An Efficient Green Synthesis Method for the Synthesis of Silver Nanoparticles Using the Extraction of Catha Edulis Leaves

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Abstract

The synthesis of nanoparticles using plant extracts has received great attentions during the last two decades. That is plausibly due to its simple, rapid, toxic-free, and efficient reactions. In this study, a unique green method for preparing silver nanoparticles (Ag NPs) using the extract of Qat (or Khat) leaves is reported. The method is cheap, easy and has a potential for mass production of nanoparticles. Qat is a fast growing plant used mostly as stimulant in Yemen and South African countries and contains dozens of phytochemicals in its leaves. These chemicals are extracted from Qat leaves in an aqueous solution and used as a reducing agent and surfactant in the reaction. The structure and morphology of Ag nanoparticles are confirmed using multidisciplinary characterization tools. The results showed well dispersed spherical particles with an average size of 18.11 nm. The surfactant coated on the particles are confirmed using FTIR technique. Moreover, this green method is applicable for large scale production with an efficient cost due to rapid reaction and the wide availability of the plant leaves.

الملخص

حظيت تقنية انتاج الجسيمات النانوية باستخدام المستخلصات النباتية اهتمامًا كبيرًا خلال العقدين الماضيين. ويعزى ذلك بشكل منطقي إلى تفاعلاتها البسيطة والسريعة والخالية من السمية والكفاءة. في هذه الدراسة ، تم استخدام طريقة خضراء فريدة لإعداد جسيمات الفضة النانوية (Ag NPs) باستخدام مستخلص أوراق القات. هذه الطريقة رخيصة وسهلة ولديها إمكانية إنتاج كميات كبيرة من الجسيمات النانوية. القات هو نبات سريع النمو يستخدم في الغالب كمنشط في اليمن ودول جنوب إفريقيا ويحتوي على العشرات من المواد الكيميائية النباتية في أوراقه. يتم استخراج هذه المواد الكيميائية من أوراق القات في محلول مائي وتستخدم كعامل اختزال وعامل سطحي في التفاعل. يتم تأكيد هيكل ومورفولوجيا الجسيمات النانوية Ag باستخدام أدوات التوصيف متعددة التخصصات. أظهرت النتائج جزيئات كروية منتشرة جيدًا بمتوسط حجم 18.11 نانومتر. تم اكيد وجود الأغلفة السطحية على الجسيمات باستخدام تقنية FTIR. علاوة على ذلك ، فإن هذه الطريقة الخضراء قابلة للتطبيق على إنتاج واسع النطاق بتكلفة فعالة بسبب لتفاعله السريع والتوافر الواسع لأوراق النبات

Keywords: *Qat leaves, Green synthesis, Silver nanoparticles; Antibacterial; Green reducing agents.*

1. Introduction

Silver is a noble metal that possesses novel properties among all other metals. The fabrication of Silver at the nanoscale has boosted its properties several folds [1]. That is why silver is the most synthesized nanoparticles in the literature. Nowadays, the preparation of silver at nanoscale attracts a variety of industrial, healthcare and domestic applications *[2]*. For instance, it was found that silver NPs properties such as antibacterial activity depend mainly on their size, shape and structure *[3]*.

The synthesis of silver nanoparticles has been successfully reported using different physical and chemical routes *[3]*. However, most of these methods deal with hazardous substances for both reduction and stabilization purposes. For sensitive applications such as medical and environmental fields, hazardous materials being coated on the surface of the particles are annoying and cannot be totally removed from the final particles. As a result, the presence of hazardous reactants even with low concentration in the final products has a negative effect on their sensitive applications, especially in medical and environmental applications. Green synthesis of nanoparticles is the optimum solution to the aforementioned constraints.

The synthesis of nanoparticles using plant extracts has widely been explored for almost two decades [4]. Numerous publications worldwide are reported for the synthesis of nanoparticles using plant extracts and natural materials [5,6]. Noble metals such as Gold, silver and Platinum are the most synthesized nanoparticles using plant extracts [6]. Recently, researchers have been directed towards metals other than noble metals such as zinc [7,8], manganese [9], and many other metals [10]. Studies have shown that silver nanoparticles prepared using plant extract are less toxic [11], showed enhanced properties [12] and wider applications than nanoparticles prepared by conventional methods [13]. In our previous studies, several Yemeni natural products have been chosen as a reducing agent for the synthesis of nanoparticles. Dragon blood has been effectively tested for the synthesis of silver and silver oxide [14] and ZnO [15] nanoparticles. Furthermore, glucose extracted from Yemeni honey and palm dates has shown amazing results for the synthesis of Cu_2O nanoparticles with controlled morphologies [16-17].

Qat (*Catha edulis*) is an effective, fast growing plant mostly cultivated in east Africa and the southern Arabian Peninsula. People, mostly male, in many countries such as Yemen, Ethiopia and Somalia are widely masticating the leaves of Qat for long hours daily due to its stimulant action; believing that it improves performance and increases work capacity [18]. The plant grows easily in a variety of environments such as in high altitude areas and waterless soils [18-25]. It is a seedless plant and condition resistant. Chemical investigation to the constituents of Qat leaves has been widely studied. It contains more than forty alkaloids, glycosides, amino acids, vitamins and minerals [19-24]. Qat leaves also contain considerable amounts of tannins ranging between 10% to 14% in dried leaves and different types of flavonoids[22-28]. The large content of Tannins in Qat leaves is reasonable reason for its growing in almost all climates and environments. Flavonoids, Tannins and amino acids are plausibly the most active groups in the Qat extract solution for the reduction and stabilization of Ag NPs [29-30].

A research group [31] has published a research work regarding the synthesis of Ag NPs using different local plant extracts; Qat extract was among them. However, nothing was written about the reaction mechanism and the characterization was also poor. Except the previous study [31] and to the best of the researchers' knowledge, the preparation of nanoparticles from Yemeni Qat leaves extraction is not reported anywhere. That is plausibly due to the regulation rules that prevent planting it in many countries worldwide. The leaves of *Catha Edulis* are selected in the present study as a reducing and surfactant agent owing to their availability with huge amounts and negligible costs. the plausible chemical reactions are precisely investigated. Furthermore, multi-disciplinary characterization tools are used to indicate the structure and morphology of the synthesized Ag Nanoparticles.

2. Materials and Experiments

2.1 Extract Preparation

It is worthy mentioning that synthesis experiments use natural materials only. Green leaves were prepared from Yemeni Qat (Taiz, Sharaab), while silver Nitrate (99%) was purchased from Merck. Distilled water was purchased from an authenticated local agent. In the first step, the green leaves were naturally dried for a few days and kept for further use. In the next step, 100 ml of distilled water was heated at 100^{o}C in a magnetic stirrer. After that, 20 g of dried Qat leaves were poured in the heated water solution and kept for 20 minutes until the water color transferred to a red-like solution. Fig. 1(a) shows a photograph of the extracted solution

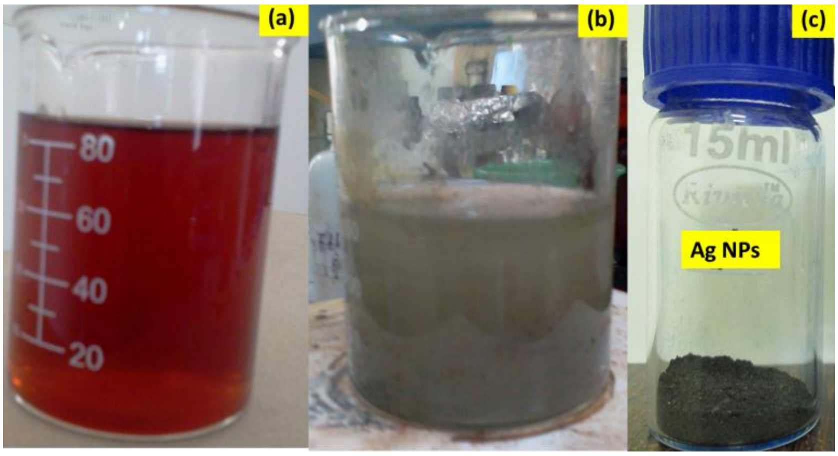

Figure 1. Photographs show the preparation procedure of (a) extract solution, (b) Ag NPs solution, and (c) Ag NPs powder.

2.2 Synthesis Experiment

It is worthy mentioning that the experiment was carried out without any chemical additives. The synthesis procedure of Ag NPs can be described in the following steps. In the first step, 1.7 g of $AgNO_3$ (Merck) was added to 50 ml of distilled water and kept to totally dissolve under vigorous stirrer. In the next step, 20 ml of the extract solution was slowly added to the previous solution and kept for 1 hour at room temperature. The pH of the resultant solution was measured to be 8.5. The resultant solution was kept to naturally precipitate (Fig. 1(b)) and the water were removed. In the final step, the obtained powder was washed twice with distilled water and ethanol and then dried at 120 $^{\circ}$C for 2 h to remove all water contents from the nanoparticles. The powder was weighed to be 1.44 g and then kept in a small glass bottle for further use as shown in Fig. 1(c).

3. Results and Discussions

The grey color (**Fig. 1(c)**) is the first indication of the synthesis of Ag NPs. Our repeated experiments at the lab scale showed that performing the reaction at high pH (adding NaOH) enhances the reaction kinetics and oxidation of Ag NPs. Powder XRD analysis (Bruker's AXS Model D8 Advance System, (λ=1.54 Å)) was performed to show the XRD pattern of Ag NPs. **Fig. 2(a)** shows the X-Ray Diffraction pattern of the prepared Ag powder. The diffraction pattern showed characteristic diffraction peaks similar to those of pure silver, which confirms the reduction process from silver nitrate to silver nanoparticles using this novel plant extraction. The high-intensity peaks indicated that the particles are of high crystallinity. Furthermore, the peak positions appeared at 38.18°, 44.29°, 64.57°, 77.41° and 81.6° can be indexed as (111), (200), (220), (311), (222) crystal planes of Ag respectively. All these diffraction peaks can be indexed to the face-centred cubic (FCC) crystalline structure of pure Ag NPs.

Debye- Scherer equation, a well-known formula, was first invented by Scherrer in 1918 and then subjected to different modifications [32]. It is usually used to identify the main grain size of the particles by analyzing XRD peaks as shown in Fig. 2(b). The following equation is the Debye-Scherer equation:

$$\delta = \frac{0.9\,\lambda}{B\cos\theta}$$

(Eq. 1)

Where δ is the grain size diameter, B(2θ) is FWHM (Full Width at Half Maximum) in radians and can be determined using Gaussian curve, λ = 1.54 nm (a tool characteristic) and θ is the Bragg angle. However, the value of (0.9) is the constant of proportionality (Scherer constant) and generally chosen between (0.89 – 0.94).

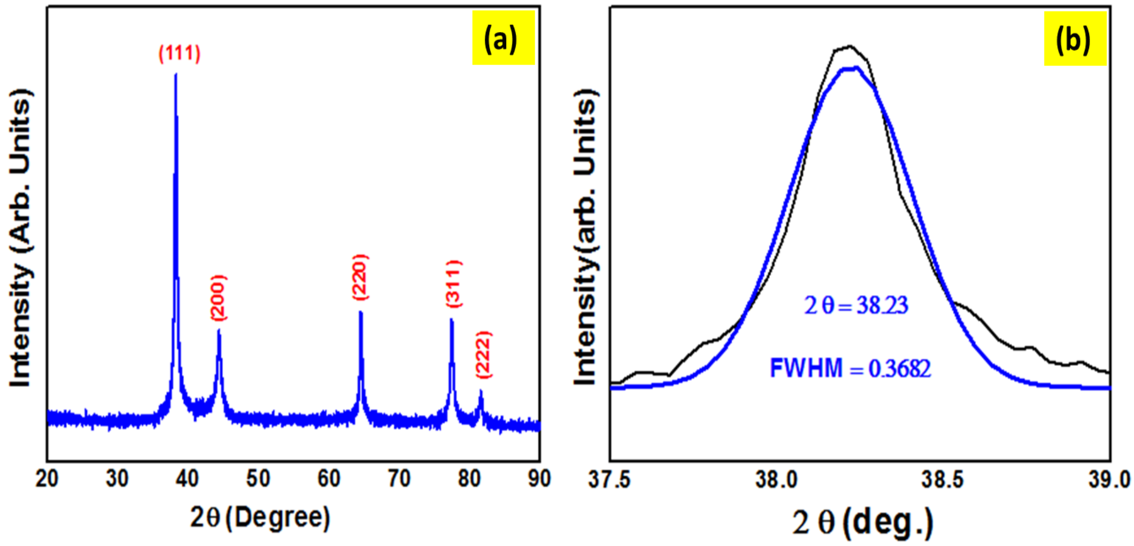

Figure 2, (a) X-Ray Diffraction pattern and (b) Debye- Scherer analysis of Ag NPs prepared from the extraction of Qat leaves.

The calculation could be performed by drawing the Gaussian fitting for the highest intensity peak (Fig. 2b) and measuring the values of (***2θ***) and Full Width at Half Maximum (***B= FWHM***). The analysis is performed and the results showed that the average grain size is d= 23.86 nm, while the lattice strain is 0.0046. The obtained crystallite size from the Scherer equation is to be compared with the results of electron microscope images.

To identify the particle sizes and morphologies, Ag powder was characterized using a TEM microscope (*FEI Technai G2 S-Twin, 200 kV voltage*). Fig. 3(a-c) show TEM images of Ag NPs. Most of the particles are of round morphology, but with different sizes ranging from 2–50 nm. Generally, the particles prepared using plant extracts are of a wide size range. Further investigation to control the size and shape of the particles is out of the scope of the present study.

The average particle size was calculated by measuring the diameter of an arbitrary 114 particles from TEM images. Fig. 3(d) shows a histogram of particle size distribution in the range 01 – 45 nm. Few particles above this range were excluded. The average particle size based on the above measurements is 18.11 nm. This value is in-line with the previous calculation made using Scherer equation (Fig. 2(b)).

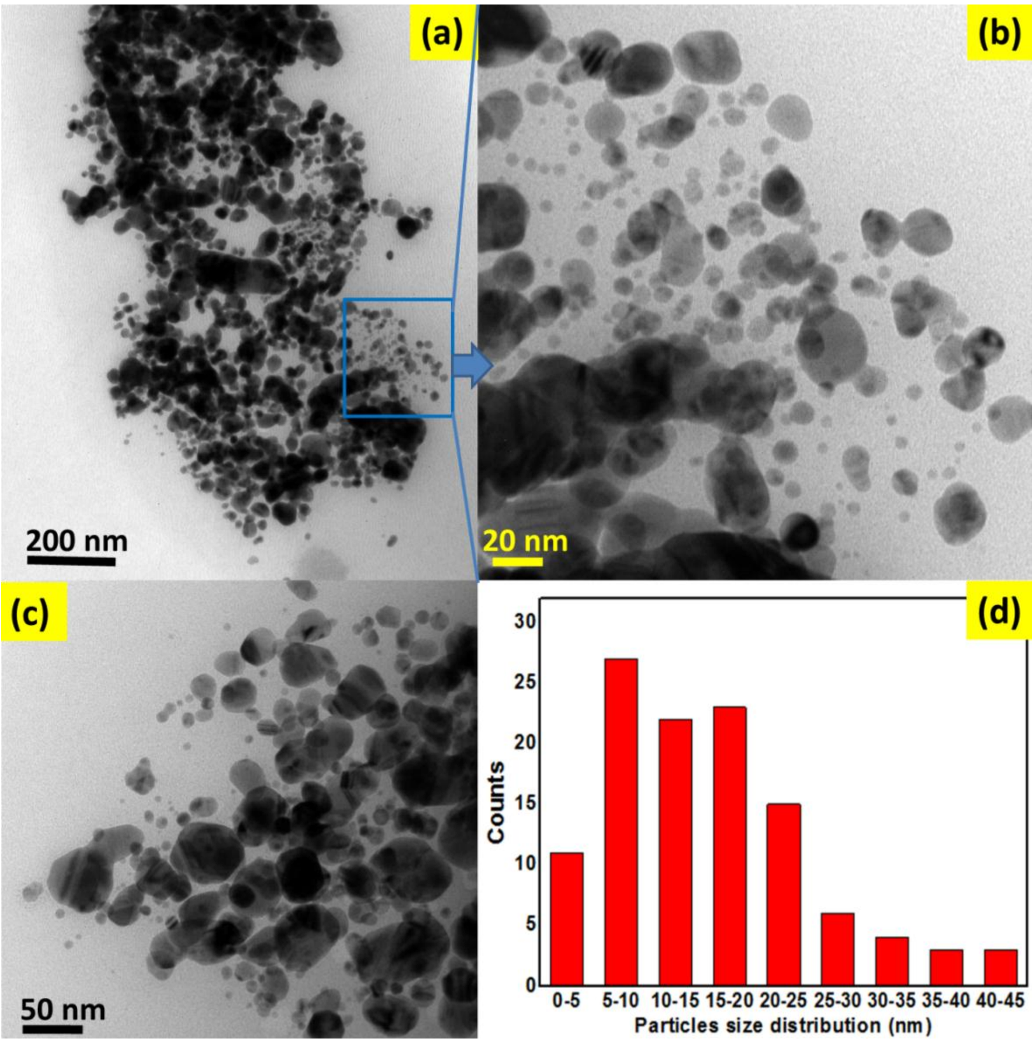

Figure 3, TEM micrographs of Ag NPs prepared from Qat leaves at pH= ~8. (a) Low resolution image, (b) & (c) are high magnification TEM images. (d) is the Particles size distribution

The chemistry of Qat constituents confirms the availability of several active chemical compounds in its leaves. Some of these chemicals have been found with high concentrations in the analytical analysis of qat leaves. These chemicals are flavonoids, cathinone, amino acids and cathine [20-21] and maybe they are the most responsible compounds for reducing silver precursor to silver ions surfactant. Although, The particle size range of NPs prepared using a green synthesis of plant extracts are wide and irregular shapes, the range in the present study is relatively narrow between 2 - 50 nm in size and the particles are with spherical shape in almost all particles. Moreover, silver nanoparticles in this size range are an excited area in many applications such as antibacterial applications in water purification or in medical and pharmaceutical applications as well as in environment fields. The wide range in particle size is attributed to the change of the chemical concentrations responsible for reducing Ag ions due to their difference in concentration from leaves to another and from tree to other based on the soil where the plant is growing.

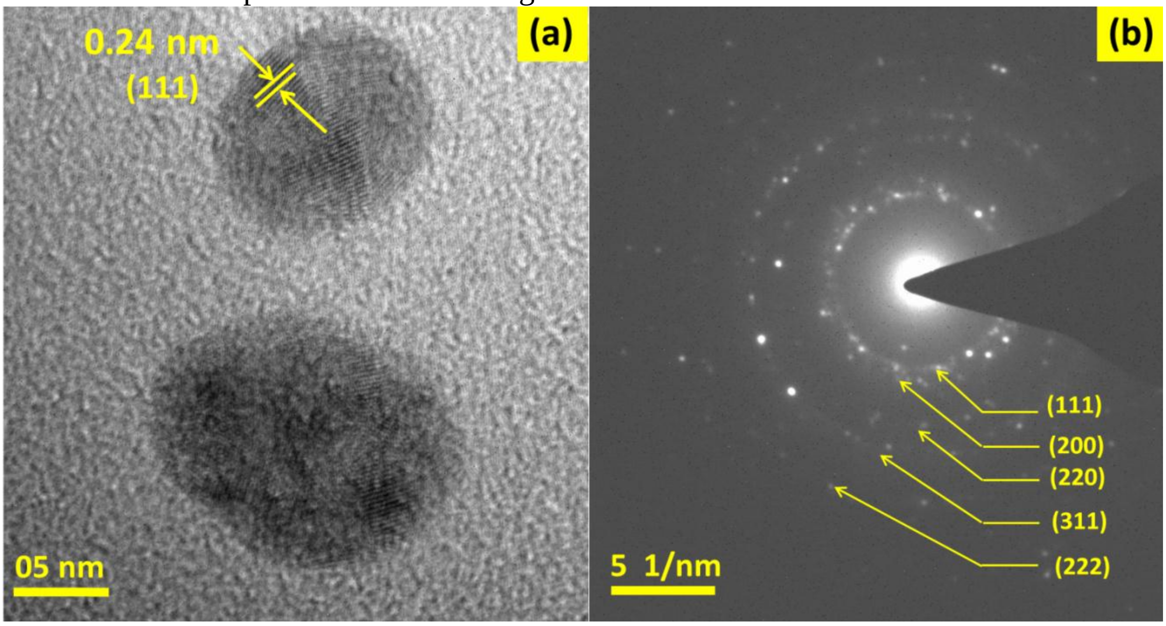

Figure 4. (a) HRTEM micrograph and (b) SAED pattern of Ag NPs prepared with the help of Qat extract.

High-Resolution TEM image of two particles is shown in **Fig. 4(a)**. The image shows a single particle that has lattice lines with a certain orientation on the particle surface, indicating the atomic distance between two adjusting atoms in the crystal structures of silver. The lattice interface is measured to be ~ 2.4 A°, which corresponds to (111) fcc single crystal plane of Ag crystal. The interference lines shown on every single particle, indicated that the atoms subjected to distortion during the reaction.

Fig. 4(b) shows the SAED pattern from Ag powder. SAED is a crystallographic experimental technique that can be performed within a transmission electron microscope (TEM). Obviously, the image is a series of spots, each spot corresponding to a satisfied diffraction condition of the sample's crystal structure. If the sample is tilted, the same crystal will stay under illumination, but different diffraction conditions will be activated, and different diffraction spots will appear or disappear. The spotted circles on the pattern are correspond to the pure phase of the Ag structure. The pattern is indexed to (111), (200), (220), (311), and (222) of fcc silver respectively. These patterns are in accordance with the XRD results. The pattern also showed that Ag powder is polycrystalline in nature.

Tannins are responsible for giving the leaves a sharp bitter taste, which makes the animals, insects, microbes, etc., are unable to feed on such leaves or at least indigestible. The presence of Tannins in Qat leaves with ~ 14% [20] makes its growing fast. Tannins by their self are weak reducing agents at neutral pH solution. However, at high/low pH, tannins hydrolyze to glucose and Gallic acid [20]. Glucose is a well-known reducing and stabilizing agent [16,17]. On the other hand, Gallic acid is considered a bad surfactant habit of the particles' agglomeration. That is plausibly the reason behind the wide particle-size distribution. Flavonoids which is a common reducing agent [14,15], is also found in the extract [22-23]. The red color of Qat extract (**Fig. 1(a)**) is an indication of the presence of polyphenolic compounds which are known as antioxidant agents [34]. These unique compounds are plausibly metal chelating agents for reducing and stabilizing Ag NPs.

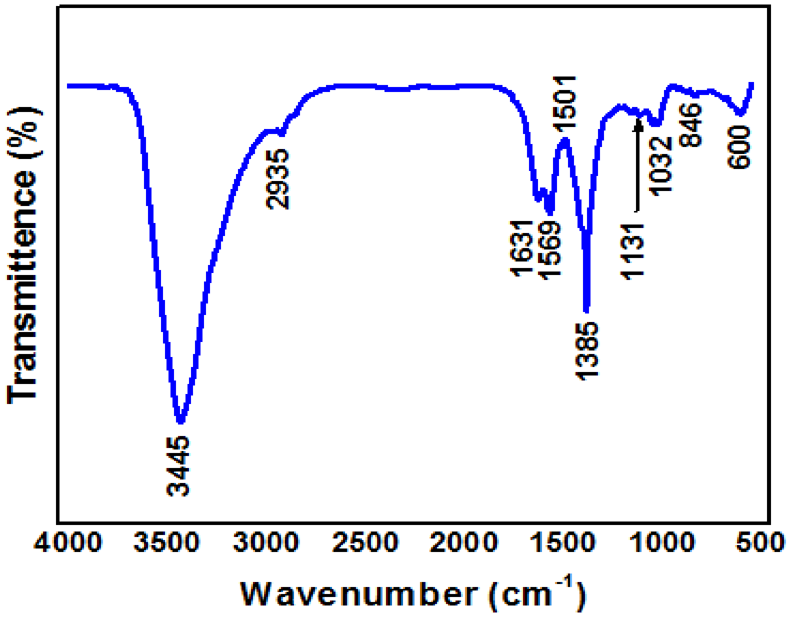

Figure 5. FTIR spectrum from Ag NPs synthesized with the help of Qat extract.

Surface contents of Ag NPs were identified using Fourier-transform infrared (FTIR) spectroscopy (*Model: Nicolet 380 of Thermo Scientific*). It is a unique characterization tool to identify the functional group on the surface of Ag NPs. In a very recent study, FTIR spectra of Qat leaves have shown peaks at 646, 1626, 3412 cm^{-1}, which are an indication of the presence of polyphenols, flavonoids, tannins and alkaloids in its leaves [36]. **Fig. 5** shows the FTIR spectra of Ag NPs that are reduced with the help of Qat extract. The presence of a large number of bands is an indication of the surface-functionalized particles. The band at 1631 cm^{-1} arising from the stretching of carbonyl in protein while the peak at 2935 cm^{-1} is for the stretching of C-H aldehyde groups. A very deep band at 3445 cm^{-1} is assigned to the O-H stretching bond in alcoholic and phenolic groups. Similarly, the peaks at 1569 cm^{-1} and 1032 cm^{-1} are attributed to the stretching of N-H of tannins and C-N groups of amines, respectively [35]. Finally, the peak at 600 cm^{-1} is an indication of the Ag-O oxide of silver crystallites [14]. **Fig. 6** shows the Energy Dispersive Spectroscopy (EDS) analysis of the obtained powder. It is an analytical study of the obtained Ag NPs powder and its percentage constituents. The spectrum shown on the figure indicated that highly pure silver particles with a few percentages of silver oxide (9.9 % by weight).

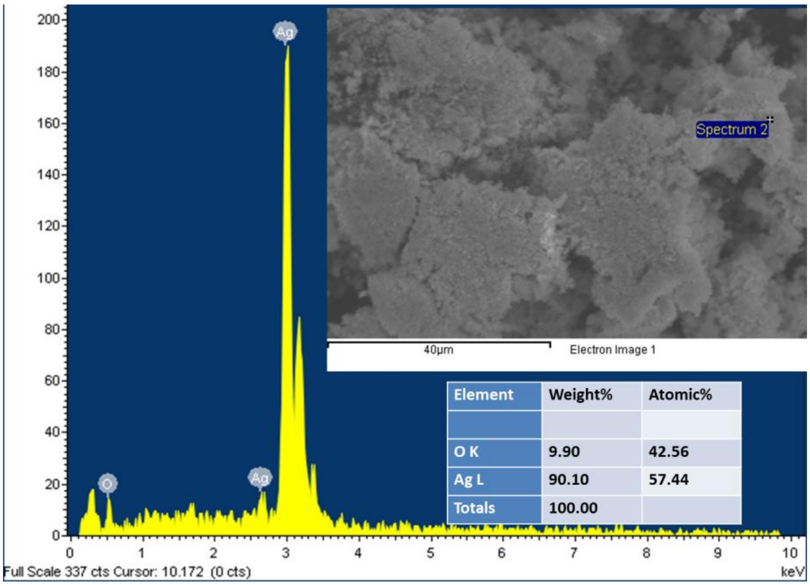

Figure 6. EDS from Ag NPs powder.

4. Conclusions

This study has presented the synthesis of highly crystalline Ag NPs with average size 18.11 nm using a facile, rapid, cost-effective and eco-friendly synthesis method using the extraction of Qat leaves. The chemistry behind Qat analysis confirms the availability of several active chemical compounds in its leaves. Some of these chemicals have been found in high concentrations in the analytical analysis of Qat leaves such as flavonoids and tannins, which are being proved as reducing and capping agents for reducing silver ions to silver nanoparticles without any additional hazardous chemicals. Multi-disciplinary characterization tools were used to prove the size, shape, structure and elemental components of the particles. The results show sphere-like Ag NPs with FCC structure and lattice distance of d = 0.24 nm. The characterization has also showed that a negligible oxidation phase was obtained in the particles, indicating the purity of the silver particles. This method is examined for mass production of Ag NPs and the obtained powder has the potential for several attractive applications.

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