Sudan University of Science and Technology
College Graduate Studies

Green Synthesis of Silver Nanoparticles Using Azadirachta Indica (Neem) leaves Extract

التحضير الآمن لجسيمات الفضه النانويه بإستخدام مستخلص اوراق النيم

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

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الآيـــــــــة

قال تعالى :

{اللَّهُ نُورُ السَّمَاوَاتِ وَالأَرْضِ مَثَلُ نُورِهِ كَمِشْكَاةٍ فِيهَا مِصْبَاحٌ الْمِصْبَاحُ فِي زُجَاجَةٍ الزُّجَاجَةُ كَأَنَّهَا كَوْكَبٌ دُرِّيٌّ يُوقَدُ مِن شَجَرَةٍ مُّبَارَكَةٍ زَيْتُونَةٍ لّا شَرْقِيَّةٍ وَلا غَرْبِيَّةٍ يَكَادُ زَيْتُهَا يُضِيءُ وَلَوْ لَمْ تَمْسَسْهُ نَارٌ نُّورٌ عَلَى نُورٍ يَهْدِي اللَّهُ لِنُورِهِ مَن يَشَاء وَيَضْرِبُ اللَّهُ الأَمْثَالَ لِلنَّاسِ وَاللَّهُ بِكُلِّ شَيْءٍ عَلِيمٌ}

صدق الله العظيم

سورة النور الآية {35}

Dedication

To my family

To my friends

Mishkat

Acknowledgements

First of all, I would like to thanks Allah for giving me the strength to finish this study

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Abstract

Noble metals nanoparticles are considered as promising material due to their unconventional characteristics owing to several technological applications. Their small size and large surface to volume ratio as compared to their bulk form leads to differences in their physical and chemical properties. As the results, these metallic nanoparticles have found a wide range of applications in almost all fields of research. Silver **(Ag)** nanoparticles are the most common one being employed in emerging interdisciplinary and brightest field due to their fascinating optical properties owing to their strong surface Plasmon resonance. As compared to the conventional chemical methods used to synthesize silver nanoparticles, biological synthesis showed some advantages such as cost effective, rapid and eco- friendly.

In this work, silver nanoparticles were synthesized by chemical reduction methods using Neem extract as reducing agent. During synthesis, the color was changed after addition of Neem extract, indicating the formation of silver nanoparticles. The obtained nanoparticles (in solution) were further characterized by UV-VIS spectrometer. The obtained absorption spectra showed an absorption peak in visible region owing to localized surface Plasmon resonance which confirms the formation of silver nanoparticles. In addition, the effect of Neem quantity and boiling time on the formation of silver nanoparticles was also investigated. The obtained results showed that the boiling time and the concentration of Neem extract had no obvious effect on the particle size but instead enhanced interaction rate. The particle size of silver was calculated using Mie theory and the average size was found to be ∼5.3 nm.

المستخلص

تعتبر جسيمات المعادن النبيلة النانوية من المواد الواعدة بسبب خصائصها غير التقليدية والتي تدخل في العديد من التطبيقات التكنولوجية .إن صغر حجمها و كبرمساحة سطحها مقارنة بحجمها ادي إلى اختلافات في خواصها الفيزيائية والكيميائية . كنتيجة لذلك، فقد دخلت هذه الجسيمات المعدنية النانوية في مجموعة واسعة من التطبيقات في جميع مجالات البحث تقريبا .تعتبر جسيمات الفضة النانوية هي الأكثر استخداما نظرًا لخصائصها البصرية الرائعة الناتجة من ظاهرة البلازمون . بالمقارنة مع الطرق الكيميائية التقليدية المستخدمة لتحضير الفضة النانوية ، أظهرت االطريقة البيولوجية بعض المزايا مثل قلة التكلفة وسرعة التحضيرو صديقة للبيئة. في هذة الدراسة ، تم تصنيع جسيمات الفضة النانوية بطريقة الاختزال الكيميائية باستخدام مستخلص اوراق النيم كعامل مختزل .أثناء التحضير ، تغير لون المحلول بعد إضافة مستخلص اوراق النيم ، مما يشير إلى تشكيل جسيمات الفضة النانوية .تم فحص الجسيمات النانوية التي تم الحصول عليها (في المحلول) بمقياس مطياف الامتصاص وأظهرت أطياف الامتصاص التي تم الحصول عليها ذروة امتصاص في المنطقة المرئية بسبب ظاهرة رنين البلازمون والذي يؤكد تشكيل جسيمات الفضة النانوية .بالإضافة إلى ذلك ، تم أيضا دراسة تأثير كمية مستخلص اوراق النيم وزمن الغليان على تكوين جسيمات الفضة النانوية .وأظهرت النتائج التي تم الحصول عليها أن زمن الغليان وتركيز مستخلص اوراق النيم لم يكن لهما تأثير واضح على حجم الجسيمات ولكنهما تحسنان من معدل التفاعل .تم حساب حجم جسيمات الفضة النانوية باستخدام نظرية ماي, حيث وجد ان متوسط حجم الجسيمات يساوي تقريبا ~ 5.3 نانومتر

Keywords and acronyms

Keywords

Neem extract -turkevich method - Localized surface Plasmon resonance (LSPR) - Mie Theory-Silver nanoparticles.

Acronyms

SPP: Surface Plasmon Polariton.

LSPs: Localized surface Plasmon.

LSPR: Localized surface Plasmon resonance.

NPs: Nanoparticles.

UV-VIS: Ultraviolet-visible spectroscopy

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CHAPTAR ONE

Introduction

1.1 Overview

Simply, the meaning of world nano is extremely small. Nano comes from the Greek word "nanos" meaning "dwarf" (Narayanan and Sakthivel, 2010). Actually there are two main field associated with the world nano. The first field is nano-science which is the study of structures and materials on the scale of nanometers. The other one is nanotechnology which is deals with the development of materials and devices by exploiting the properties of particles at the nano scale (Sanchez and Sobolev, 2010). When structures are made small enough particularly in the nanometer size range, it gives an interesting and useful properties completely different from their bulk form. Actually, nano science and nanotechnology can be used across all science fields, such as chemistry, biology, physics, materials science, industrial, military, medical, agricultural and engineering (Daniel and Astruc, 2004).

Nano-material is defined as the material that has at least one dimension in nanoscale. Moreover, nonmaterial can be synthesized in different shapes such as nanoparticles, nano-rods, nano-desk, nanocubes, etc (Sanchez and Sobolev, 2010).

Actually, nanoparticles are attracted much attention in last fifteen years due to their wide range of applications in almost all fields of research.

Nanoparticles are defined as particle having size in the range between 1-100 nm. Among nanoparticles, noble metal nanoparticles such as silver and gold exhibits fascinating physical properties owing to phenomena called localized surface Plasmon resonance (LSPR). LSPR is defined as collective oscillation of conduction electrons in metal nanoparticles (Sun and Xia, 2002).

Recently, silver nanoparticles are considered as the most important material due to increases of its applications. For example, silver nano particles can be incorporated into food supplements, medicines, cosmetics, packaging materials, disinfectants, water filters and products that range from photo voltaic to biological and chemical sensors and many others. Particular attention has been given to its applications in medicine and biology due to their activity in diagnostics and treatment of many diseases particularly cancer.

Actually, there are two different methods that have been used to synthesis nanoparticles, namely physical and chemical method. Physical methods includes exploding wire technique, plasma, chemical vapor deposition, microwave irradiation, supercritical fluids, sonochemical reduction, Gamma radiation and pulsed laser ablation, while chemical method comprise of chemical reduction of metal salts, microemulsions, thermal decomposition of metal salts and electrochemical synthesis .The most common method used to synthesis metals nanoparticles is chemical reduction by organic and inorganic reducing agents due to its advantage of low cost, very fast and producing NPs with high stability (Sharma et al., 2009). Due to increasing of uses of silver nanoparticles in diagnostics and treatment, researchers have replaced the organic and inorganic reducing agents with extract of natural plants to avoid the toxicity of these chemicals. The method that used these plants extract as reducing agent is termed green synthesis.

In this work, silver nanoparticles were synthesized using Neem extract as reducing agent. The effect of Neem concentration and boiling time on the formation of silver nanoparticles was investigated.

1.2 Literature Review

In recent years, the development of efficient green chemistry methods for synthesis of metal nano particles has become a major focus of researchers. They have investigated in order to find an eco-friendly technique for production of well-characterized nano particles (Sharma et al., 2009). One of the most considered methods is production of metal nano particles using organisms. Among these organisms, plants seem to be the best candidates and they are suitable for large-scale biosynthesis of nano particles. Nano particles produced by plants are more stable and the rate of synthesis is faster than in the case of microorganisms. Moreover, the nano particles are more various in shape and size in comparison with those produced by other organisms. The advantages of using plant and plant-derived materials for biosynthesis of metal nano particles have attracted the interest of many researchers to investigate mechanisms of metal ions uptake and bioreduction by plants, and to understand the possible mechanism of metal nano particle formation in plants (Virkutyte and Varma, 2011).

1.3 Problem Statement

Metal nano particle is so important due to its wide range of applications. These applications include many industrial, military, medical, agricultural and many others. Al though there are several chemical methods have been used to synthesized nanoparticles; however, these methods are relatively toxic due to the type of chemical used. Therefore, in this work, Neem extract was used instead of chemicals to minimize the use of unsafe product particularly in biological applications.

1.4 Research objectives

1.4.1 General objective

To Synthesis silver nanoparticles using Neem extract as reducing agent

1.4.2 Specific objective

- To synthesis silver nanoparticles using Turkevich method
- To use Neem extract as the reducing agent
- To study the effect of Neem quantity and boiling time on the formation of Ag-NPs
- To determine the absorption spectra of silver nano particle by using UV-VIS spectrometer in order to confirm the formation of Ag-NPs

1.5 Dissertation layout

This dissertation composed from five chapters. Chapter one presents general information about synthesis and application of NPs, aim of this study the problem statement. Chapter tow focuses on the physical concept of Plasmon type, interaction between electromagnetic radiation and nanoparticles **(NPs)**, effects of nanoparticles shape, size, and environmental, application metal

NPs. The techniques and methods presented in chapter three. Chapter four focuses on the results and discussions while chapter five presents conclusion, recommendations of research, and references.

CHAPTER TWO

Theoretical Background

2.1 Overview

A nanometer is a unit of measure just like inches, feet and miles. By definition a nanometer is one-billionth of a meter. A nanometer is used to measure things that are very small. Actually Atoms and molecules are the smallest pieces of everything around us, are measured in nanometers (Prema, 2011).The fields of research associated with the nanoscale are called nano sciences and nanotechnology. The ideas and concepts behind nano science and nanotechnology started with a talk entitled “There’s Plenty of Room at the Bottom” by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on december 29, 1959. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Over a decade later, in his explorations of ultra-precision machining, Professor Norio Taniguchi coined the term nanotechnology. It wasn't until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms that modern nanotechnology began. Nano science and nanotechnology are the study and application of extremely small things and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering.

The word nano-technology is considered as the most important field of research in the last fifteen years. This field deals with synthesis, manipulation and engineering of matter, particles and structures on the nanometer scale (Boisseau and Loubaton, 2011). New promising properties of materials, such as the electrical, optical, thermal and mechanical properties, can be obtained when it is size reduced to nanoscale particularly in the range between 1-100 nm (Karkare, 2010)

2-2 Synthesis of metals nano particles

Recently, the synthesis of nano particles becomes as an active area of academic and, more significantly applied research in nanotechnology. Several methods have been introduced for the synthesis of these materials. Generally, there are two approaches used to synthesis nanoparticles namely bottoms up and top down (Murphy, 2002). The top down approach involve braking the larger materials into nano particles while the bottoms up approach refers to the buildup of a materials from the bottom atom by atom, or molecule by molecule (see figure 2.1).

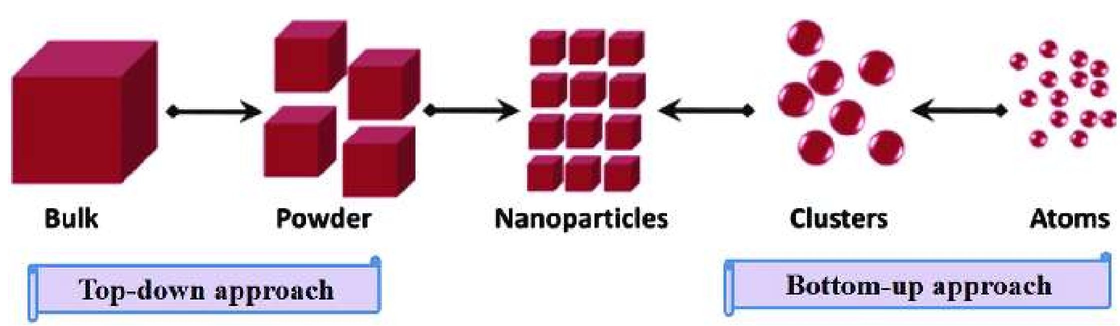


Fig.2.1 schematic diagram explaining the bottom up and top down approaches.

The techniques for synthesizing nano particles can be divided by phase into solid-phase, liquid-phase and gas-phase processes. The solid-phase techniques include mechanical ball milling and mechanochemical, the liquid-phase techniques include laser ablation, exploding wire, solution reduction, and decomposition process, whereas the gas-phase processes include gas evaporation, exploding wire, and laser ablation process (Ghorbani, 2014).

It is important to note that the above mentioned methods are also classified into physical (e.g., mechanical ball milling, laser ablation, exploding wire), chemical (e.g., solution reduction, decomposition process) and biological method. Although the physical and chemical methods have been successfully applied to synthesize nano materials with particular size and shape, they remain expensive and involve the use of hazardous chemicals. Therefore, researchers gave their concern on the biological method due its safety and low cost. This method is also called green synthesis due to uses of natural plants as the reducing agent. Still there is a need to develop environment-friendly and sustainable methods. Therefore, this work focuses on the green synthesis of silver nanoparticles by using Sudanese Neem leaves extract as reducing agent.

2.3 Nanoparticles

Nanoparticles are defined as particles having size between 1-100 nm and sometime extended to some hindered of nanometer (Korbekandi and Iravani, 2012). Recently, nanoparticles attract much attention due their fascinating physical properties. Much attention has been paid to Noble metal nanoparticles (e.g., silver, gold) due to promising properties owing to phenomena called localized surface Plasmon resonance. Nanoparticles can be classified into four main types, namely carbon based materials, metal based material, composites and dendrimers. Carbon based materials are composed mostly of carbon. It is commonly taking the form of a hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal carbon nano materials are termed as fullerenes, while cylindrical ones are called nano tubes. Metal based material are referring to quantum dots, nano gold, nano silver and metal oxides, such as titanium dioxide while Composites combine nanoparticles with other nanoparticles or with larger, bulk-type materials. Dendrimers are nanosized polymers built from branched units. This type of nano materials are commonly used as catalysis and drug delivery. Numerous shapes of nanoparticles can be constructed such as nano-spheres, nano-reefs, nano-boxes, nanoclusters, nanorods, nanodesk etc [ref]. This work will focus on silver nanoparticles and therefore, more details about its applications will be given below.

2.4 Applications of silver nano particle

2.4.1 Sensors

Peptide capped silver nanoparticle for colorimetric sensing has been mostly studied in past years, which focus on the nature of the peptide and silver interaction and the effect of the peptide on the formation of the silver nanoparticles. Besides, the efficiency of silver nanoparticles based fluorescent sensors can be very high and overcome the detection limits.

2.4.2 Optical probes

Silver nanoparticles are widely used as probes for surface-enhanced Raman scattering (SERS) and metal-enhanced fluorescence (MEF). Compared to other noble metal nanoparticles, silver nanoparticles exhibit more advantages for probe, such as higher extinction coefficients, sharper extinction bands, and high field enhancements

2.4.3 Antibacterial agents

Silver nanoparticles are most widely used sterilizing nanomaterials in consuming and medical products, for instance, textiles, food storage bags, refrigerator surfaces, and personal care products. It has been proved that the antibacterial effect of silver nanoparticles is due to the sustained release of free silver ions from the nanoparticles.

2.4.4 Catalyst

Silver nanoparticles have been demonstrated to present catalytic redox properties for biological agents such as dyes, as well as chemical agents such as benzene. The chemical environment of the nanoparticle plays an important role in their catalytic properties. In addition, it is important to know that complicated catalysis takes place by adsorption of the reactant species to the catalytic substrate. When polymers, complex ligands, or surfactants are used as the stabilizer or to prevent coalescence of the nanoparticles, the catalytic ability is usually decreased due to reduced adsorption ability. In general, silver nanoparticles are mostly used with titanium dioxide as the catalyst for chemical reactions (El-Nour et al., 2010).

2.5 Plasmon

plasmon is quantum of plasma oscillations that means the collective oscillation of free electron upon excitation by electromagnetic radiation which causes conversion of photons into plasmon (Pendry et al., 1996). plasmons are classified into three types namely volume plasmon or bulk plasmon and surface plasmon. More details about these types of plasmon will be given below.

2.5.1 Bulk plasmon

In equilibrium state, the charge of positive ions and electrons inside the bulk metal are cancel each other and metal will be neutral, and when there is an external field applied to the metal the free electrons will make a longitudinal oscillations through the metal. These oscillations occur at certain frequency called plasma frequency $\boldsymbol{\omega p}$ (Borys, 2011). This plasma frequency is given by:

$$\boldsymbol{\omega_p} = \sqrt{\frac{\boldsymbol{ne^2}}{\boldsymbol{\varepsilon_0 m}}} \qquad (\mathbf{2.1})$$

where *N* is the conduction electron density, *e* is the electron charge, m_e is the electron effective mass and ε_0 is the vacuum dielectric permittivity.

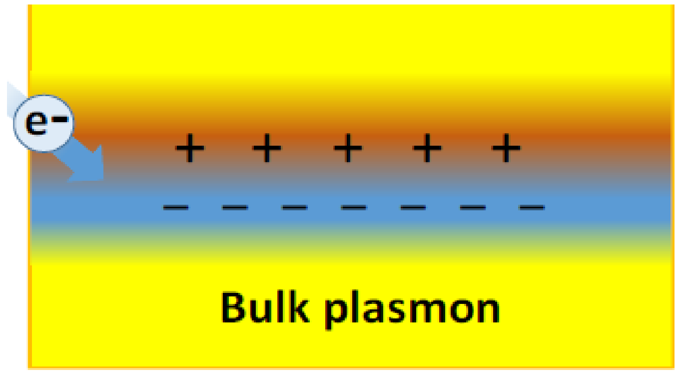


Fig.2.2 Schematic diagrams illustrating bulk plasmon

2.5.2 Surface plasmon

Surface plasmon is defined as collective oscillation of conduction electrons in metal nanoparticles (Teeling et al.). Surface plasmon is also exists in two classes namely surface Plasmon polarton and localized surface Plasmon (Stewart et al., 2008). Section 2.5.2.1 and 2.5.2.2 will give more information about these classes.

2.5.2.1 Surface Plasmon Polaritons (SPPs)

Surface plasmon polaritons are formed at the interface between metal and a dielectric material due to coupling between Plasmon and photons. The free electrons at the surface of a metal interact with the incoming photons becoming excited and collectively oscillating. This oscillation is maximized at resonance when the frequency of the incident photons match the frequency of the collective electrons (Lu et al., 2009). This resonant interaction is the basis behind surface plasmon polaritons, resulting in wave-like formations that propagate along the interface between metal and dielectric materials such as thin film (see Fig.2.2)

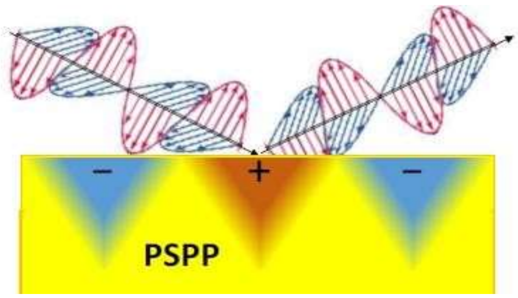


Fig. 2.3 Schematic diagrams illustrating SPP (Amendola et al., 2010).

2.5.2.2 Localized surface plasmon (LSP)

This type of surface Plasmon is refers to the confinement of a surface plasmon in a nano particle of size comparable to or smaller than the wavelength of light used to excite the plasmon (see figure 2.3). The LSP has two important effects namely electric fields near the particle's surface are greatly enhanced and the particle's optical absorption has a maximum at the plasmon resonant frequency. The enhancement falls off quickly with distance from the surface. This phenomenon is so important in noble metal nano particles due to the fact that the resonance occurs at visible wavelengths and often in the near-infrared and mid-infrared region (Amendola et al., 2010).

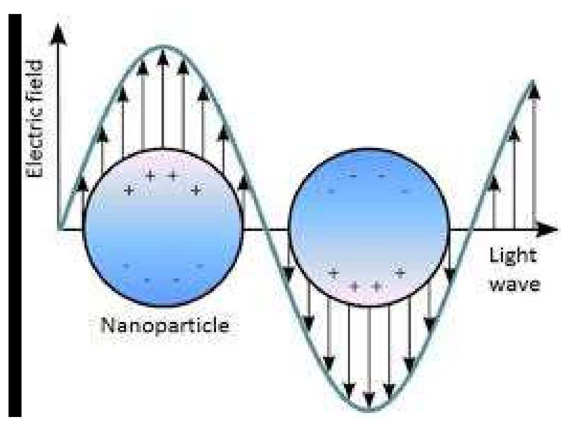


Fig.2.4 schematic illustration of Localized surface Plasmon (Borys, 2011)

2.6 Tuning of the localized surface Plasmon resonance

Actually, the resonance frequency is depends on three different parameters, namely shape and size of nano particles as well as the dielectric constant of the environment. This is due to the fact that the changes in these parameters can alter the surface polarization and therefore causes a change in plasmon resonance frequency. Details about these parameters will be given below.

2.6.1 Effect of shape

It is important to note that the exact solutions to Maxwell's equations based on analytical formulations such as Mie theory which are desirable only in cases of spherical concentric spherical shells, a spheroid, and an infinite cylinder. For other particles with arbitrary geometrical shapes, numerical calculations with some approximations are required (Amendola et al., 2010). Among available electromagnetic numerical approaches, the discrete dipole approximation (DDA) method has been widely utilized to simulate the interaction of light with metal particles of arbitrary shape (Pillai and Kamat, 2004). Figure 2.4 shows the effect of particle shapes on theoretical and experimental extinction spectra for Ag nano particles having size of 40 nm (Rycenga et al., 2011).

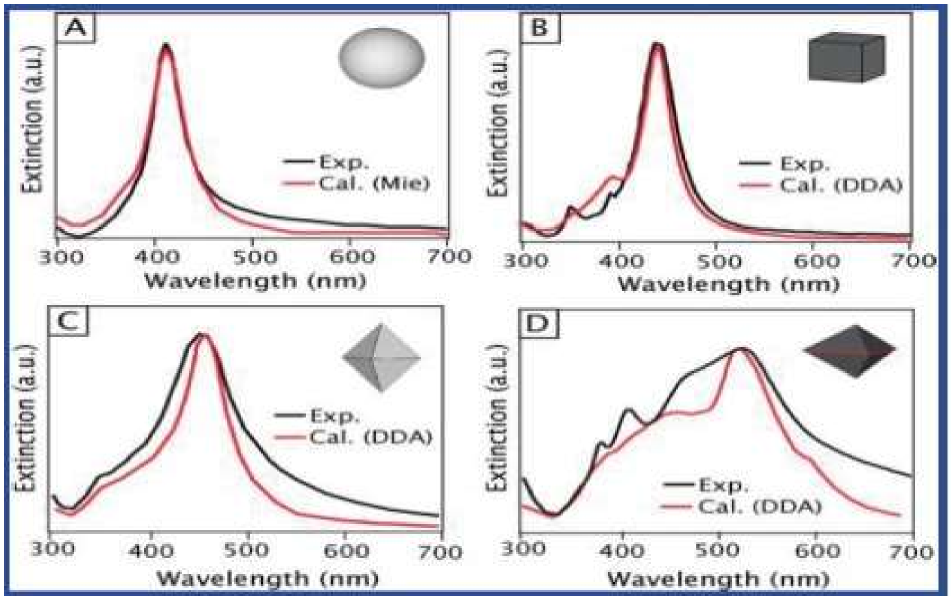


Fig.2.5 Extinction spectra for different shapes of silver nano particles having size of 40 nm (Kamat, 2002)

2.6.2 Effect of size

Metal particles in the nanometer size range have gained considerable interest in recent years as they serve as building blocks of next generation Nano devices (Kamat, 2002). Nano particles possess unique optical, electrical, and magnetic properties, which are strongly dependent on the size and shape of the particle. The size of nanoparticles determines Plasmon features that include the ratio of absorption to scattering, the number of LSPR modes and the peak position of LSPR absorption band. Therefore, size is an important variable that must be carefully considered to achieve a balance between many competing factors. Figure 2.5 show in **(A)** Extinction (black), scattering (Greenhall), and absorption spectra of Ag Nano spheres **(A)** 40nm and **(B)** 140nm in diameter calculated using Mie theory in water(El-Nour et al.). The extinction spectrum for the larger spheres **(B)** is dominated by scattering and has a broad shoulder due to contributions from the quadruple Plasmon modes. The smaller spheres have a narrow LSPR peak, and the absorption and scattering cross sections are nearly equal.

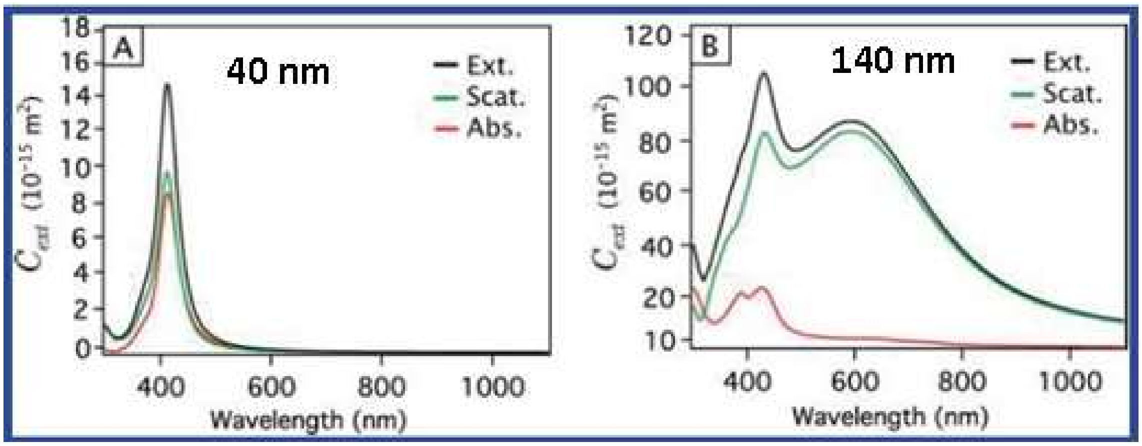


Fig.2.5 shows the absorption, scattering, and extinction spectra of silver Nano sphere with diameter (A) 40 nm and (B) 140 nm (Hutter and Fendler, 2004)

2.6.3 Effect of dielectric of the environment (Kamat, 2002)

The dielectric environment of nano particle has a good impact in the localized surface Plasmon resonance. It is plays a role in plasmon shifting effect. An increase in the relative permittivity of the dielectric medium results in a decrease in the restoring force of electron oscillation and therefore shifts the Plasmon resonance towards longer wavelength (Kelly et al., 2003).

CHAPTER THREE

Methods and techniques

1.3 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 silver nano particles is presented. The UV-VIS spectroscopy was used to determine the absorption band of localized surface plasmon resonance (LSPR).

2.3 Materials and tools

Materials and tools used to synthesis silver nano particles were:

- Silver nitrate ($AgNO_3$) with purity 99%**.**
- Distilled water and ethanol.
- Beakers and magnetic stirrer with hot plate (see fig.3.1).
- Neem leaves (see fig.3.3).

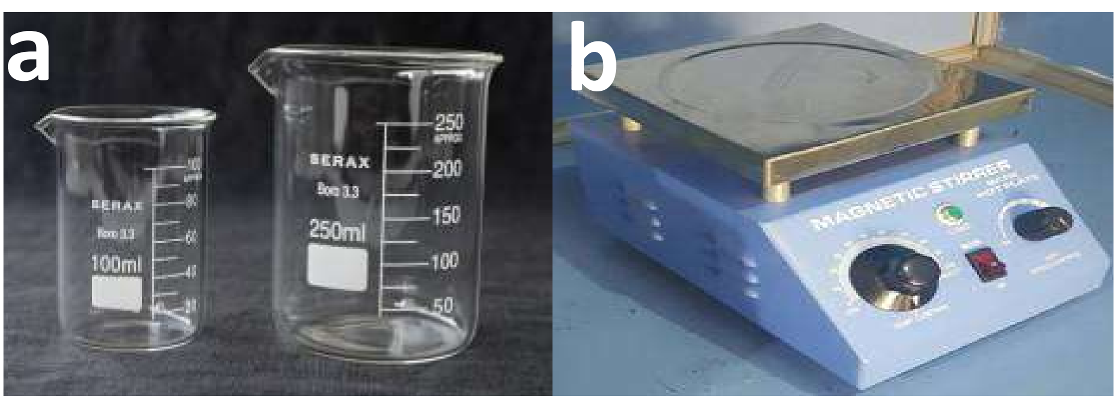


Fig 3.1 (a) beakers (b) Magnetic stirrer with hot plate

3.3 Silver nitrate

Silver nitrate is an inorganic compound with chemical formula $AgNO_3$. Pure silver nitrate is an intermediate in the preparation of other silver salts, including the colloidal silver compounds used in medicine and the silver halides incorporated into photographic emulsions. Figure 3.2 showed chemical formula of silver nitrate.

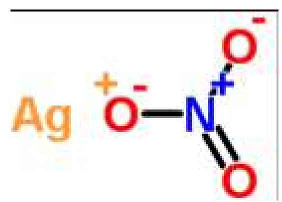


Fig.3.2 chemical formula of silver nitrate

3.4 Neem

To give a brief background, chemical investigations of neem were undertaken by Indian pharmaceutical chemists in 1919, whereby they isolated acidic principle in neem oil, which they named as 'margosic acid". However, real chemical research originated in 1942 with isolation of three active constituents, viz, nimbin, nimbidin and nimbinene (Völlinger and Schmutterer, 2002).

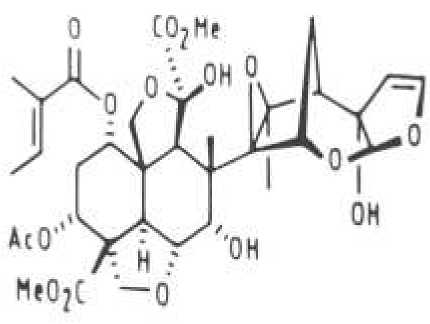


Fig.3.3 (a) natural Neem leaves (b) chemical syntax of neem (Völlinger and Schmutterer, 2002).

3.5 Experimental procedure to synthesize Ag nano particles

Silver nitrate ($AgNO_3$, 99%) was purchased from loba Chemie (india). All glassware was washed with ethanol and distilled water and dried before used. Neem leaves was collected from neem trees Khartoum, Sudan. Neem leaves was washed several times with distilled water to remove dust. Neem extract was prepared as follow: 40g of washed Neem leaves was added to 200ml distilled water in beaker and boiled for 10min. The obtained solution was filtered and stored at low temperature for further use. To optimize the synthesis parameters, different boiling time and Neem to silver salt solution ratio were applied. In typical experiment, Neem extract with different quantities was added to silver nitrate solution (1mM) in beaker to get different neem to silver nitrate solution ratio (0.5:25, 1:25, 1.5:25and 2:25).The mixed solution was boiled for 20 min. In other experiment, the optimum ratio (1.5:25) which showed more pronounced peak with high intensity related to absorption band of LSPR was used to optimize boiling time. Similarly, the mixture of Neem and silver nitrate with the ratio of 1.5:10 was boiled at different time (10, 30, 40 and 50 min). In both experiments, after few minutes, the color was changed indicating the formation of silver nanoparticles. Figure 3.4 showed the steps of preparation of silver nanoparticles.

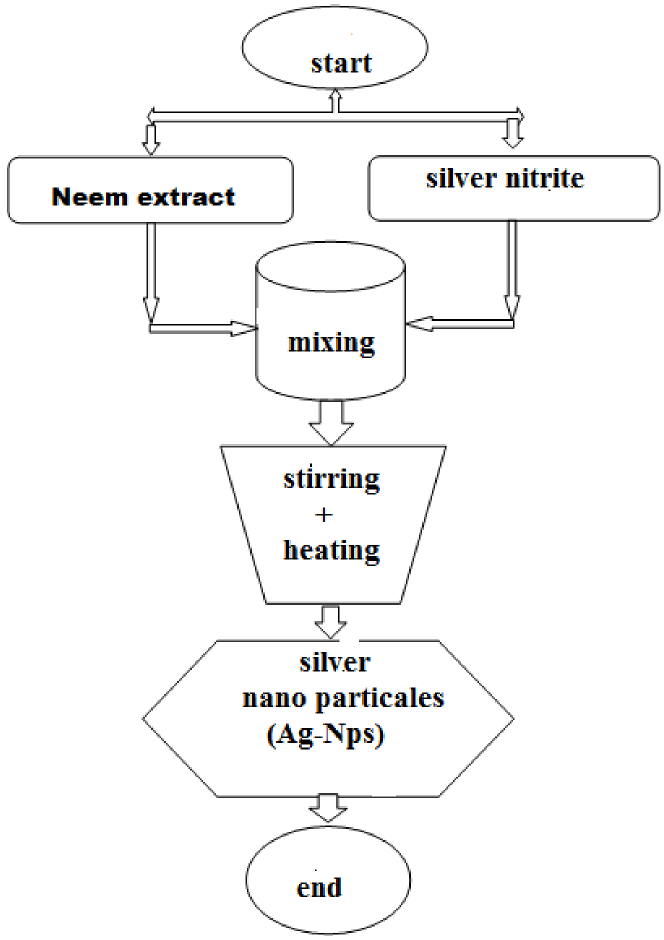


Figure 3.4 Schematic diagrams for preparation of silver nano particles.

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/I_o) is called the transmittance. The UV-visible spectrophotometer can also be configured with an integrated share 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 Fig.3.4). 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 cuvettes. 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.

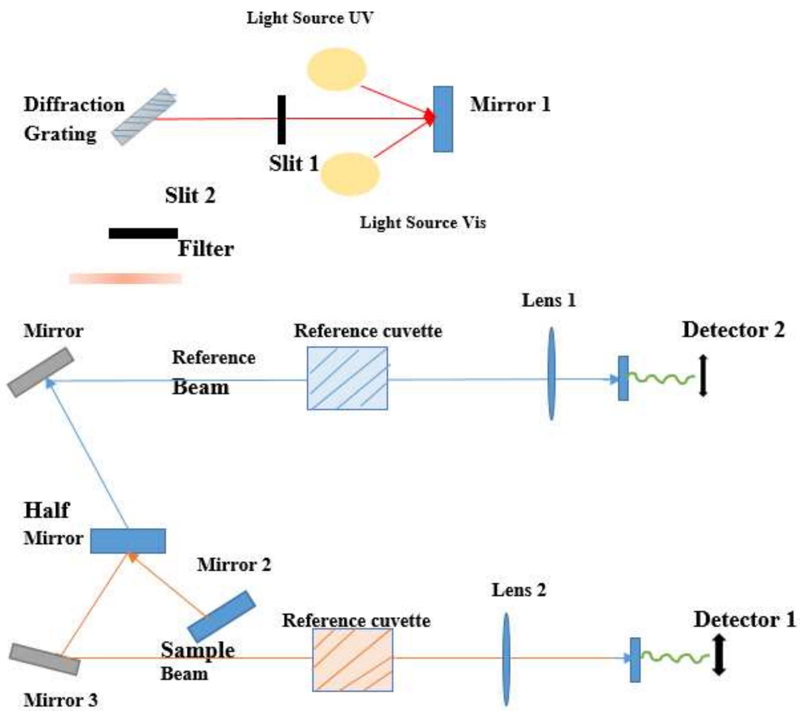


Fig. 3.4 A dual-beam UV-VIS spectrophotometer

Fig.3.5 UV-vis spectrophotometer.

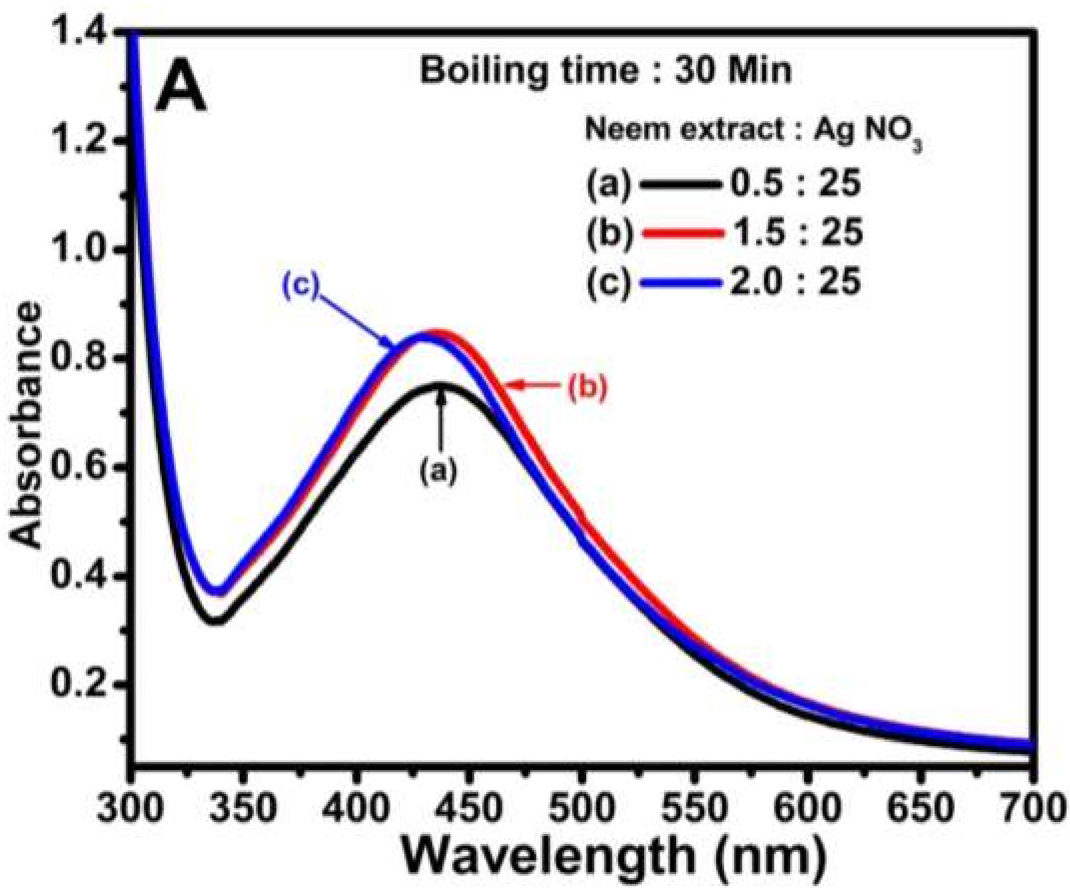
CHAPTER FOUR

Result and Discussion

This work is focuses on the synthesis of silver nanoparticles (Ag-NPs) using Sudanese Neem extract as reducing agent. Actually, Ag-NPs are playing an important role in wide range of applications. The reason of Ag-NPs success lies in a favourable combination of physical and chemical properties. The main characteristic of Ag-NPs is surface Plasmon absorption, which has 10^5-10^6 larger extinction cross sections than the ordinary molecular chromospheres (Mayer and Hafner, 2011). Moreover, the absorption intensity is also higher than that of other metal nanoparticles due to the weak coupling to interband transitions. It is also important to note that in case of Ag-NPs, the absorption is varying between visible and IR regions depending on the particle sizes and shapes. These properties is completely different from their bulk form (Kelly et al., 2003). In practical, the appearance of this absorption band in absorbance spectra and the change of color during experimental process are considered as the strong evidence for the formation of metal nanoparticles.

In this work, Ag ions (silver nitrate dissolved in distill water with concentration of 1mM) is reduced to Ag NPs using Neem extract. To optimize the synthesis method, different boiling time and concentration of Neem extract were used (see figures 4.1 and 4.2). The first indication of the formation of Ag NPs was observed during the experimental process which is changing of color from pale yellow to yellowish brown and finally to dark brown as function of boiling time. It was suggested that compound like margosic acid which is one of the Neem content is responsible for reducing Ag ion in solution to silver nanoparticles (Kelly et al., 2003)

. Further confirmation of the formation of silver nano particles can be obtained from UV-Vis results (see figure 4.1 and 4.2).



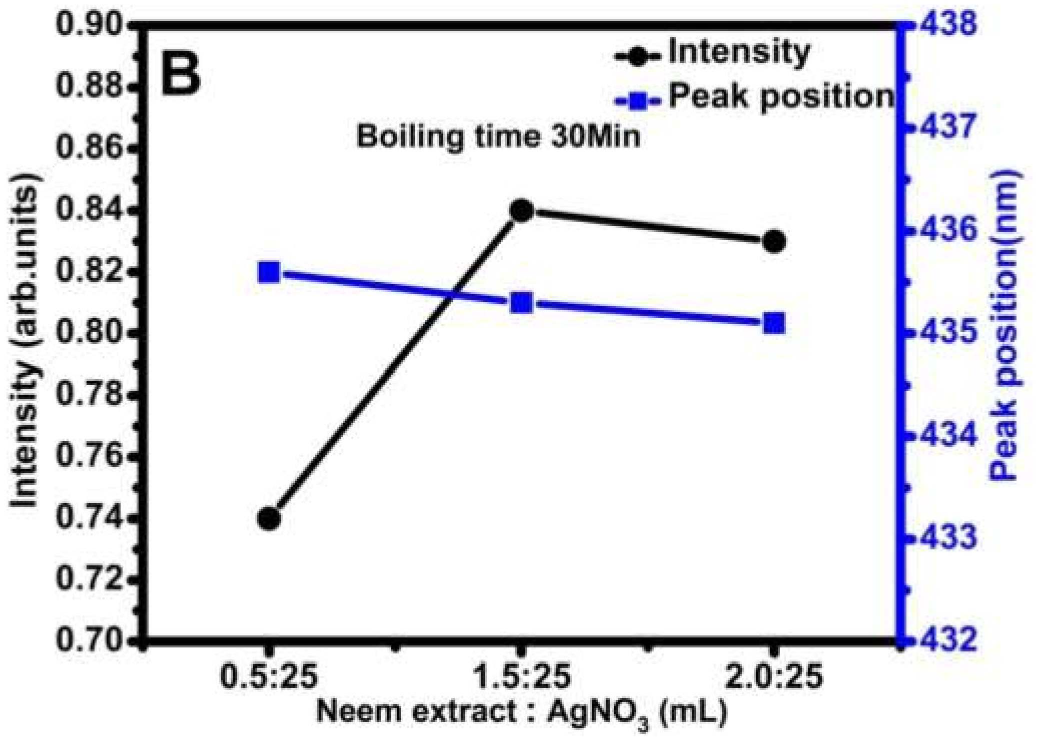
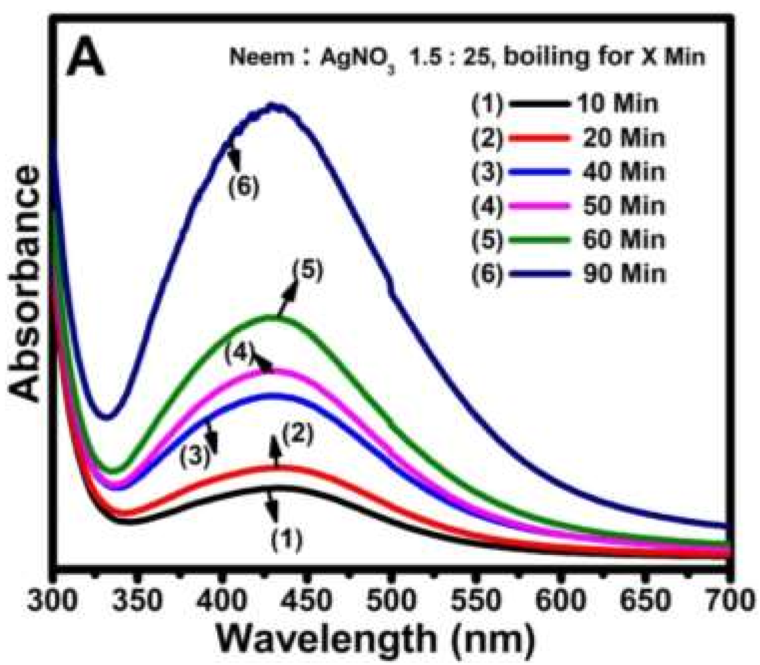


Fig. 4.1 (A) UV-Vis spectra of Ag-NPs produced using different concentration of cinnamon bark. (B) Effect of neem extract concentration on the intensity of the absorption band and Peak position.

Fig.1. Shows (A) UV-Vis spectra of Ag-NPs produced using different concentration of Neem extract. (B) Effect of Neem extracts concentration on the intensity of the absorption band and the peak position. Figure (4.1A) shows absorption spectra for silver nitrate (25 ml) mixed with different quantity of Neem extract boiled for 30 minutes. As can be seen when 0.5 ml of Neem extract mixed 25 ml Ag NO_3, a broad peak appeared at 430 nm. This peak is assigned to localized surface Plasmon resonance, indicating the formation of silver nanoparticles (Kelly et al., 2003). When the quantity of Neem extract increased to 1.5 ml, the intensity of the absorption band was increased. This may be due to enhancement of the interaction rate. Upon

further increase the quantity of Neem extract to 2ml, the intensity of the absorption band was decreased, indicating that the optimum ratio between Neem extract and silver salt solution is 1.5: 25, respectively (see figure 4.1B). Of interest is that there is no significant shift in the peak position was observed (see figure 4.1B). It has been reported that the shift in the peak position of the LSPR absorption band is due to changes in particle sizes or/and shapes or the dielectric constant of the environment (see chapter 2, sections 2.6). In our case, this very small shift may be correlated with the change in the dielectric constant due to increasing of the Neem concentration.

To study the effect of boiling time on the formation of Ag-NPs, the optimum concentration ratio between Neem extract and silver salt (1.5:25) obtained from the above experimental results (Fig. 4.1) was used. Different boiling time in the range between 10-90Min was applied. The obtained absorption spectra from these samples are shown in figures 4.2 below.



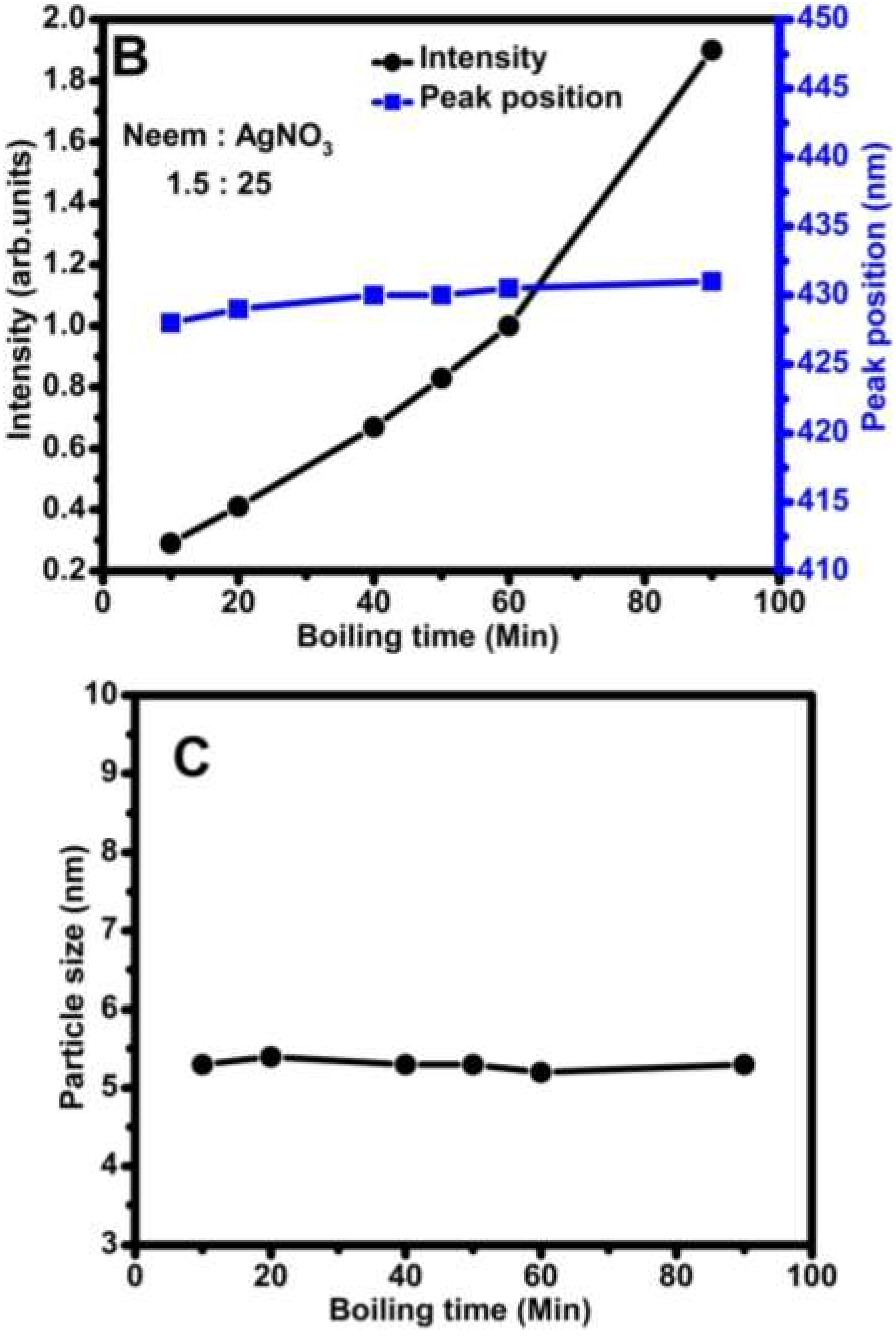


Fig. 4.2 shows (a) UV-Vis spectra of Ag-NPs produced using silver nitrate mixed with Neem extract with the ratio of 1.5:10 for neem and silver salt, respectively. (b) Effect of boiling time on the intensity of the absorption band and peak position. (c) Effect of boiling time on NPs size.

Figure 4.2A shows absorption spectra of Ag-NPs produced at different boiling time when the ration between Neem extract and silver salt was 1.5-25. Figures 4.2 (B and C) showed the effect of boiling time on the intensity, peak position and particle size, respectively. As can be seen from figure 4.2A, even at less boiling time (10 Min) there is an obvious peak appeared at 430 nm. This peak is attributted to LSPR absorption, indicating the formation of Ag-NPs. The intensity of this peak is increased with increasing the boiling time (see figure 4.2B). This indicate that more boiling time produes more Ag-NPs (enhancement in the reduction rate). Of interest is that all spectra showed single peak, indicating that the NPs is smaller than the mean free path of the conduction electrons (50 nm for Ag) and have spherical shape, since shapes other than sphere produces multiple peaks due to existence of high order modes. Therefore, in this case the Mie theory can be applied to calculate the size of NPs.

According to Mie theory, there is the relationship between the resonance broadening (γ) and the sizes of nanoparticles (R) given by the following relation.

$$\gamma(R) = \Gamma_0 + \frac{AV_f}{R} \qquad (4.1)$$

where $\gamma(R)$ is resonance broadening, A is scattering process (3/ 4 in case of Ag), Γ_0 is the velocity of bulk scattering ($5 \times 10^{12} S^{-1}$, for Ag) and V_f is the Fermi velocity (1.4×10^6m/s, $for\ Ag$).

Figure 4.2 C showed the particle sizes calculated using equation 4.1 as the function of boiling time. As can be seen, there small variation in the particle size (5.2-5.4), indicating that the boiling time has no significant effect on particle size.

CHAPTER FIVE

Conclusion and Recommendation

5.1 Conclusion

In this study, the silver nanoparticles were synthesized by using Turkevich chemical method using Neem extract as the reducing agent. The prepared samples were characterized using UV-VIS spectroscopy. The change in colour during synthesis processes and the presence of pronounced peak in the visible region in absorption spectra confirm the formation of Ag-NPs. The optimum ratio between Neem extract and silver nitrite is found to be 1.5:25. It is also found that the boiling time do not has significant effect on the particle size but instead increased the reduction rate. Depending on the Mie theory calculations, the average particle size was found to be 5.2 nm.

5.2 Recommendation

- In this study Neem extract has been used to synthesis silver nanoparticles. Other Sudanese plants can be used.
- Only two parameters have been optimized (concentration and boiling time). Other parameters such as temperature and PH can be optimized.
- Only UV-Vis technique was used to characterize the samples. Other techniques can be used such as TEM, XRD for further information.

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