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Sudan University of Science and Technology
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Natural Plants Extract Mediated Synthesis of Silver Nanoparticles

تحضيرجسيمات الفضة النانوية بأستخدام مستخلص النباتات الطبيعية

A dissertation Submitted in Partial Fulfillment for the Requirement of a Master Degree (M. Sc) in General Physics

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Abstract

Recently, noble metal nanoparticles have gained the interest of researchers due increases of its application in almost all fields particularly in biological application. This is actually due to their fascinating optical properties owing to localized surface Plasmon resonance. Among metal nanoparticles, silver is known to have special properties such as high resistance to oxidation and antibacterial activity which make it desirable for biological application. This encourages researchers to develop new synthesis method using material with low toxicity such as natural plants. Later on, this method is termed green method or biological method.

In this work, Acacia Nilotica fruits and Guiera Senegalensis leaves extracts were used as the reducing agent and silver nitrate as the source of silver to synthesis silver nanoparticles. During synthesis process the color was changed after addition of these plants extract, indicating the formation of silver nanoparticles. UV-Vis spectrometer was further confirm the formation of silver nanoparticles due appearance of absorption band in visible range owing to localized surface Plasmon resonance. In addition, the effect of plant extract quantity and heating time on the formation of silver nanoparticles was investigated in details. The optimum ratio between plants extract and silver nitrate solution is found to be 2.0:20 and 0.2:20 for Acacia Nilotica and Guiera Senegalensis, respectively. The obtained results showed that the heating time has no significant effect on the particle size but instead enhanced the reduction rate. It also found that the using of Acacia extract produces bigger particles compare with Guiera extract.

المستخلص

في الآونة الأخيرة ، اكتسبت جسيمات المعادن النبيلة النانوية اهتمام الباحثين بسبب الزيادة في تطبيقاتها في جميع المجالات تقريبًا وخاصة في التطبيقات البيولوجية. هذا يرجع إلى خصائصها البصرية المميزه الناتجة من ظاهرة رنين البلازمون. من بين جسيمات المعادن النبيلة النانوية تتميز الفضة بخواص خاصة مثل المقاومة العالية للأكسدة والنشاط المضاد للبكتيريا مما جعلها ملائمه في الاستخدامات البيولوجية. هذه المميزات شجعت الباحثين على تطوير طريقة جديدة لتحضيرها باستخدام مواد ذات سمية منخفضة مثل النباتات الطبيعية. سميت هذة الطريقة في وقت لاحق بالطريقة الخضراء (الآمنة) أو الطريقة البيولوجية .في هذا البحث ، تم استخدام مستخلص ثمار القرض(Acacia Nilotica) ومستخلص أوراق الغبيش (Guiera Senegalensis) كعامل اختزال ونترات الفضة كمصدر للفضة لتحضير جسيمات الفضة النانوية. أثناء عملية التحضير ، تغير اللون بعد إضافة مستخلص هذه النباتات ، مما يشير إلى تكوين جسيمات الفضة النانوية. تم تأكيد هذه النتيجة باستخدام مطياف الاشعة الفوق بنفسجية حيث ظهرت ذروة الامتصاص في النطاق المرئي بسبب رنين البلازمون. بالإضافة إلى ذلك ، تم دراسة تأثير كمية المستخلصات النباتية وزمن التسخين على تكوين جسيمات الفضة النانوية بالتفصيل. حيث اظهرت النتائج ان النسبة المثلى بين مستخلص النباتات ومحلول نترات الفضة هي 2.0: 20 و 0.2: 20 لمستخلص القرض و الحرجل، على التوالي. أوضحت النتائج المتحصل عليها أن زمن التسخين ليس له تأثير كبير على حجم الجسيمات ولكن بدلاً من ذلك عزز معدل التفاعل. كما وجد أن استخدام مستخلص القرض ينتج جسيمات أكبر مقارنة بمستخلص الحرجل.

Keywords and acronyms

Keywords

Acacia Nilotica fruit extracts - Guiera Senegalensis leaves - Turkevich method - Green method- Localized surface Plasmon resonance (LSPR) - Mie theory - Silver nanoparticles.

Acronyms

SPP: Surface Plasmon Polariton.

LSPs: Localized Surface Plasmon.

LSPR: Localized Surface Plasmon Resonance.

Ag-NPs: Silver Nanoparticles.

UV-VIS: Ultraviolet-Visible Spectroscopy.

MNPs: Metal Nanoparticles.

EMR: Electromagnetic Radiation

DDA: Discrete dipole approximation

QDs: quantum dots

List of figures

Figures	page
Fig. 2.1 Schematic diagram explaining approaches that used to synthesis nanomaterials	**10**
Fig. 2.2 Schematic diagram illustrating Bulk Plasmon	**13**
Fig. 2.3 Schematic diagrams illustrating SPP	**15**
Fig. 2.4 Schematic diagram illustrating localized surface Plasmon	**15**
Fig. 2.5 Extinction spectra of Ag nanoparticles with different shapes	**17**
Fig. 3.1 (a) beaker (b) Magnetic stirrer with hot plat	**26**
Fig. 3.2 Sensitive balance	**27**
Fig.3.3 chemical formula silver nitrate $AgNo_3$	**28**
Fig. 3.4 Preparation flowchart of silver nanoparticles.	**31**
Fig.3.5 UV-Vis spectroscopy diagram.	**33**
Figure 4.1 showed changing in color during the experimental process of (A) Acacia Nilotica (B) Guiera senesegalensis.	**35**
Fig.4.2 diffuse absorption for the mixture of silver salt and (A) Acacia fruits extract (B) Guiera leaves extract with different ratio.	**36**
Fig.4.3 Effect of the amount of Acacia fruits extract or Guiera leaves extract on the intensity of the absorption band.	**37**
Fig.4.4 diffuse absorption for the mixture of silver salt and (A) Acacia fruits extract (B) Guiera leaves extract heated at different time.	**38**
Fig.4.5 Effect of heating time on the absorption band intensity of the mixture of silver salt and Acacia fruits extract or Guiera leaves extract.	**39**
Fig.4.6 Effect of heating time on particle size for both Acacia and Guiera samples.	**40**

Table of Contents

Acknowledgements i
Abstract ii
المستخلص iii
Keywords and acronyms iv
Keywords iv
Acronyms iv
List of figures v
Table of Contents vi
Dedication viii
CHAPTER ONE 1
INTRODUCTION 1
1.1 Overview 1
1.2 Problem statement 4
1.3 literature review 4
1.4 Research Objectives 5
1.4.1 General Objective 5
1.4.2 Specific Objectives 6
1.5 Thesis layout 6
CHAPTER TWO 7
2.1 Overview 7
2.2 Nanoparticles 7
2.3 Synthesis of Metals Nanoparticles 9
2.4 Silver Nanoparticles 11
2.5 Plasmon 12
2.5.1Bulk Plasmon 12

2.5.2 Surface Plasmon Resonance....13
2.5.2.1 Surface Plasmon Polaritons (SPPs)....14
2.5.2.2 Localized Surface Plasmon (LSP)....15
2.6 Tuning of the Localized Surface Plasmon Resonance....16
2.6.1 Effect of Shape....17
2.6.2 Effect of Size....18
2.6.3 Effect of Dielectric of the Environment....20
2.7 Applications of Silver Nanoparticles....21
2.7.1 Applications in Medicine....21
2.7.2 Applications in Industrial....21
2.7.3 Scientific applications....22
2.7.4 Biological applications....23
CHAPTER THREE....26
METHODS AND TECHNIQUES....26
3.1 Introduction....26
3.2 Materials and tools....26
3.3 Silver Nitrate....27
3.4 Acacia Nilotica....28
3.5 Guiera....30
3.5 Experimental Procedure to Synthesize Ag Nanoparticles....30
3.6 Characterization Techniques....32
3.6.1 UV-VIS Spectrophotometer....32
CHAPTER FOUR....35
RESULTS AND DISCUSSIONS....35
CHAPTER FIVE....42
CONCLUSION AND FUTURE WORK....42
5.1 Conclusion....42
5.2 Recommendation....42
References....**Error! Bookmark not defined.**

Dedication

This study is wholeheartedly dedicated to our beloved parents, who have been our source of inspiration and gave us strength when we thought of giving up, who continually provide their moral, spiritual, emotional, and financial support. To my brothers, sisters, relatives, mentor, friends, and classmates who shared their words of advice and encouragement to finish this study. And lastly, thank you my God for the guidance, strength, power of mind, protection and skills and for giving us a healthy life.

CHAPTER ONE
INTRODUCTION

1.1 Overview

The prefix nano associated with the word “nanotechnology” is actually comes from Greek word "nanos" which mean dwarf. In recent years, nanotechnology has become one of the most important fields of research in physics, chemistry, engineering and biology (Kuppusamy et al., 2015). Actually, the science of nanometer scale objects is the so called nanoscience while the resulting technology is called nanotechnology (Bayda et al., 2020). Nanotechnology deals with various structures of matter having dimensions between 1-100 nm (Ramsden, 2011) Moreover, Nanotechnology creates and uses structures that have novel properties because of their small size and it builds on the ability to control and manipulate materials at the atomic scale (Ramsden, 2011). The other important field of research associated with the word “nano” is the nanoscience which is defined as the study of materials having size in nanoscale (Ramsden, 2011). Moreover, nanoscience is considered as cross disciplinary, therefore scientists from different fields such as chemistry, physics, biology, medicine, computing, materials science and engineering are studying it to better understand the world around us (Kakani and Kakani, 2006, Panja et al., 2016). Both nanoscience and nanotechnology are deals with the materials at the nano scale which called in more generic name “nanomaterials”. It is typically a nanoscale material having size between 1-100 nm and sometimes extended to some hundreds of nanometers. It is actually created from a natural or synthesized material through chemical, physical or mechanical processing (Sharma et al., 2009, Khan et al., 2017). The most common examples of nanomaterials are, nanotubes, nanowhiskers, Nanofiber, Nanosheet, Nanoparticles, etc.,. Nowadays, nanoparticles have attracted much attention due to their multifunctional properties and very interesting applications in various fields such as physics, chemistry, biology, medicine, nutrition and energy. Recently, noble metal nanoparticles have gained great interest due to their distinctive properties resulting from the localized surface plasmon resonance (LSPR) (Panja et al., 2016). LSPR is defined as collective oscillation of the conductions electrons in the noble metals nanoparticles (Panja et al., 2016). This phenomena occurs when the frequency of the natural oscillations of free electrons in metals match with the frequency of incident light, resulting in strong absorption of light at particular wavelength. Among metal nanoparticles, silver nanoparticles have exhibit promising properties which are extremely important for wide range of applications (Natsuki et al., 2015). Moreover, silver is known to have stronger plasmon resonance because its interband transition occurs at higher energy (in ultraviolet region) compared to the LSPR energy (in visible or near infrared regions) (Awwad et al., 2013).

Basically, there are two approaches used to synthesis nanoparticles namely the bottom- Up and top down approach (Balasooriya et al., 2017). The Top-down approach refers to slicing or successive cutting of a bulk material to get nano sized particle (the ball milling is a typical example) while bottom-up approach refers to the buildup of a material from the bottom: atom by atom, molecule by molecule or cluster by cluster (chemical synthesis is a typical example) (M Ramya1, 2012).

It is well-known that the chemical methods is more advantageous than the physical methods (I.e., ball milling, laser oblation, etc.,..) because the former have a better chance of producing nanomateial with good stability, more homogenous chemical composition, and better short- and long-range ordering in addition to its ease and low cost (Sharma et al., 2009). One of the more popular chemical method used to create nanoparticles is chemical reduction of metal salts (Fernando et al., 2018). In this method some organic and inorganic material was used as reducing agent to convert metal ions to metal nanoparticles. Recently, due to increasing of the uses of metal NPs in a wide range of applications particularly in diagnostic and medical treatment, researchers have replaced this toxic chemicals (organic or inorganic) by some extract of natural plants (Sharma et al., 2009, Ahmed et al., 2016). The method that used the extract of natural plants as reducing agent is called green synthesis or biosynthesis. Biosynthesis or green synthesis methods have more compensation over other classical synthesis procedures due to the availability of more biological entities and eco-friendly procedures (Mondala et al., 2011). The rich biodiversity and easy availability of plant entities have been highly explored for the nanomaterials synthesis. The low cost of cultivation, short production time, safety, and the make plants an attractive ability to up production volumes platform for nanoparticle synthesis are some advantages of the green synthesis compare to the other chemical methods (V.V.Makarova, 2014, Aparajita Verma, 2015).

This work aims to synthesis Ag NP_s using extract of two Sudanese plants namely Acacia Nilotica fruit extract and Guiera leave extract based on turkevish method (Turkevich et al., 1951). To optimize the reaction rate of experiment, different heating time and different ratio between $AgNO_3$ solution and extract was applied. To confirm the formation of Ag NPs, UV-Vis spectrophotometer was used.

1.2 Problem statement

Nowadays, metal NPs gained much attention due to increase of uses in several applications like agriculture, medicine field, industrial- sciences, and etc., (Kuppusamy et al., 2015). Moreover, it provides solution to most of technological problems and environmental challenges on the earth, e.g. medicine, solar energy conversion, catalysis, water sanitation, etc,.. (Rycenga et al., 2011). These metal nanoparticles have been successfully synthesized using different methods (Natsuki et al., 2015). Among these methods, chemical reduction of metals salt by some organic or inorganic chemicals were commonly used due to its advantage of low cost, very fast and producing NPs with high stability (Sharma et al., 2009). However, these chemicals are toxic and therefore it cannot be used in some applications particularly biological applications. Therefore this work is utilized to use extract of two Sudanese natural plants namely Acacia Nilotica fruit and Guiera leave as the reducing agent to synthesis Ag NPs for possible application in biological fields.

1.3 literature review

The first relation between human life and nano scale was developed naturally in Ayurveda, which is 5000 years old Indian system of medicine (T. S. Santra1, 2014).

Nanotechnology is a fast emerging technology, that not only in physics and chemistry but also in the field of biology. Generally, nanoparticles are prepared by a variety of chemical and physical methods such as chemical reduction, photochemical reduction, electrochemical reduction, heat evaporation, etc. (T. S. Santra1, 2014). Among methods mentioned above, green synthesis of Ag NPs received great attention due to their versatile properties (Shanmuganathan et al., 2018). The synthesis of either silver or gold nanoparticles using some plants extract have been reported (Santra et al., 2014). The potential of green synthesis for both silver and gold nanoparticle has been reported intensively in literature (Santra et al., 2014, Kuppusamy et al., 2015, M Ramya1, 2012). For example, (Huang et al., 2007), reported the formation of both silver nanoparticles (55-80nm) and triangular or spherical gold nanoparticles when Sun-dried biomass of Cinnamomum camphora leaf incubated with aqueous silver or gold precursors at ambient temperature. In other report, the Neem (Azadirachtaindica) leaf broth has also been used for the extracellular synthesis of pure metallic silver, gold and bimetallic Au/Ag nanoparticles (Yadav, 2008).

1.4 Research Objectives

1.4.1 General Objective

To synthesis silver nanoparticles (Ag NP_s) using Acacia Nilotica fruits and Guiera Senegalensis leaves extracts as the reduction agents for silver nitrate solution.

1.4.2 Specific Objectives

- To develop and establish safe, eco-friendly, cheaper method for the synthesis of Ag-NPs using natural plants extract.
- To synthesis Ag-NPs using modified Turkevich method.
- To use extract of Acacia Nilotica fruits and Guiera Senegalensis leaves as the reducing agent and silver nitrate as source of silver to produce Ag NPs.
- To investigate the effect of Acacia Nilotica fruits and Guiera Senegalensis leaves quantity and heating time on the formation of Ag-NPs.
- To determine the absorption spectra of Ag-NPs by using UV-Vis spectrometer in order to confirm the formation of Ag-NPs and to calculate the particle size of Ag-NPs.

1.5 Thesis layout

This thesis contained five chapters. Chapter one including shorts introduction, literature review, problem statement, and the aim of this study. Chapter two focuses on the theoretical background, overview, nanoparticles, synthesis of metals nanoparticles, Plasmon properties, and type of plasmon, effects on the shape and size, effect of environmental, the applications. In chapter three studied materials, methods, and techniques. chapter four yielded the results and discussions. Finally, conclusions, recommendations, and references are presented in chapter five.

CHAPTER TWO

THEORETICAL BACK GROUND

2.1 Overview

This chapter focus on the definition and synthesis of nanoparticles. In addition, the theoretical background was also presented.

2.2 Nanoparticles

Nanoparticles (NPs) are defined as an objects having size between1 to 100 nm (Ramsden, 2011). Nanoparticles exist in the natural world and are also created as a result of human activities. Because of their submicroscopic size, they have unique material characteristics, and manufactured nanoparticles may find practical applications in a variety of areas, including medicine, engineering, catalysis, and environmental remediation (Roh and Cho, 2005, Fernando et al., 2018).

In 2008 the International Organization for Standardization (ISO) defined a nanoparticle as a discrete nano-object where all three Cartesian dimensions are less than 100 nm. The ISO standard similarly defined two-dimensional nano-objects (i.e., nanodiscs and nanoplates) and one-dimensional nano-objects (i.e., nanofibres and nanotubes). But in 2011 the Commission of the European Union endorsed a more-technical but wider-ranging definition.

Under that definition a nano-object needs only one of its characteristic dimensions to be in the range 1-100 nm to be classed as a nanoparticle, even if its other dimensions are outside that range. The lower limit of 1 nm is used because atomic bond lengths are reached at 0.1 nm. That size range from 1 to 100 nm overlaps considerably with that previously assigned to the field of colloid science from 1 to 1,000 nm which is sometimes alternatively called mesoscale. Thus, it is not uncommon to find literature that refers to nanoparticles and colloidal particles in equal terms. The difference is essentially semantic for particles below 100 nm in size.

Nanoparticles can be classified into any of various types, according to their size, shape, and material properties. Some classifications distinguish between organic and inorganic nanoparticles; the first group includes dendrimers, liposomes, and polymeric nanoparticles, while the latter includes fullerenes, quantum dots, and nanoparticles (Khan et al., 2017). Other classifications divide nanoparticles according to whether they are carbon-based, ceramic, semiconducting, or polymeric. In addition, nanoparticles can be classified as hard (e.g., titanium (titanium dioxide), silica (silica dioxide) particles, and fullerenes) or as soft (e.g., liposomes, vesicles, and nanodroplets). The way in which nanoparticles are classified typically depends on their application, such as in diagnosis or therapy versus basic research, or may be related to the way in which they were produced.

There are three major physical properties of nanoparticles, and all are interrelated: (1) they are highly mobile in the free state (e.g., in the absence of some other additional influence, a 10-nm-diameter nanosphere of silica has a sedimentation rate under gravity of 0.01 mm/day in water); (2) they have enormous specific surface areas (e.g., a standard teaspoon, or about 6 ml, of 10-nm-diameter silica nanospheres has more surface area than a dozen doubles-sized tennis courts; 20 percent of all the atoms in each nanosphere will be located at the surface); and (3) they may exhibit what are known as quantum effects. Thus, nanoparticles have a vast range of compositions, depending on the use or the product.

In general, nanoparticle-based technologies centre on opportunities for improving the efficiency, sustainability, and speed of already-existing processes. That is possible because, relative to the materials used traditionally for industrial processes (e.g., industrial catalysis), nanoparticle-based technologies use less material, a large proportion of which is already in a more "reactive" state. Other opportunities for nanoparticle-based technologies include the use of nanoscale zero-valent iron (NZVI) particles as a field-deployable means of remediating organochlorine compounds, such as polychlorinated biphenyls (PCBs), in the environment. NZVI particles are able to permeate into rock layers in the ground and thus can neutralize the reactivity of organochlorines in deep aquifers. Other applications of nanoparticles are those that stem from manipulating or arranging matter at the nanoscale to provide better coatings, composites, or additives and those that exploit the particles' quantum effects (e.g., quantum dots for imaging, nanowires for molecular electronics, and technologies for spintronics and molecular magnet.

2.3 Synthesis of Metals Nanoparticles

Over the last decade, novel synthesis approaches/methods for nanomaterials (such as metal nanoparticles, quantum dots (QDs), carbon nanotubes (CNTs), graphene, and their composites) have been an interesting area in nanoscience and technology (Ramsden, 2011). To obtain nanomaterials of desired sizes, shape, and functionalities, two different fundamental principles of synthesis (i.e., top down and bottom up methods) have been investigated in the existing literature (see fig 2.1) (Murphy, 2002). In the former, nanomaterials/nanoparticles are prepared through diverse range of synthesis approaches like lithographic techniques, ball milling, etching, and sputtering (Tapaszto et al., 2008). The use of a bottom up approach (in which nanoparticles are grown from simpler molecules) also includes many methods like chemical vapor deposition, sol–gel processes, spray pyrolysis, laser pyrolysis, and atomic/molecular condensation and aerosol processing (Pokropivny et al., 2007).

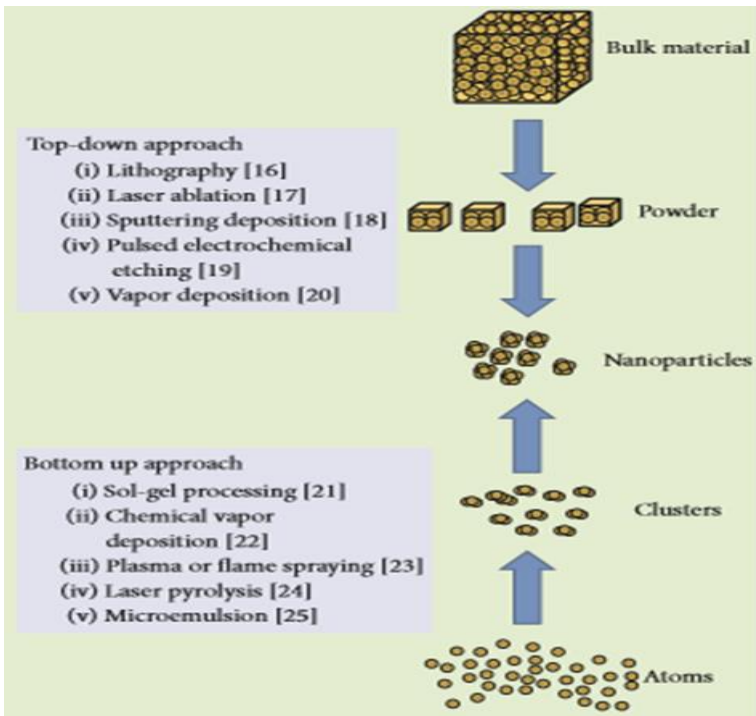

Fig. 2.1 Schematic diagram explaining approaches that used to synthesis nanomaterials (Balasooriya et al., 2017).

Actually, the synthesis methods mentioned above are categorized into two group namely chemical and physical methods. All these methods produce pure and well-defined nanoparticles, but the chemicals used in the synthesis are toxic, energy consuming, expensive, and not suitable for biological applications. Since silver NPs proved its activity in biological applications such as antimicrobial agents in wound dressings, as topical creams to prevent wound infections, and as anticancer agents, the researchers replaced these toxic chemical with natural plants. The method used these natural plants is called green method or biosynthesis method (Huang et al., 2007, Hussain et al., 2016).

2.4 Silver Nanoparticles

Silver nanoparticles are nanoparticles of silver of between 1-100 nm in size (Bayda et al., 2020). While frequently described as being 'silver' some are composed of a large percentage of silver oxide due to their large ratio of surface to bulk silver atoms. Numerous shapes of nanoparticles can be constructed depending on the application at hand. Commonly used silver nanoparticles are spherical, but diamond, octagonal, and thin sheets are also used extensively. Their extremely large surface area permits the coordination of a vast number of ligands. The properties of silver nanoparticles applicable to human treatments are under investigation in laboratory and animal studies, assessing potential efficacy, toxicity, and costs.

Silver is a soft, white and lustrous belonging to transition metals. It is possessing high electrical and thermal conductivity. It has been known since ancient time due to its medical and therapeutic application even before the realization that microbes are agents for infections. Moreover, it was used in many forms as coins, vessels, solutions, foils, sutures, and colloids as lotions, ointments, and so forth. It is the foremost therapeutic agent in medicine for infectious diseases and surgical infections. After discovery of the promising properties of nonmaterial, silver NPs have found new applications in almost all fields of research. Among metal nanoparticles, silver shows special optical properties owing to phenomenon called surface plasmon resonance (SPR). This phenomenon is occur due to a collective oscillation of free electrons in metal nanoparticles when interact with electromagnetic radiation. As the result, strong absorption of electromagnetic radiation occurs at visible and infrared regions.

2.5 Plasmon

Plasmon is defined as the collective oscillations of the free electrons in the conduction band of metals due to existence of an internal electric field. According to the dimensions of metal there are two main types of Plasmon namely bulk Plasmon (three dimensions (3D) and surface Plasmon (two or one dimension (2D or 1D)). More details about these types of plasmon will be given in the following sections.

2.5.1Bulk Plasmon

This mode of Plasmon occurs only in bulk metals. When an external field is applied to a given metal, the free electrons will make longitudinal oscillations through the metal. These oscillations occur at certain frequency called plasma frequency and is given by following equation (Borys, 2011). Bulk Plasmon can be well defined using Durde model through the following equation.

$$\boldsymbol{\omega_p = \sqrt{N\, e^2/\varepsilon_0 m_e}} \qquad (2\text{-}1)$$

where $\boldsymbol{N}$ is the conduction electron density, $\boldsymbol{e}$ is the electron charge, $\boldsymbol{m_e}$ is the electron effective mass and $\boldsymbol{\varepsilon_0}$ is the vacuum dielectric permittivity. Actually, most of Bulk metals have plasmon frequency with corresponding energy above 5 ev. Moreover, bulk Plasmon cannot be excited by photons, because the electrons in the bulk metals have longitudinal oscillations while photons have transfers oscillations which are not coupled together. Due to these mentioned properties, bulk Plasmon have no real practical in photonic applications.

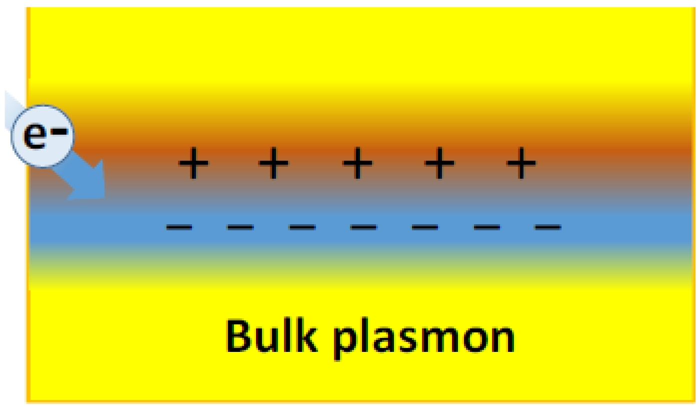

Fig.2.2 Schematic diagram illustrating Bulk Plasmon(Amendola et al., 2010)

2.5.2 Surface Plasmon Resonance

Surface Plasmon resonance (SPR) is the resonant oscillation of conduction electrons at the interface between negative and positive permittivity material stimulated by incident light. SPR is the basis of many standard tools for measuring adsorption of material onto planar metal (typically gold or silver) surfaces or onto the surface of metal nanoparticles. It is the fundamental principle behind many color-based biosensor applications, different lab-on-a-chip sensors and diatom photosynthesis. Actually, there are two types of SPR namely Surface Plasmon Plariton (SPP) and Localized Surface Plasmon (LSP) (Xianmao Lu et al., 2009). Details about these types will be discussed below.

2.5.2.1 Surface Plasmon Polaritons (SPPs)

Surface Plasmon Plariton (SPP) occurs when electromagnetic waves practically in the infrared or visible region travel along a metal–dielectric or metal–air interface (see Fig.2.3) (Amendola et al., 2010). The term "surface plasmon polariton" explains that the wave involves both charge motion in the metal "surface plasmon" and electromagnetic waves in the air or dielectric "polariton".

The surface plasmon polariton is a non-radiative electromagnetic surface wave that propagates in a direction parallel to the negative permittivity/dielectric material interface. Since the wave is on the boundary of the conductor and the external medium (air, water or vacuum for example), these oscillations are very sensitive to any change of this boundary, such as the adsorption of molecules to the conducting surface.

To describe the existence and properties of surface Plasmon polaritons, one can choose from various models (quantum theory, Drude model, etc.). The simplest way to approach the problem is to treat each material as a homogeneous continuum, described by a frequency-dependent relative permittivity between the external medium and the surface. This quantity, hereafter referred to as the materials' "dielectric function", is the complex permittivity. In order for the terms that describe the electronic surface plasmon to exist, the real part of the dielectric constant of the conductor must be negative and its magnitude must be greater than that of the dielectric. This condition is met in the infrared-visible wavelength region for air/metal and water/metal interfaces (where the real dielectric constant of a metal is negative and that of air or water is positive). Plasmon are photonic data storage, light generation, and bio-photonics (Barnes et al., 2003).

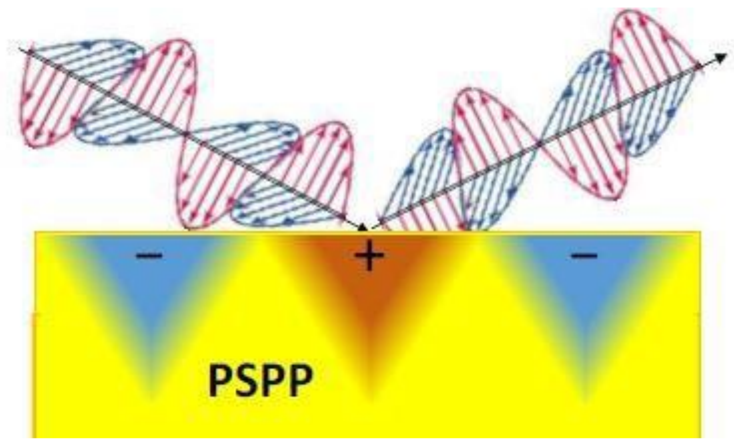

Fig. 2.3 Schematic diagrams illustrating SPP (Amendola et al., 2010)

2.5.2.2 Localized Surface Plasmon (LSP)

Localized Surface Plasmon Resonances (LSPRs) is defined as collective electron charge oscillations in metallic nanoparticles that are excited by light (see Fig.2.4). In case of small NPs compare to the wavelength of electromagnetic radiation (EMR), the electrons in these NPs oscillate transforming the energy from EMR into thermal energy in an absorption process.

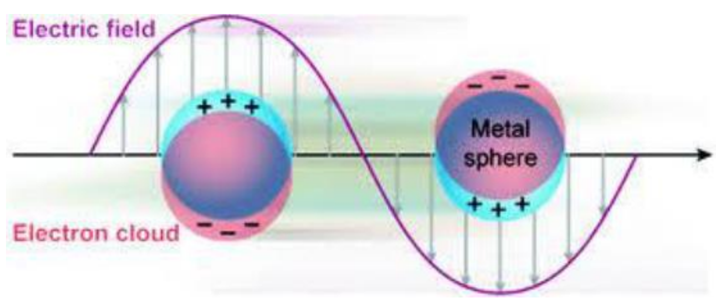

Fig. 2.4 Schematic diagram illustrating localized surface Plasmon (Borys, 2011)

The enhancement of this process is called near-field enhancement. Of interest is that this field is highly localized at the nanoparticles surfaces and decays rapidly away from the nanoparticles. For big NPs, these electrons can be accelerated, and they radiate energy in scattering process. The enhancement of this process is called far-field enhancement. Actually, the theory of the interaction between metal NPs and Electromagnetic radiation (EMR) was developed by scientist Mie 1908 and Later on called by Mie theory (Hergert and Wriedt, 2012). In general, this theory expressed the electromagnetic extinction C_{ext} as the sum of absorption C_{abs} and scattering C_{sca} (Kakani and Kakani, 2006).

$$C_{ext} = C_{abs} + C_{sca} \quad (2\text{-}2)$$

Light intensity enhancement (in both cases of absorption or scattering) is a very important aspect of LSPRs. The localization means that the LSPR has very high spatial resolution (sub wavelength), limited only by the size of nanoparticles. Because of the enhanced field amplitude, effects that depend on the amplitude such as magneto-optical effect are also enhanced by LSPRs.

2.6 Tuning of the Localized Surface Plasmon Resonance

When metal nanoparticles are excited by electromagnetic radiation, they exhibit collective oscillations of their conduction electrons known as localized surface plasmons. The wavelength corresponding to the extinction maximum (λ max), of the LSPR is highly dependent on the sizes and shapes of metal NPs and dielectric function of the environment. Details about these parameters will be discussed below.

2.6.1 Effect of Shape

It is well known that the shape of metal nanoparticles (MNPs) strongly affects their SPR. For many metal nanoparticles (MNPs), there are indications of the presence of polyhedral shapes with well-defined facets and vertices, including icosahedral (I h), decahedral (dh), face-centered cubic (f cc), and truncated cubes (t c). The SPRs for polyhedral nanoparticles have been recently studied and a general relationship between the SPR and the morphology or the shape of each nanoparticle was shown in figure 2.5. For instance, the optical properties have been investigated computationally for spherical, cubes and decahedra as well as for their different truncations (Rycenga et al., 2011).

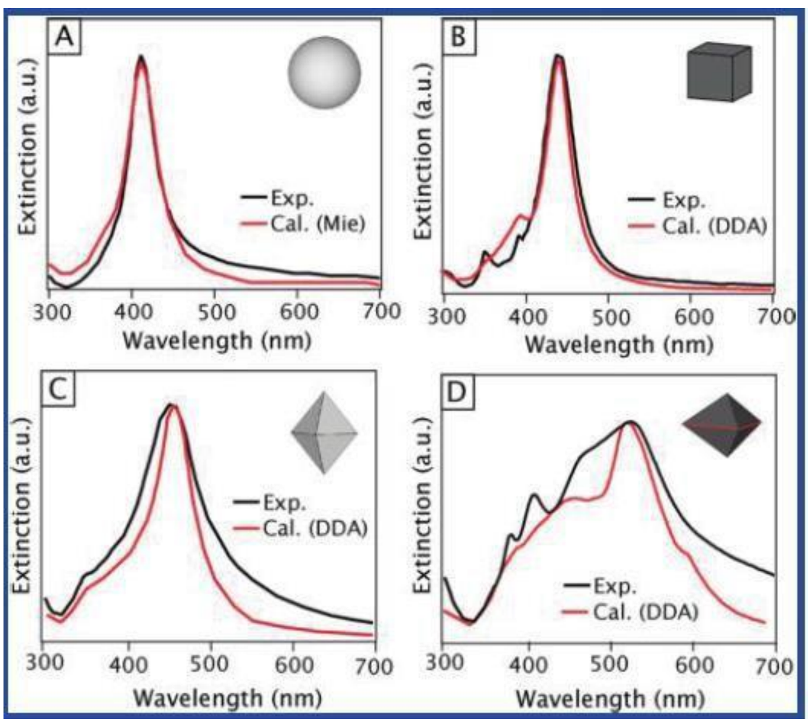

Fig.2.5 Extinction spectra of Ag nanoparticles with different shapes (Rycenga et al., 2011).

2.6.2 Effect of Size

As mentioned before, the extinction coefficient responsible for the measured UV-Vis spectrum of metal nanoparticles has contributions from electronic absorption and scattering. The scattering effect becomes increasingly more important for larger particles. For metallic nanoparticles of less than about 30 nm of diameter, the scattering processes are usually negligible, and the particle mainly absorbs light energy through either SPR or inters band electronic transitions. SPR is dependent on the particle shape, size, embedding environment and chemical nature of the material. Due to the small size and thereby large surface-to-volume (S/V) ratio, surface dispersion or scattering of the "free" electrons, especially when their mean free path is comparable to the dimension of the nanoparticles, is an important process to consider, e.g. in electronic energy relaxation or dissipation. For metal NPs smaller than ∼10 nm, collision of electrons with the particle surface becomes important, which usually results in broadening and blue-shift of the SPR absorption band (Horvath and Mie, 2009, Hodak et al., 2000)

From a quantum viewpoint, for particles containing about 100 atoms the electronic energy bands are quantized and energy level spacing may become comparable to thermal energy $k\ T$. This affects intra band transitions of the conduction electrons and leads to a damping of electron motion, which, in turn, influences the dielectric constant (Taleb et al., 1998).

One way to account for the size or surface effect is to divide the contribution to the dielectric constant into two parts: one from interband transitions and the second from intraband transitions including the surface effect (Noguez, 2007, Johnson and christy, 1972, Ashcroft and Mermin, 1976).

$$\mathcal{E}_1(\omega) = \mathcal{E}_1^{intra}(\omega) + \mathcal{E}_1^{inter}(\omega) \qquad \text{(2-3)}$$

$$\mathcal{E}_2(\omega) = \mathcal{E}_2^{intra}(\omega) + \mathcal{E}_2^{inter}(\omega) \qquad \text{(2-4)}$$

where ε_1 and ε_2 are the real and imaginary parts of the complex dielectric constant of the metal particle with a radius *R*. The intraband contribution can be calculated using the Drude model for the nearly free electrons (Ashcroft and Mermin, 1976):

$$\mathcal{E}_1^{intra}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} \qquad \text{(2-5)}$$

$$\mathcal{E}_2^{intra}(\omega) = 1 - \frac{\omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)} \qquad \text{(2-6)}$$

where $\boldsymbol{\omega}_p$ is the plasmon frequency, which is related to the free electron density *N*, and $\boldsymbol{\Gamma}$ is a damping constant. For metals such as Al and Ag, where the onset of interband transitions is well separated from the plasmon band, the plasmon band width is controlled by $\boldsymbol{\Gamma}$. For metals such as Au and Cu, where the interband transitions occur in the same spectral region as the plasmon band, the bandwidth is determined by both $\boldsymbol{\Gamma}$ and $\mathcal{E}^{\text{intra}}(\omega)$, which makes the analysis more difficult. In either case, however, the dependence of the bandwidth on particle size can be accounted using the following expressing (Kreibig and Vollmer, 1995, Johnson and christy, 1972, Hodak et al., 2000, Amendola et al., 2010).

$$\Gamma = \Gamma_0 + A\frac{Vf}{R} \qquad \text{(2-7)}$$

where R is the particle radius, V_F is the Fermi velocity of the electrons, A is a constant dependent on the electron- surface interaction and is usually on the order of unity (Hodak et al., 2000) and Γ_0 stands for the frequency of inelastic collisions of free electrons within the bulk metal, e.g. electron–phonon coupling or defects, and is on the order of hundredths of an electron Violate. For small-size particles, the second term in Eq. (2-5) which accounts for dephasing due to electron-surface scattering, can greatly exceed the bulk scattering frequency Γ_0, which accounts for bulk contribution to the electronic dephasing.

In general, the SPR depends weakly on the particle radius R. As R increases, one generally expects a shift and broadening of the SPR and the absorption cross section per particle will increase mainly due to an increase in particle volume.

2.6.3 Effect of Dielectric of the Environment

Besides the influence of nanoparticle morphology such as size and shape, the physical environment also modifies SPRs (Noguez, 2007). It has been shown that SPRs are shifted if the dielectric properties of the surrounding media are changed. In particular, the SPRs in a medium with density more than one are red-shifted with respect to those in vacuum. The SPR is also dependent on the geometry of the system including distance between the metal NP and substrate. The effects of both the dielectric properties and the physical environment of the nanoparticles are often of interest, since they have implications in processes such as SPR detection and surface enhanced raman scattering (SERS), catalytic processes, and plasmonic devices.

2.7 Applications of Silver Nanoparticles

Recently, silver nanoparticles have found wide range of applications in all most all fields of research. For examples, their applications in medicine, industrial, and scientific will be discussed in details below:

2.7.1 Applications in Medicine

For long time ago, silver was used for a variety of clinical conditions including epilepsy, venereal infections, acnes and leg ulcers. Moreover, silver foil was applied to surgical wounds for improved healing and reduced post-operative infections, while silver and 'lunar caustic' (pencil containing silver nitrate mitigated with potassium nitrate) was used for wart removal and ulcer debridement. Although some centers still use these solutions, they have been shown to be very impractical to use on large wounds or for extended time periods due to instability. With nanotechnology, the availability of silver nanoparticles has enabled the use of pure silver to achieve a rapid growth in medical practice. Since the size, shape and composition of silver nanoparticles can have a significant effect on their efficacy; extensive research has gone into synthesizing and characterizing silver nanoparticles. The application of nanosilver can be broadly divided into diagnostic and therapeutic uses.

2.7.2 Applications in Industrial

Ag-NPs have been in use for more than 150 years and are recognized as antimicrobial agent in United States (USA) since 1954.There are many assumptions about the use of silver by the ancient Egyptian and Romans. The most stable oxidation state of Ag is +0 and +1 although it can exist in other oxidation states as well and can form various complexes. Ag(NO3) is considered as a precursor for the synthesis of Ag-NPs. The size and geometry of Ag-NPs are dependent on the synthetic route adopted for its synthesis; however it can be found in spherical, rod, and triangular shape, or coated with polymer, biomolecules, and sugars. Ag-NPs has numerous chemical, physical and biological functions which are explained point by point.

2.7.3 Scientific applications

Nanomaterials have a wide range of applications in automotive catalyst, membranes, fuel cells, photocatalysts, propellants, scratch-resistant coatings, structural ceramics and solar cells (Bhargava and Sharma, 2013). High surface area and high surface energy predetermine metal nanoparticles for being effective catalytic medium. The growing small silver particles have been proved to be more effective catalysts than stable colloidal particles. These growing particles catalysed the borohydride reduction of several organic dyes. As compared with the stable and larger silver particles, the rate of reduction catalysed by growing particles was found to be faster.

Catalysis is due to efficient particle-mediated electron transfer from the BH4- ion to the dye. The catalytic activity of the particles depends on their size, *E*1/2 of the dye, and the dye-particle interaction. By controlling the size of nanoparticles, its catalytic activity can be controlled, as the redox potential depends on the nanoparticle size (Jana, *et al*., 2000). Using Kashayam and Guggulutiktham an ayurvedic medicine, the size-dependent catalytic activity of the synthesized Ag NPs was observed in the reduction of methylene blue dye by using NaBH4 (Suvith and Philip, 2014). The synthesized Ag NPs from the plant extract of *Gloriosa superb* has the electron relay effect which influences the degradation of methylene blue at the end of the 30 min (Ashokkumar et al., 2013). The catalytic activities of Ag-NPs synthesized by *Dimocarpus longan* seed extract were assessed against the photocatalytic degradation of methylene blue and chemo-catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). The results suggest that the prepared Ag-NPs have strong chemo-catalytic activity with a complete reduction of 4-NP to 4-AP within 10min (Khan et al., 2017). Hence, it can be said that silver nanoparticles find good applications in catalysis.

2.7.4 Biological applications

Silver is being used from centuries as a non-toxic, safe inorganic antibacterial agent capable of killing about 650 microorganisms that cause various diseases (Annamalai and Nallamuthu, 2016) It has a significant potential for a wide range of biological application such as antibacterial agents for antibiotic resistant bacteria, preventing infections, healing wounds and anti-inflammatory (Atiyeh et al., 2007). Silver ions and the compounds made from it have a very strong destructive effect on many bacterial species and also have low toxicity towards animal cells. Therefore, silver ions, being an antibacterial component, are employed in the formulation of dental resin composites, bone cement, ion exchange fibers and coatings for medical devices (Panáček et al., 2006, Alt et al., 2004).

Silver nanoparticles also have antimicrobial properties. It was reported that Ag in nanoforms is considered less toxic than Ag^{+} ions (Pattabi and Pattabi, 2013). The antimicrobial properties of silver nanoparticles caused the employment of those nano-metals in numerous fields of medication, numerous industries, agriculture, packaging, accessories, cosmetics, health and military (Roh and Cho, 2005, Hussain et al., 2016, Khan et al., 2017).

Silver nanoparticles with their large surface to volume ratio have been widely studied as a valuable material for their strong antimicrobial effect (Song et al., 2012). The toxicity of silver nanoparticles has been well-known to a wide range of microorganisms. The antibacterial property of silver nanoparticles against Staphylococcus aurous, Pseudomonas aeruginosa and Escherichia coli has been investigated (Birla et al., 2009). It was considered that silver nanoparticles of 1 -10 nm range attach to the surface of the cell membrane and disturb its proper function like permeability and respiration (Morones et al., 2005).

The biosynthesized silver nanoparticles displayed antimicrobial activity against a range of pathogenic microorganisms, such as C. albicans, V. parahaemolyticus, S. enterica, B. anthracis, B. cereus, and E. coli (Singh et al., 2015). Biogenic synthesis of silver nanoparticles(Antibacterial and cytotoxic potential) (Algebaly et al., 2020). Antimicrobial activity of the synthesized Ag NP's from the leaf extracts of C. torulosa D.Don and fungal endophytes Pestalotiopsis versicolo was done against three pathogenic bacteria Bacillus subtilis, Salmonella entrica and Pseudomonas aeruginosa showed promising medicinal drug activity against all the pathogens (Rajput et al., 2017, Baletto and Ferrando, 2005, Tao et al., 2006).

The exact mechanism of antimicrobial action is not clearly known, but studies suggest that silver nanoparticles have the ability to damage the cell membrane permeability, damage the respiration functions of the cell, and encourage the formation of free radicals. The antimicrobial activity of silver nanoparticles was investigated by using fluorescent bacteria (Gogoi et al., 2006, Nikoobakht and El-Sayed, 2003). A different conclusion was drawn from the study that silver nanoparticles get attached to the sulfur containing bacterial cell which causes the death of the bacteria. The fluorescent measurements of the cell-free supernatant reflected the effect of silver on recombination of bacteria.

Several studies have shown that the combination of silver nanoparticles with antibiotics leads to an enhanced effect of the antibiotics against microorganisms (Fayaz et al., 2010, Algebaly et al., 2020). This is probably due to the increase in cell wall penetration by antibiotics with the nanoparticles. The synergistic effect of the antibiotics (vancomycin, novobiocin lincomycin, oleandomycin, penicillin G, and rifampicin) in association with biosynthesized silver nanoparticles increased the sensitivity of the tested microorganisms (S. enterica, E. coli, V. parahaemolyticus, B. anthracis, and B. Cereus) (Singh et al., 2015, Bagherzade et al., 2017).

Many researchers have demonstrated the synergistic effect of biosynthesized silver nanoparticles with commercially available antibiotics (Dar et al., 2013, Fayaz et al., 2010). However, the exact mechanism behind this activity is still not well understood and must be explored.

CHAPTER THREE

METHODS AND TECHNIQUES

3.1 Introduction

In this chapter, the experimental method and materials used were described in details. At the end of the chapter, a brief description of the UV-Vis spectrometer used in the characterization of Ag-NPs is presented.

3.2 Materials and tools

Materials and tools used to synthesis Ag-NPs were:

- Silver nitrate ($AgNO_3$) with purity 98%.
- Distilled water and ethanol.
- Beakers and hot plate with magnetic stirrer (see Fig.3.1)
- Acacia Nilotica fruit and Guiera leave extract.
- Sensitive balance (accuracy=0.0001g) (see Fig.3.2a).

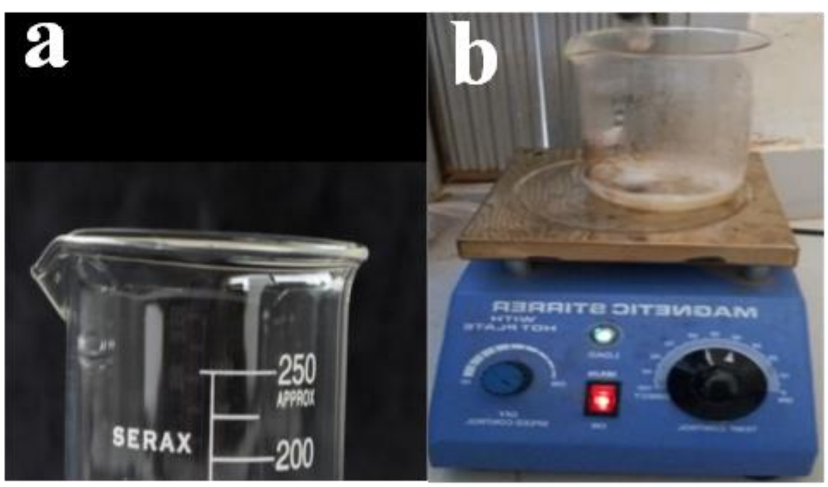

Fig. 3.1 (a) beaker (b) Magnetic stirrer with hot plat.

Fig. 3.2 Sensitive balance

3.3 Silver Nitrate

It is an inorganic compound with chemical formula Ag NO_3. This salt is a versatile precursor to many other silver compounds, such as those used in photography. It is far less sensitive to light than the halides. It was once called *lunar caustic* because silver was called *Luna* by the ancient alchemists. It can be prepared by reacting silver, such as silver bullion or silver foil, with nitric acid, resulting in silver nitrate, water, and oxides of nitrogen. Reaction byproducts depend upon the concentration of nitric acid used.

3 Ag + 4 HNO_3 (cold and diluted) → 3 $AgNO_3$ + 2 H_2O + NO

Ag + 2 HNO_3 (hot and concentrated) → $AgNO_3$ + H_2O + $\underline{NO_2}$

This is performed under a fume hood because of toxic nitrogen oxides evolved during the reaction. molar mass: 169.87 g/mol, formula: $AgNO_3$, density: 4.35 g/cm³,melting point: 413.6°F (212°C), boiling point: 824°F (440°C), soluble in: water, glycerol.

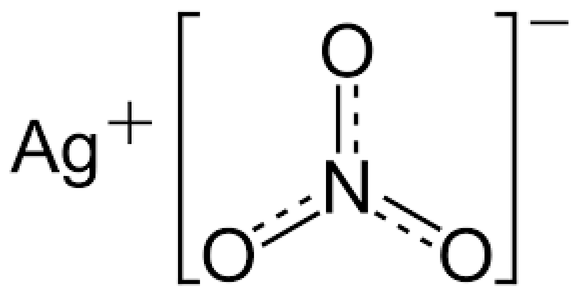

Fig.3.3 chemical formula silver nitrate $AgNo_3$

3.4 Acacia Nilotica

Acacia is a genus of shrubs and trees belonging to the subfamily mimosoideae of the family fabaceae or leguminosae. It is indigenously known as 'babul' or 'kikar' is moderate sized with a spreading crown tree and is broadly scattered in tropical and subtropical countries. It is indigenous to the indian sub-continent as also in tropical Africa, Burma, Srilanka, Saudi arabia, Egypt and in west and east of Sudan. In India, natural babul forests are generally found in Maharashtra, Gujarat, Andhra Pradesh, Rajasthan, Haryana and Karnataka. However, scattered trees in groups occur naturally and also widely planted in almost all states and Union territories except north-eastern states, Kashmir and Kerala. A. *nilotica* is truly a multipurpose tree and extensively used in traditional agro-forestry system. In the present scenario of climate change, agro-forestry practices, emerging as a viable option for combating negative impacts of climate change (Pattanayak et al.,

2014) (Abhishek., R., et al., 2015, Toppo, j., et al., 2018, Uthappa, A. R., et al., 2017). It is reported to be well nodulated with rhizobium species (Dreyfus and Dommergues, 1981). This nodulation behavior helps in biological nitrogen fixation which helps to meet the nitrogen requirement in nutrient-poor soils and application of nitrogen. In addition, this species form symbiotic associations with naturally occurring soil fungi called vesicular arbuscular mycorrhizae (v a m) (Abiala et al., 2013) (Linderman, R.G., 1992, Toppo, R., et al., 2018). This association assists the roots to exploit more soil volume and to gain improved access to available nutrients especially phosphorus under stress and also makes the unavailable forms of nutrients into utilizable forms (Renge, 2008). Its timber is valued by rural folks, its leaves and pod are used as fodder and gum has a number of uses. acacia nilotica is an imperative multipurpose plant that has been used broadly for the treatment of various diseases (Atif et al., 2012, Asgarpanah et al., 2017). Furthermore, acacia nilotica, butea monosperma, terminalia arjuna, albizia procera and zizyphus mauritiana are an integral part of the rural agroforestry practices of the region and have tremendous importance in poverty alleviation and income generation (Zlatic, M., 2015). The tree has a special significance to resource-poor farmers, who have a long tradition of growing it on their farms along with crops (Viswanath et al., 2000). Moreover gum produced from this resource is very valuable in pharmaceutical purpose, calico-printing, sizing paper, cloth and textiles and encapsulation etc.

3.5 Guiera Senegalensis

Guiera senegalensis is also called Sabara in hausa (African tripe) language. It is shrubby of savannah region of west and Central Africa. Its leaves arecommonly used in traditional medicine in gastrointestinal disorders, respiratory infections, and rheumatism and as antimalarial agent. It is known to have significant activities against cough, respiratory congestion and fever. Moreover, Guiera senegalensis is prescribed as an antitussive, hypertension and hypotension as well as venereal diseases to ease breathing and to treat lung and bronchial disorders (Dénou*et al., 2016).

Previous studies indicated the presence in leaves of two alkaloids (harman, tetrahydroharman or eleagnine), flavonoids, naphthopyrans, tannins, and a naphthyl butenone (guieranone A); in roots, were only obtained tannins and the same beta-carboline alkaloids than in leaves (Fiot et al., 2006). In different research, the phytochemical analysis of Guiera senegalensis revealed the presence of bioactive compounds which includes alkaloids, flavonoids, saponnins and tannins (Mohammed et al., 2016).

3.5 Experimental Procedure to Synthesize Ag Nanoparticles

Silver Nitrate ($AgNO_3$, 98%) was obtained from chemical laboratory of Sudan University science and Technology. Acacia and Guiera were purchased from Omdurman market. It was picked in 2017 from Al hawatia western Sudan in al Gatareef state, and kept in local store. All glass ware was cleaned with distilled water and dried before used. To prepare Acacia and Guiera extract, it was cleaned for several times with distilled water to remove dust and dried at room temperature. Then 10g of Acacia and Guiera were added separately to 100ml of distil water in beaker and heated of 70^0C for 25 min. The obtained mixtures were filtered and stored at room temperature for further use.

To prepare homogenous solution of Ag NO_3 with concentration of 1mM, 0.169g of $AgNO_3$ was added to 1 litter of distiled water and stirred for 30 min at room temperature.

To optimize the synthesis parameters, different heating time and different ratios between acacia nilotica or Guiera extracts and silver nitrate solution were applied. In the first experiment, different amount of acacia nilotica extract (1ml, 2ml, 3ml, and 4ml) was added separately to 20 ml of silver nitrate solution to get different ratios (1:20, 2:20. 3:20 and 4:20). In other experiment, different amount of Guiera extract (0.2ml, 0.5ml, 1.0ml, and 2.0ml) was added separately to 20 ml of silver nitrate solution to get different ratios (0.2:20, 0.5:20. 1.0:20 and 2.0:20). These mixtures were heated separately at fixed temperature of 70^oC for 10 minutes. In the second experiment, the optimum ratios obtained from the first experiment for acacia nilotica (2.0:20) and for Guiera (0.2:20) were used to optimize the heating time. These ratios were used because they showed highest intensity of the absorption band of LSPR compared to other ratios. The obtained mixtures with optimum ratio were heated at 70^oC for different time (5 min, 10 min, 20 min, 30 min, 50 min and 70 min for acacia nilotica and 10min, 20min, 40min, 60min and 90min for Guiera). Of interesting is that for both experiments the color was changed after addition of plants extract (acacia nilotica or Guiera), indicating the formation of Ag-NPs. Figure 3.4 showed the preparation flowchart of Ag NPs.

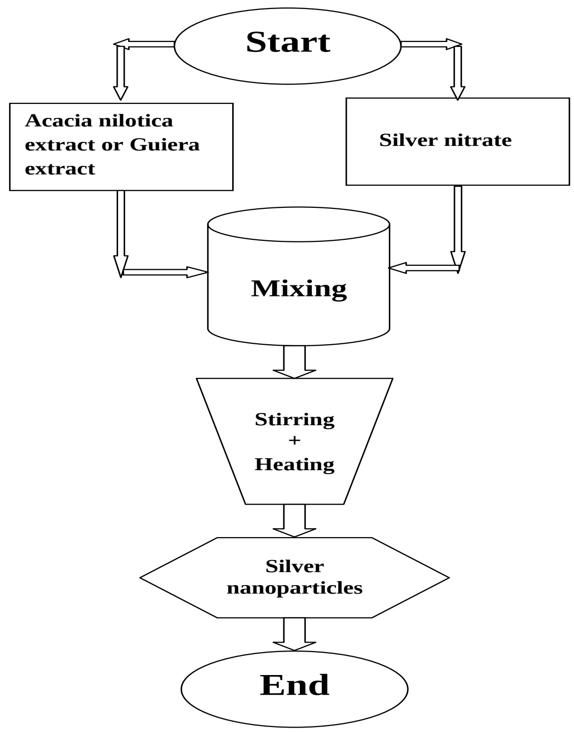

Fig. 3.4 Preparation flowchart of silver nanoparticles.

3.6 Characterization Techniques

Ultraviolet and visible light spectrophotometer was used to conform silver nanoparticles under more details.

3.6.1 UV-VIS Spectrophotometer

The instrument used in ultraviolet-visible spectroscopy is called a UV-Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o).The ratio (I/Io) is called the transmittance.

The UV-visible spectrophotometer can also be configured with an integrated sphere to measure reflectance. In this case, the spectrophotometer measures the intensity of light reflected from a sample (I), and compares it to the intensity of light reflected from a reference material (I_o). The ratio (I/I_o) is called the reflectance. In a UV-Vis (ultraviolet-visible light) spectroscopic measurement, light absorption as a function of wavelength provides information about electronic transitions occurring in the material (Förster, 2004). There are two types of UV spectrophotometer (single beam and double beam).

In a single beam UV spectrophotometer, all of the light passes through the sample cell (Chen et al., 2013). Io must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs. In a double-beam UV spectrophotometer, the light is split into two beams before it reaches the sample (see Figure 3.5). One beam is used as the reference and the other beam passes through the sample. The measured UV-Vis spectrum can be obtained as absorption, transmission and reflection spectrum. Absorption and transmission apply for gas and solution or transparent glass samples, while reflection applies only for solid samples. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape and commonly with an internal width of 1 cm. Cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions.

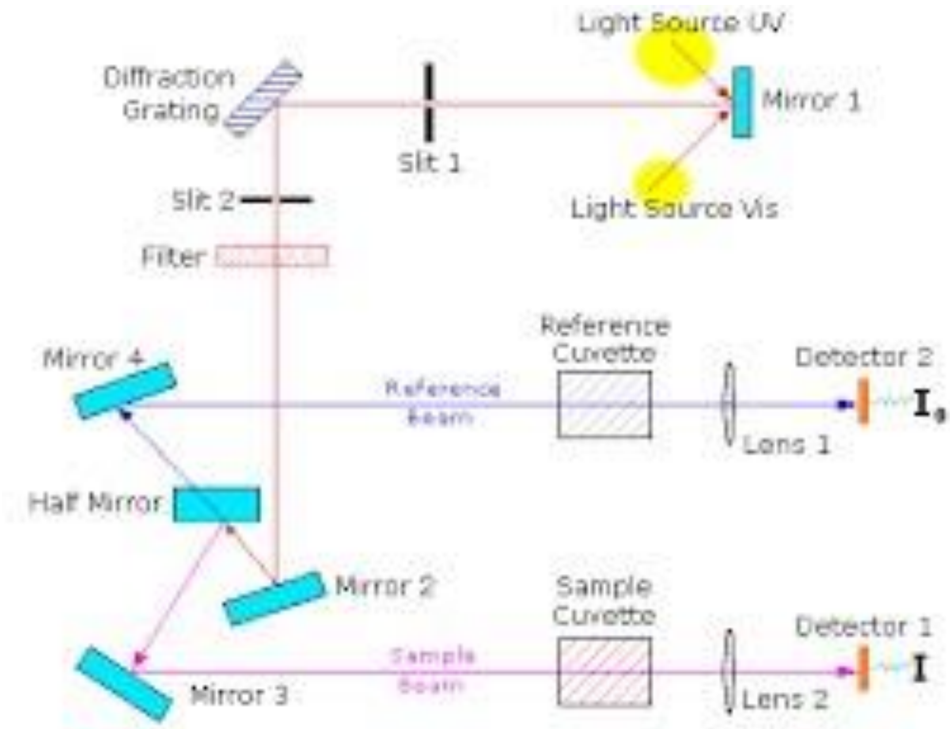

Fig.3.5 UV-Vis spectroscopy diagram.

The main objective of this instrument is to determine the absorption band of LSPR which confirm the formation of Ag NPs.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

Result and Discussion

The chemical synthesis of metals nanoparticles by reduction of the corresponding metal salts (metals ions in solution) is an apparently simple process, which only requires the mixing of the reagents (metals ions with reducing agent) at suitable conditions. These conditions (I.e., heating temperature, heating time and the concentration) can affect, in subtle ways, the final morphology of the particles (Harihar Nath Verma 2014). One of the most characteristic properties of metals nanoparticles is physical phenomenon called LSPR (see chapter 2). Among metals NPs, Ag is known to have strong absorption band in visible range due to LSPR. The appearance of the absorption band in the visible range is considered as a strong evidence of the formation of silver NPs (Awwad et al., 2013, Mondala et al., 2011). Therefore UV-Vis spectrometer technique is commonly used to confirm the formation of metal NPs. . It is important to note that some significant parameters such as temperature, and reaction time inferred a quantifiable influence on the absorbance intensity and position of the LSPR band (Rajasree Shanmuganathan et al., 2018). Therefore these two parameters were investigated in this work.

In this study Ag ions (silver nitrate dissolved in distil water), was reduced to the silver Ag-NP_s using natural plants namely Acacia Nilotica fruits extract, and Guiera senegalensis leaves extract. To optimize the synthesis parameters, different heating time (see Fig 4.4A for Acacia fruits and Fig. 4.4B for Guiera leaves) and different ratio between the natural plants extract

(Acacia fruits or Guiera leaves) and silver salt solution was applied (see Fig 4.2A for Acacia fruits and 4.2B for Guiera leaves). The first indication of the formation of Ag NPs is observed during the experimental process which was the colour change after addition of plant extracts. When the Acacia fruit extract, or Guiera leaves extract, added to silver nitrate aqueous solution, the colour was changed to yellow pale after 5min and then to red murkily and finally to brown ((see Fig 4.1A for Acacia fruits and 4.1B for Guiera leaves)).

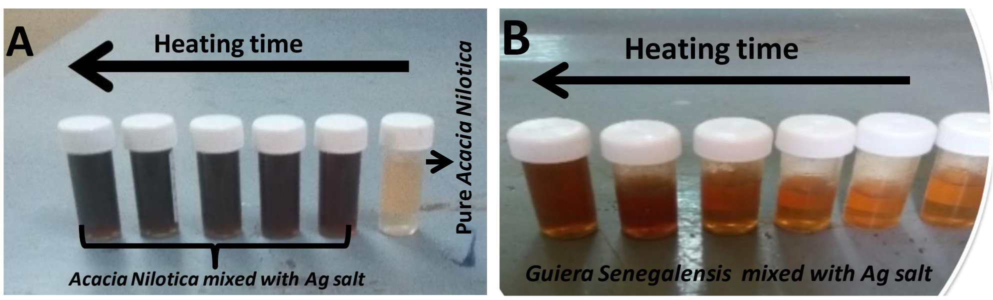

Figure 4.1 showed changing in color during the experimental process of (A) Acacia Nilotica (B) Guiera senegalensis.

To confirm the formation of Ag NPs, the obtained samples were characterized using UV-Vis spectrometer. The diffuse absorption for the mixture of Acacia fruits or Guiera leaves extract with silver salt is shown in Figure 4.2A and 4.2B, respectively.

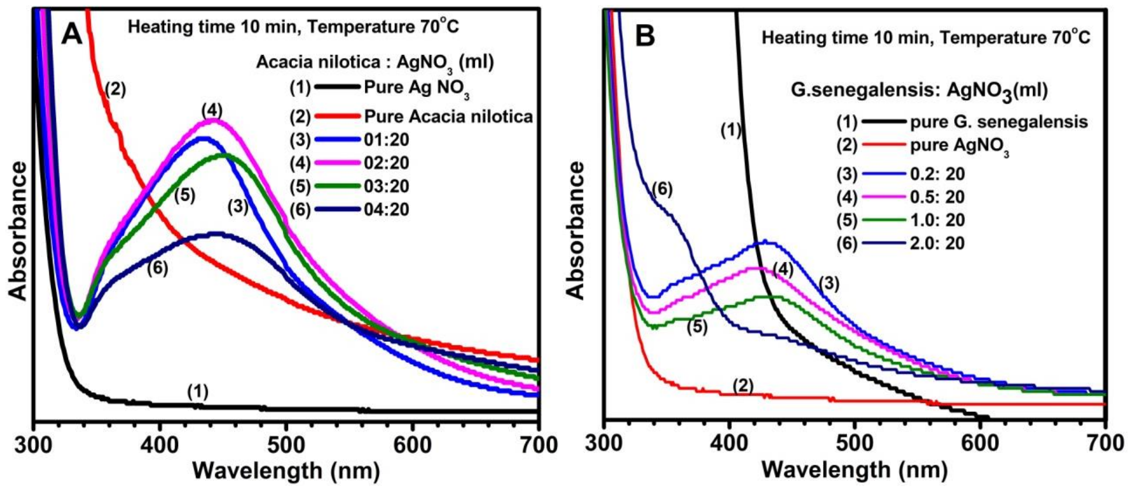

Fig.4.2 diffuse absorption for the mixture of silver salt and (A) Acacia fruits extract (B) Guiera leaves extract with different ratio.

As can be seen from figure 4.2 that the pure $AgNO_3$, Acacia fruits extract (Fig4.2A) and Guiera leaves extract (Fig4.2B) showed no peak in the visible region. But when aqueous solution of silver salt mixed with Acacia fruits extract (Fig4.2A) or Guiera leaves extract (Fig4.2B), pronounce peak is appeared in the visible region. This peak is attributed to LSPR which confirm the formation of Ag NPs (Shankar et al., 2004, Dubeya et al., 2010). As can be seen from figure 4.2A when the amount of Acacia fruits extract increased from 1ml to 2 ml with respect to 20 ml of silver salt solution, the intensity of the absorption band was increased, while the intensity of this band was decreased when the amount of Acacia fruits extract was further increased to 3 and 4 ml. This indicates that the optimum ratio between Acacia fruits extract and silver salt solution is 2.0:20 (see Fig 4.3).

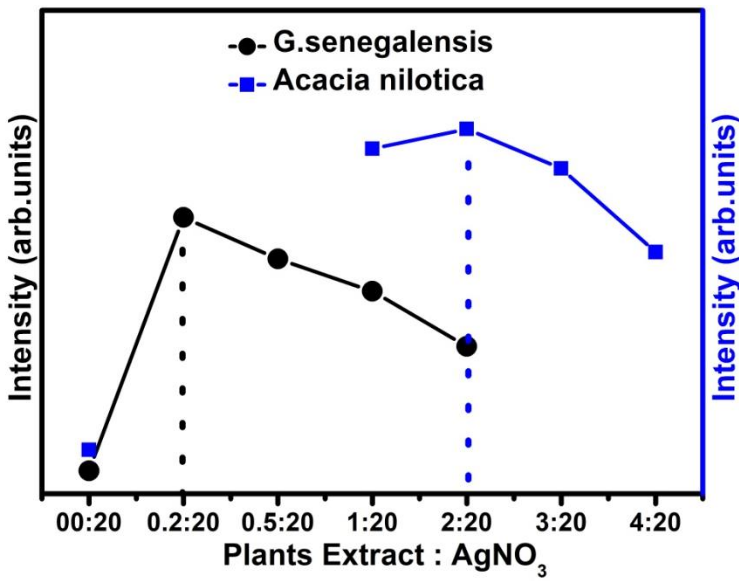

Fig.4.3 Effect of the amount of Acacia fruits extract or Guiera leaves extract on the intensity of the absorption band.

Similarly, figure 4.3B showed the effect of the Guiera leaves extract amount on the intensity of the absorption band. It can be seen from figure 4.3 that the optimum ratio between Guiera leaves extract and silver salt solution is 0.2:20. It has been reported that the plant metabolites such as sugars, terpenoids, polyphenols, alkaloids, phenolic acids, and proteins play an important role in the reduction of metal ions into nanoparticles (V.V.Makarova, 2014). In our case, alkaloids and proteins Are within the components of Acacia fruits extract and Guiera leaves extract which may be responsible of reducing silver ions to silver nanoparticles. It is well known that the shift in the peak position of the LSPR absorption band is due to changes in particle sizes or/and shapes or the refractive index of the environment (Kreibig and Vollmer, 1995). Since the shift is random, the changes in particle sizes or/and shapes is ruled out. Therefore the small random shifting in the absorption peaks in both figure 4.2A and 4.2B may be due changing in the refractive index during the preparation of samples for characterization where the samples were diluted with different amount of distil water. To investigate the effect of heating time, different heating time were applied for both Acacia and Guiera samples (see Fig 4.4) using the optimum ratio between plant extract and silver salt obtained from experimental results shown above (see Fig. 4,3) and heating temperature of 70^{o}C.

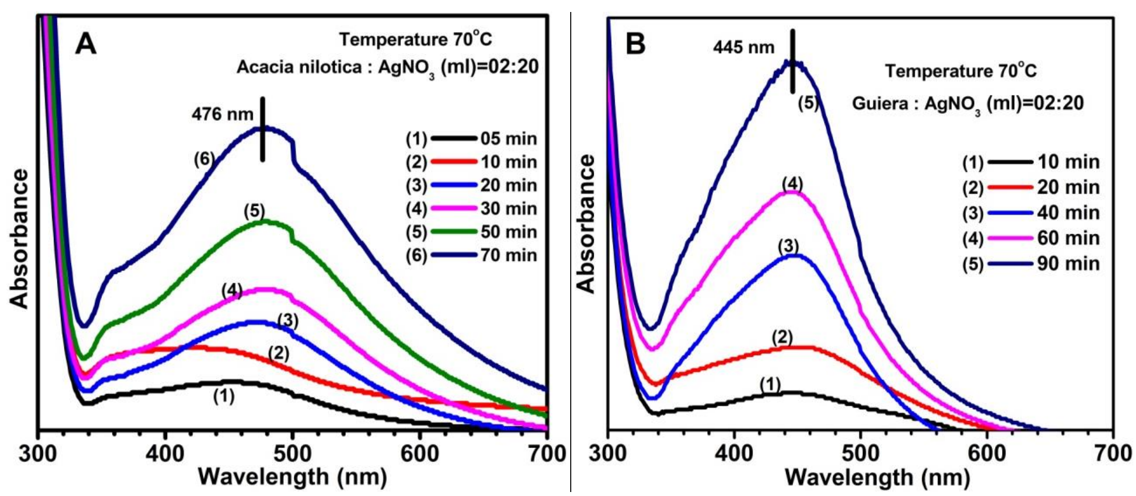

Fig.4.4 diffuse absorption for the mixture of silver salt and (A) Acacia fruits extract (B) Guiera leaves extract heated at different time.

Figure 4.4 shows the absorption spectra of the (A) Acacia sample and (B) Guiera sample. As can be seen from both figures (A&B), as the heating time increases the absorption intensity is increased (see fig 4.5). This indicates that the increasing of the heating time enhanced the reaction rate and therefore more silver ions are reduced. Of interest is that there is no shift in peak position as the function of heating time for both samples, indicating that the particle size produces at different temperatures for each sample were mostly similar in shapes and sizes. It is also seen that the both figures showed single absorption peaks related to the LSPR centred at 476 nm and 445 nm for Acacia and Guiera sample, respectively. It has been reported that the red shift of absorption band is correlated with increasing of particle size and changing of particle shape (Eichelbaum and Rademann, 2009). In addition, for shapes others than spherical produces multiple peaks in absorption spectra due to high order mode dipoles (I.e. Double, triple, quadruple, , …) (Xianmao Lu et al., 2009) . Since both figures showed single peaks, the effect of the shape is ruled out. Therefore, the difference in the absorption band position between figure 4.4A and 4.4B is due to particle size, indicating that the addition of Acacia extract produces bigger particles compare with Guiera extract. To confirm this, Mie theory was used to calculate the particle size using the results shown in figure 4.4 (A and B).

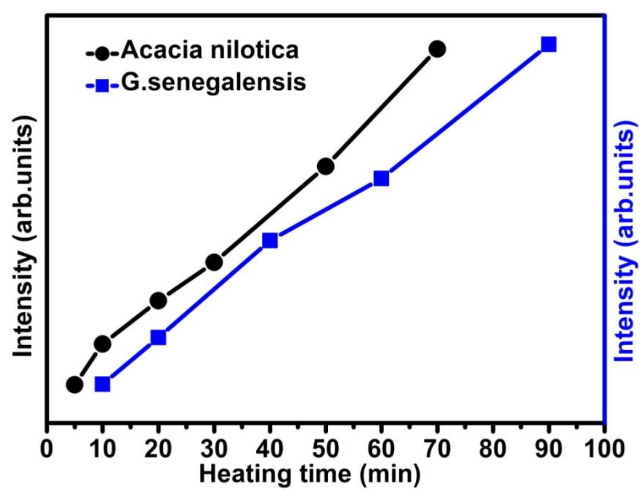

Fig.4.5 Effect of heating time on the absorption band intensity of the mixture of silver salt and Acacia fruits extract or Guiera leaves extract.

According to Mie theory there is relationship between the resonance broading, and the sizes of nanoparticles as shown in equation 2.7 chapter two. In our case, for silver the $v_f = 1.4\text{x}10^6 \text{m/s}$, $A = 3/4$ and $\Gamma_0 = 4.4 \times 10^{14}$ Hz (Hodak et al., 2000).

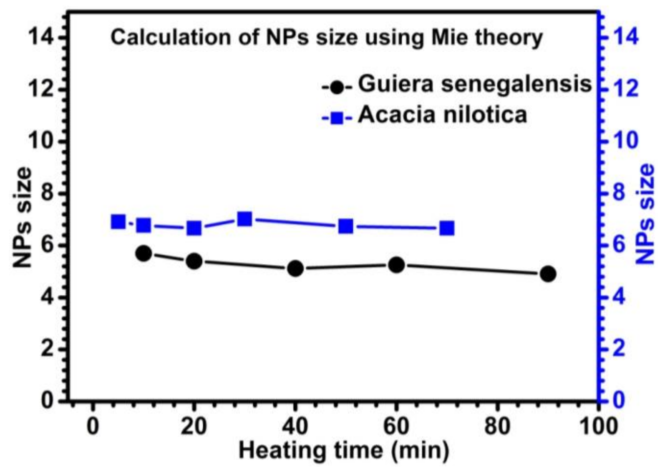

Fig.4.6 Effect of heating time on particle size for both Acacia **and Guiera samples.**

Figure 4.6 shows the effect of the heating time on the particle size for both Acacia and Guiera samples. As can be seen, the heating time has no significant effect on the particle size. It also seen that the in case of Acacia extract the particle size is found to be 7nm while for Guiera is found to be 5 nm which confirm that the difference in absorption band position between figure 4.4A and 4.4B is due to the particle size.

CHAPTER FIVE
CONCLUSION AND FUTURE WORK

5.1 Conclusion

In work, silver nanoparticles were successfully synthesized using Acacia Nilotica fruits and Guiera Senegalensis leaves extracts as reducing agent and silver nitrate as the source of silver. All samples were characterized by UV-Vis spectrometer. The presence of an absorption band in visible range in absorption spectra and the change of color during synthesis process confirm the formation of silver nanoparticles. According to Mie theory calculations, it found that the using of Nilotica fruits extract produced bigger particles compare to the particles produced in case of Guiera Senegalensis extract. It is also found that the heating time had no effect on the particle size but instead enhanced the reaction rate.

5.2 Recommendation and future work

- In this work, Acacia Nilotica fruits, and Guiera senegalensis leaves were used as reducing agent. Other plants extract can be used to reduce silver ion into silver nanoparticles.
- Acacia Nilotica fruits and Guiera senegalensis leaves extracts were used to synthesis silver nanoparticles only. In future work, other noble metals such as gold, copper…etc. should be used.
- Only UV-Vis spectrometer is used to confirm the formation of Ag-NPs. Appling other characterization techniques such transmission electron microscope (TEM) and x-ray diffractometer (XRD) for

further information (I.e., morphology, distribution, size and shape) should be done.

- Other synthesis parameters such PH, heating temperature will be applied to optimize synthesis method.

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