticles for Pb (II) and Cd (II) ion detection in wastewater. Last, we hope this study will serve as a useful resource, raising the understanding and appreciation of the role that these electrochemical sensors may play in protecting our environment.

5.2 Recommendations and Future Work

Recommendations for future work include the following:

- The synthesis of silver nanoparticles using different plant extracts targeted different shapes of silver nanoparticles and checked their efficiency in the detection of heavy metal ions.
- Detection of heavy metal ions at different temperatures to check the stability of the silver nanoparticles.
- The results from the fabricated sensor are compared with results from known analytical quantification techniques.
- Increasing the current response of the biosynthesized Ag NP/CPE modified electrode by using instrumental optimization results in pulse amplitude, frequency, and step potential.

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