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Rapid Formation of Stable Silver Nano Particles Using Aqueous Seed Extract of Jatropha-curcas.

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ABSTRACT

This investigation reports the reduction of silver ions to silver nano-particles as a rapid single step green process using Jatropha seeds extract, which is successfully reducing and stabilizing agent. In this study, silver nano-particles were synthesized from silver nitrate solution using locally prepared aqueous extract from crushed dry jatropha seeds. Effect of various operating conditions including pH, heating and the ratio between $AgNO_3$ and aqueous extract Jatropha- curcas seeds were examined and confirmed by the ultra violet-visible spectra (UV-VIS) which gave surface plasma resonance for silver nano- particles at 430 nm. The produced nano silver was characterized by transmission electron microscope (TEM) and Scattered area electronic diffraction (SAED) which revealed that the produced nano-particles are of spherical shape within size range (20-50) nm. Higher conversion of nano silver particles was achieved at pH ≈ 10.6 and in absence of heat which was confirmed by UV-VIS spectra.

Keywords: Nano silver, Jatropha extract, reducing agent, green synthesis.

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INTRODUCTION

Nanotechnology is an important and attractive field of modern research concerning synthesis of materials with particle sizes range from approximately 1-100 nm. Nano-particles (NPs) and nano-science have wide applications in different areas such as chemical industries, medical sciences, agriculture and electronics applications [1]. Also, nanotechnology is applied in fields of energy, materials, electrochemistry, optical devices, environmental health and catalysis [2-8].Our environment is rich with crude extracts from plants or microorganisms which can be used as simple alternatives to chemicals that were synthesized by chemical methods and physical procedures [9-10]. Several studies have been made to prepare nano – materials employing physical, chemical and biological methods [11]. Synthesis of silver nano-particles can be achieved by various methods such as thermal decomposition [12], microwave assisted process [13], electrochemical [14] and green chemistry [15]. Nowadays great efforts have been done by researchers for biosynthesis of inorganic materials in nano-size using whole plants, plant tissue, plant extract, fruits and marine algae [16-18]. Therefore, green synthesis of nano materials especially metal nano-particles using microorganisms is considered as a great achievement [19-25].Reduction of metal ions using plant extracts has started since 1900s [26]. However, the use of whole plant extract and plant tissue for reducing metal salts to nano-particles attracted great attention within the last 30 years [27-31]. The main target of the present investigation is to study the synthesis of nano silver particles by eco-friendly process using Jatropha seeds extract as naturally reducing agent and characterize synthetic nano silver particles by different analysis such as ultra violet-visible spectra (UV-VIS), transmission electron microscope (TEM) and Scattered area electronic diffraction (SAED) . From previous studies, it was concluded that, the most important operating conditions of nano silver synthesis are pH, Seed extract concentration, and reaction temperature so these parameters were investigated.

EXPERIMENTAL

Materials

Egyptian crude Jatropha seeds were delivered from Ministry of Agriculture and stored at 20ºC until ready for use. Also, Silver nitrate (extra pure) was purchased from Sigma Aldrich, min. assay (99%). Sodium hydroxide was used for pH adjustment; it was obtained from El-Nasr Company, min. assay (95.5%). All the aqueous solutions were prepared using de-ionized water.

Jatropha Seeds Preparation:

Weight of 50 g Jatropha seeds were milled using an ordinary coffee grinder, then boiled in 500 ml de-ionized water for 2h with stirring at 150rpm by using magnetic stirrer and cooling flux. The clear seed extract liquid was obtained after filtration using filter paper (No 4), seed extract is ready for further use. The measured pH of the obtained extract was 6.4.

Synthesis of Stable Silver Nano-particles:

In a typical reaction procedure, different concentrations of stock $AgNO_3$ (1.1 g $AgNO_3$ in 100 ml de-ionized water) were mixed with 1 ml of seed extract. It is well known that particles size and its shape is pH dependant. After preparing of jatropha extract, pH of the sample was adjusted using either dilute sulfuric acid or sodium hydroxide. The mixture was then subjected to stirring at 150 rpm under either heating at 60ºC or without heating. The resulting solution became reddish in color after 15 min. However, the most important indication for the conversion of silver nitrate to nano silver is the change in color from colorless to yellow ending with dark brown. This is indicating the formation of silver nano-particles gradually. The reaction was repeated at various concentration of $AgNO_3$ at different pHs and various concentrations of the extract. The complete conversion to nano size was tested by using of sodium chloride solution. While, on addition of sodium chloride to the reaction medium if white preciptate is formed, this will indicate that non complete conversion of silver to the nano- form. However, without formation of this precipitate, complete conversion of silver nitrate to nano-particles was predicted as shown in the following equation:-

$$Ag\,NO_3 + NaCl \longrightarrow NaNO_3 + AgCl\downarrow \quad \text{(white precipitate)} \qquad (1)$$

Analytical Technique.

Ultra Violet Visible Spectra (UV-Vis)

The formation of silver nano-particles is detected by using a 50 ANALYTIKA JENA Spectrophotometer to determine the surface Plasmon resonance (SPR) band at 425- 430 nm. Color intensity increases with increasing $AgNO_3$ concentration at fixed volume fraction of seed extract bathing from yellow to reddish brown ending with dark brown.

Higher resolution transmission electron microscope (HRTEM).

A JEOL-JEM-1200 transmission electron microscope was used to identify the shape and size of silver nano-particles. Also the same microscope was used for morphology Scattered area electronic diffraction (SAED)

Scattered area electronic diffraction (SAED)

A JEOL-JEM-1200 transmission electron microscope was used to identify Scattered area electronic diffraction (SAED) of produced nano silver.

Specifications of Jatropha- curcas extract

Aqueous extract of Jatropha- curcas seeds which is used in silver nano-particles synthesis, consists of fats, proteins, carbohydrates, water and amides 1-bond which derived from proteins and act as capping ligands of the nanoparticles [32]. Also the major composition of fatty acids is oleic acid, linoleic acid and stearic acid [33]. These fatty acids have in their structure carbonyl and hydroxyl groups (high molecular weight) as illustrated in Table1. These groups are responsible for reduction of silver ions to the nano-form and also stabilizing the created silver nano-particles. The fatty acid composition was determined by gas chromatography.

Table (1): Fatty acid Composition of Jatropha- curcas Extracts Seeds

Fatty acid	Composition (% wt.)
Palmitic (16 : 0)	18.04
Stearic (18 : 0)	6.08
Oleic (18 : 1)	28.18
Linoleic (18 : 2)	47.79

RESULTS AND DISCUSSION

A green method to synthesize silver nano-particles by aqueous seeds extract of jatropha-curcas can be synthesized at different concentrations of $AgNO_3$ with fixed volume fraction (0.25) of seed extract. Absorption band for silver nano-particles that were reduced by seed extract was detected at 430 nm as shown later in Fig.8, 9. Based on literature review, the silver nano-particles could be applied in surfaces disinfectants for glass, metals, etc. Moreover, it is recommended to use silver nano-particles in the range of (5-25) nm. However, it is not safe to use silver particle size less than 15nm. In this study, the synthesized silver nano-particle size was 20 nm.

Effect of pH

Figures 1 to 4 show the effect of pH on the particle size and shape at operating conditions for nano-silver preparation as: silver ion concentration of 0.673 g/l, jatropha concentration of 1.4g/l, reaction temperature 70^oC, stirring rate 150rpm, and reaction duration of 15min. The results show that as the pH value increased, the particle size also increased and the shape of the particles changed from sphere shape at pH10.6 as clear from Fig.1 to flakes like shape at pH 12.5 as shown in Fig.4. The reductive properties of jatropha extract are substantially enhanced owing to the oxidative degradation with the formation of low molecular

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weight reducing chains. From the above results pH of 10.6 was taken as the optimum pH for silver nano-particles synthesis. The increment of pH leads to the decrement of the medium viscosity which gives the chance for the reduced silver nano particles to aggregate. This fact leads to increase of particles size and also changes the shape from circular to flakes like one.

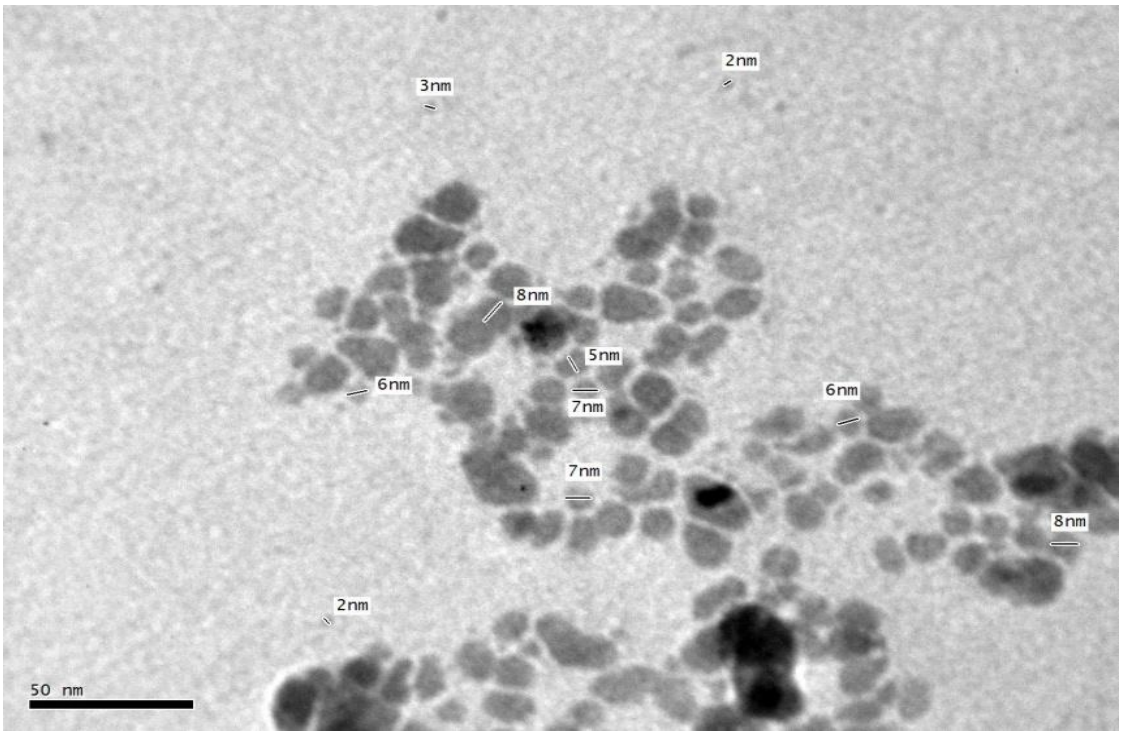

Fig 1: TEM of nano silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 4ml, 60°C, 150rpm, 15min and pH 9.

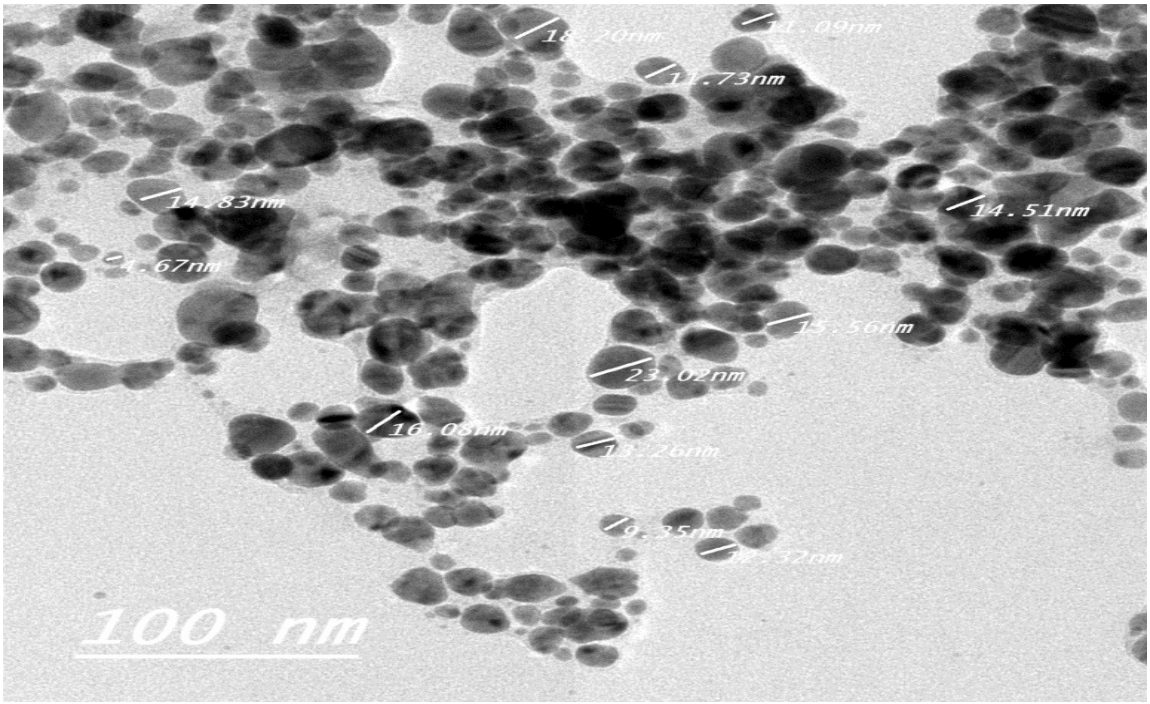

Fig 2: TEM of nano silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 4ml, 60°C, 150rpm, 15min and pH10.6.

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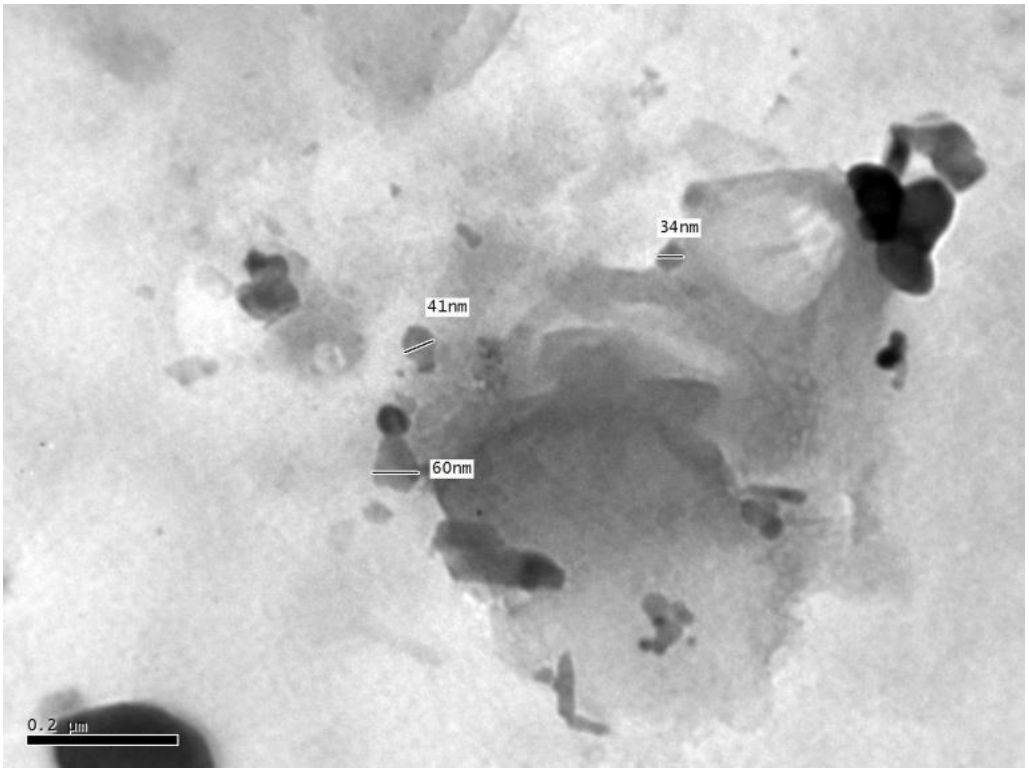

Fig 3: TEM of nano -silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 4ml, 60°C, 150rpm, 15min and pH11.5.

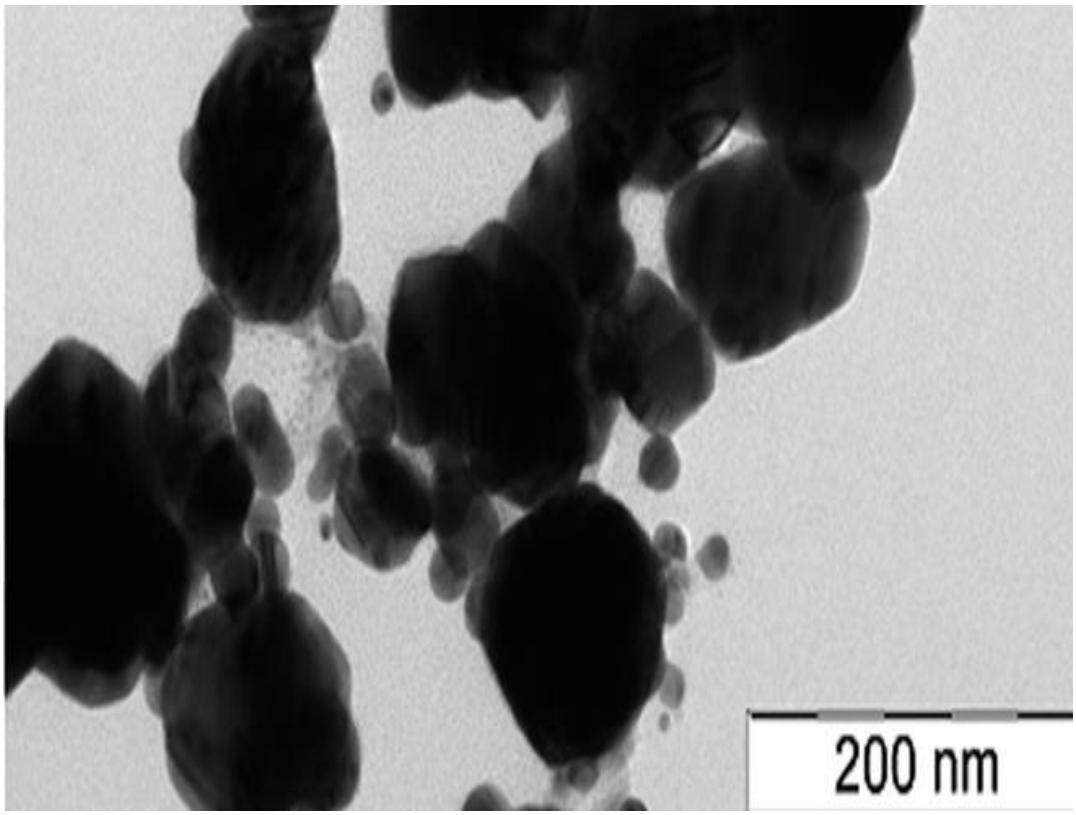

Fig 4: TEM of nano silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 4ml, 60°C, 150rpm, 15min and pH12.5.

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The UV–Vis absorption spectra of silver nano-particles prepared using jatropha extract show similar Plasmon bands formed at wavelength 425nm with the formation of the ideal bell shape which is characteristic for the formation of Ag^0 nano-particles, as clear in Fig.5.

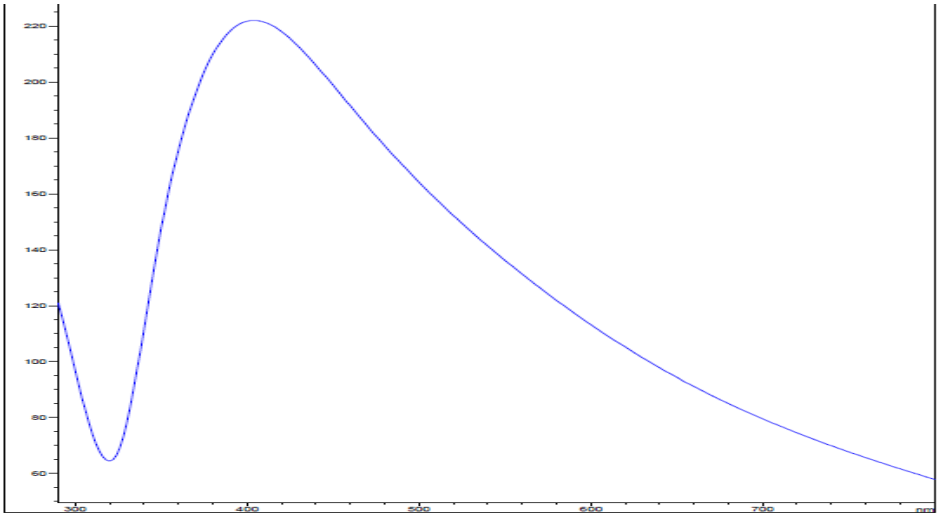

Fig. 5 UV-Visible scan at silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 4ml, 60°C, 150rpm, 15min and pH10.6

Effect of Jatropha Extracts Concentration

Figure 2, 6 and 7 show effects of different volumes of jatropha extract on the shape and particle size of synthesized nano silver at operating conditions of initial pH of 10.6, Silver ion concentration 0.673g/l and temperature of 60°C for 15min at stirring rate of 150rpm. As the extract volume increased the particle size increased, where it reached to about 10 nm on using of 1ml of extract and about 23nm at 4ml extract volume. Also, it reached more than 90 nm when10ml of the extract was added. From the above data, it was concluded that the target particle size was obtained when 4ml of the extract was taken as the optimum, although 10 nm particle size was more effective and according to nano safety, particle size of 23 nm was preferred. The study of variation of $AgNO_3$concentration showed that higher concentration of $AgNO_3$ leads to the formation of larger particles.

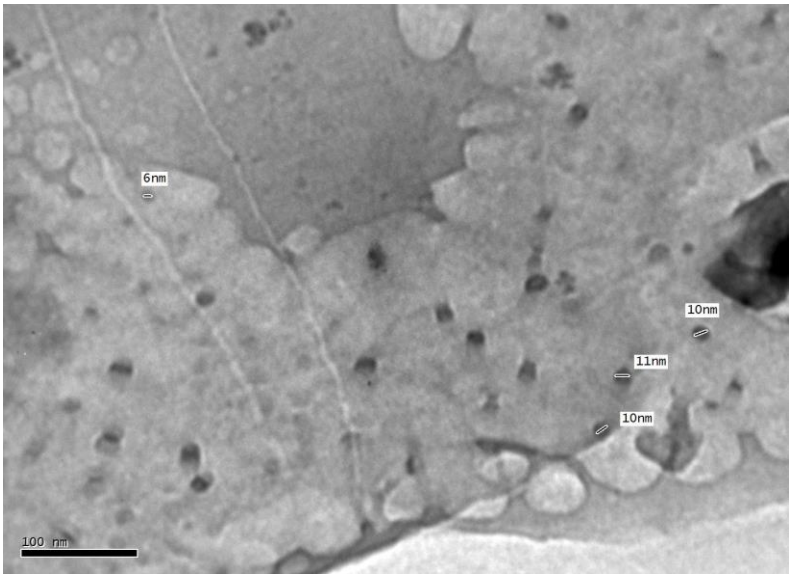

Fig 6: TEM of nano silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 1ml, 60°C, 150rpm, 15min and pH 10.6.

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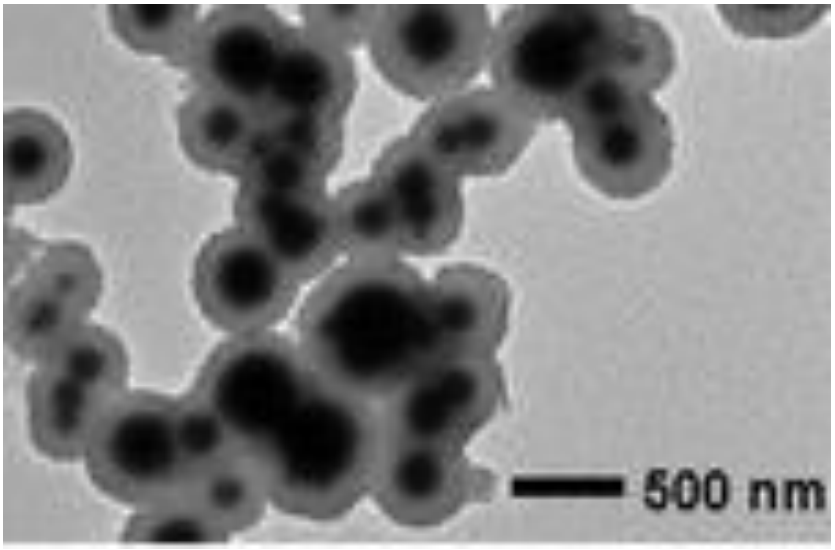

Fig 7: TEM of nano silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 10ml, 60°C, 150rpm, 15min and pH10.6

It is clear also that there is a gradual decrease in the absorption intensity, by decreasing the extract volume up to 1ml as clear from Figs. 5 and 8 and also formation of brown precipitate could be attributed to the disturbance in the stabilization efficiency of the formed silver nano-particles.

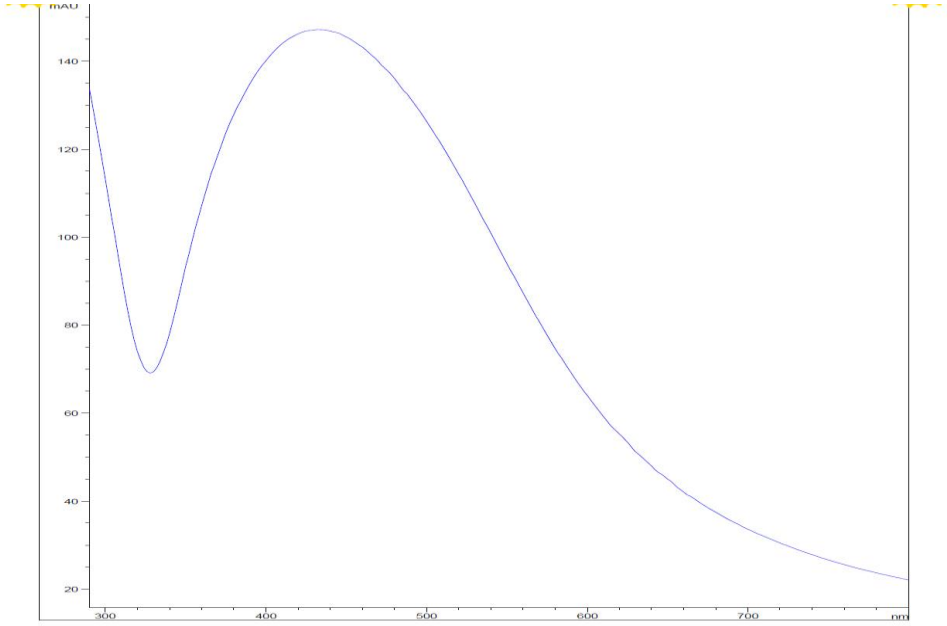

Fig 8: UV-Visible scan at silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 1ml, 60°C, 150 rpm, 15min and pH 10.6

Effect of Reaction Temperature

Figure 2 and 9 illustrate the effect of temperature on the obtained silver nano-particle size and shape at operating conditions: initial pH 10.6, Silver ion concentration 0.673g/l and jatropha extract volume was 4ml for 15min at stirring rate of 150rpm. The results showed that as the temperature increased the particle size increased .Moreover, in absence of heating the obtained average particle size was 10 nm as shown in Fig. 9, while by heating to 60°C the average particles size was 20 nm. From these results, it was concluded that,

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heating was not adequate for silver nano-particles synthesis which was spherical in shape. Also, on increasing temperature, a precipitation occurred that may be attributed to reaction of both oleic and linoleic acids (OH^- groups) with the silver ions and resulted in the increment of particle size up micro size causing precipitation.

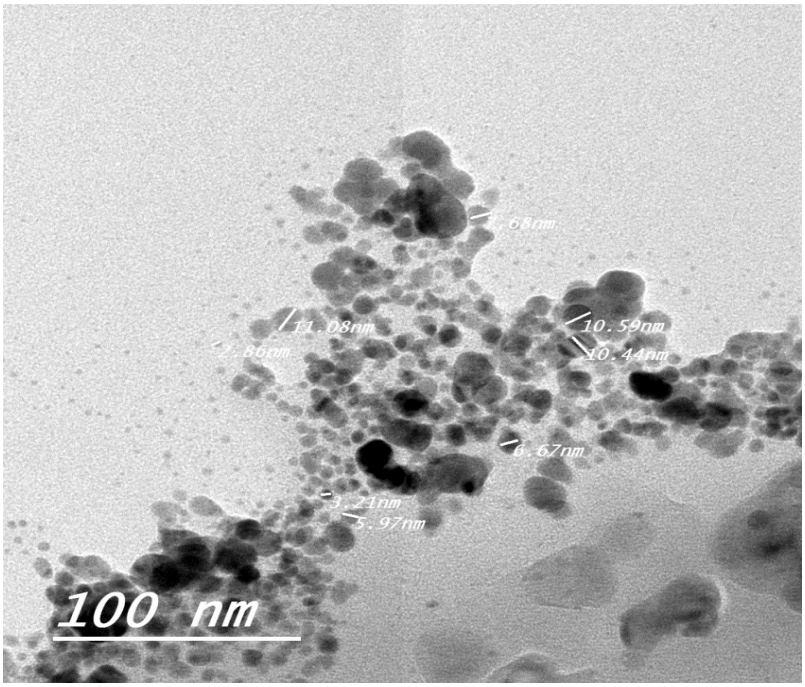

Fig 9: TEM of nano silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 4ml, 25°C, 150rpm, 15min and pH10.6.

Also, as seen in Figs 5 and 10, there was a high increase in the absorption intensity from 220 mAu at 60°C to 450 mAu at 25°C which confirmed that heating was ineffective in synthesis of silver nano-particles.

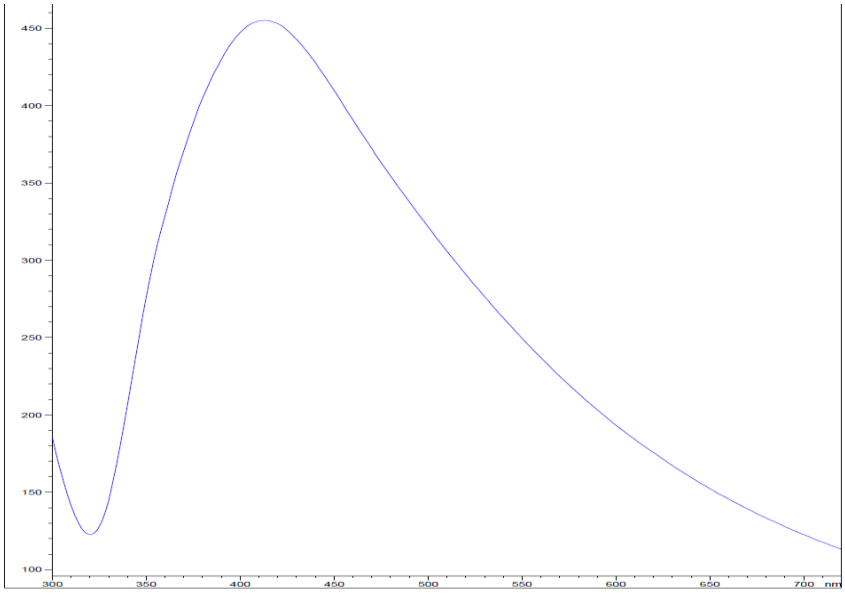

Fig 10: UV-Visible scan at silver prepared at $AgNO_3$ (1ml 0.1M) jatropha extract 4ml, 25°C, 150rpm, 15min and pH10.6

On applying the selected area for the electronic diffraction (SAED) test, it was confirmed that the obtained material was silver in the nano-form as shown in Fig. 11

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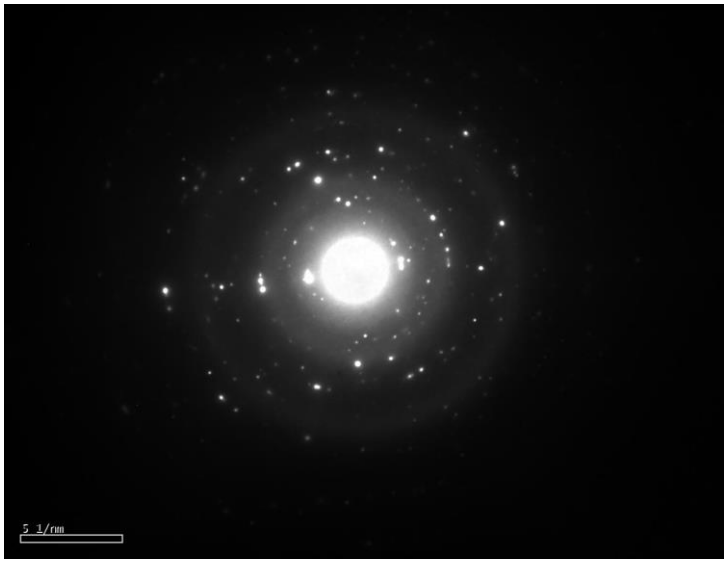

Fig 11: electronic diffraction (SAED) of the obtained nano silver using jatropha extract

CONCLUSIONS

-This study showed that the aqueous seed extract of Jatropha-curcas can be used for both reducing Ag^+ to Ag and stabilizing the particles during the synthesis process; also no toxic chemicals were needed as reducing and stabilized agent.

-Particles are mostly spherical in shape and by varying concentration of $AgNO_3$; size of particles can be controlled.

-Silver nano-particles having diameter from 20 nm to 50 nm some larger particles are uneven shape.

-optimum results were obtained at spherical nano-particles , pH 10.6, fixed volume ratio of $AgNO_3$ to Jatropha-curcas extract (0.25), 150r.p.m. for 15 minutes and in absence of heating.

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