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Gamma Radiation Effect on Characterizations of Gold Nanoparticles Synthesized Using Green Method

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Abstract
Biocompatible gold nanoparticles were successfully synthesized by hibiscus plant leaf extract as a bioreactor. The prepared nanoparticles were evaluated using UV/Vis spectroscopy, Atomic Force Microscopy (AFM), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction and Scanning Electron Microscopy (SEM) . The study also investigated the effect of the different gamma irradiation doses on the size and dispersion of the produced nanoparticles. In UV-Vis spectra, the peak of Au NPs' surface plasmon resonance (SPR) was detected as a single peak at 543 nm. The gamma irradiation induced a blue shift in the SPR peak, which indicates that it might be applied as affective factor for size control. Physical as well as chemical compound of gold with extract was discovered using Fourier Transform Infrared (FT-IR) analysis. SEM results indicated that the nanoparticles size was in the range from (25.61 - 48.36) nm and most of particles appeared within the nanoscale with spherical and semi-spherical shapes, moreover, the irradiation process led to development in the shape and size of synthesized nanoparticles

Keywords: green synthesis, hibiscus plant, gold nanoparticles, gamma radiation.

تأثير أشعا عكاما على توصيف جسيمات الذهب النانوية المركبة باستخدام الطريقة الخضراء

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الخلاصة
تم تحضير جسيمات الذهب النانوية المتوافقة حيويا بنجاح بواسطة مستخلص اوراق نبات الكركديه كمادة حيوية متفاعلة . تم تقييم الجسيمات النانوية المحضرة باستخدام التحليل الطيفي للاشعة فوق البنفسجية / المرئية, والفحص المجهري للقوة الذرية والتحليل الطيفي للاشعة تحت الحمراء وانحراف الاشعة السينية و بتقنية الفحص المجهري الالكتروني . كذلك تضمنت الدراسة التحقق من أن جرعات اشعة كاما المختلفة أثرت على حجم وتشتت الجسيمات النانوية المنتجة. وجد ان ذروة رنين البلازمون السطحي في طيف الاشعة فوق البنفسجية / المرئية للذهب النانوي تقع عند 543 نانومتر . تسبب استخدام التشعيع بكاما في حدوث تحول في الذروة نحو اللون الزرق وهذا يشير الى استخدامه كعامل مشارك للتحكم في الحجم . تم اكتشاف التركيب الفيزياوي والكيميائي للذهب مع المستخلص باستخدام تحليل فوربيه للاشعة تحت الحمراء واشارت النتائج الى

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ان حجم الجسيمات النانوية في المدى من (25.61−48.36) نانومتر وظهور معظم الجسيمات ضمن المدى النانوي باشكال كروية وشبه كروية , علاوة على ذلك ادت عملية التعيع الى تطور بشكل وحجم الجسيمات النانوية المركبة .

1. Introduction

Nanotechnology is a relatively new branch of science concerned with the design, development, and application of nanoparticles. The creation of green metal nanoparticles (MNPs) is a technology that is both environmentally benign and time efficient [1]. Secondary metabolites are plentiful in plants and are used in a range of biological activities, including MNPs synthesis [2]. Gold nanoparticles (AuNPs) have become a focus of nanomaterial studies due to their broad variety of applications in different fields such as, biomaterial synthesis, sensing, catalysis, and electronics [3]. The composites of noble MNPs, which include AuNPs, have lately gained interest for their capacity to enhance dye degradation and minimize organic pollutants in the environment [4].

As a result, the physiological impact of green nanoparticle creation is greater [5]. The creation of nanoparticles utilizing beneficial plant components is an exciting concept when compared to typical synthesis methods. This synthesis approach has been developed and implemented since plants are widely available, have a large dispersion, and are simple and safe to utilize [6]. The shape, size, surface area distribution, and aggregation of nanoparticles must all be determined before toxicity or biocompatibility can be determined [7]. The main benefit of plant extracts is that they are gentle, renewable, and non-toxic reducing and stabilizing agents, obviating the need for chemical reducing agents as well as costly polymeric capping agents and stabilizers [8,9]. Gold nanoparticles prepared by green method are more efficient than all other nanoparticles due to their considerable plasmon resonance and bio-conjugation behavior with bimolecular medium [10]. AuNPs offer perfect features such as biocompatibility, size control, and stability, making them useful in a variety of domains such as biological transmission electron microscopy, colorimetric DNA sensors, and catalysis [11], also, the most effective drug nano-carriers and promising agents for cancer diagnosis and treatment [12]. The extracts of some plant such as pineapple, acacia gum and more plant components have also been used to create AuNPs [13-15].

Ionizing radiation is a type of energy that comes in the form of electromagnetic waves (such as X-rays and gamma rays) or particles (alpha, beta, neutrons, etc). They transfer energy to the materials they come into contact with. Faster or heavier particles leads to a harder effects [16].

Because of metal tendency to organize, ionizing radiation, such as gamma radiation, is useful in metal reduction process. It aids to controlling the size and distribution of metal nanoparticles [17].

Water radiolysis produces transient radicals in an aqueous solution that has been bombarded with high-energy gamma radiation. The metal ions are reduced by the solvated electrons(e–aq.) which are produced in the radiolysis process and the metal atoms combine to form aggregates [18].

In the current study, AuNPs were prepared from non-toxic natural components from hibiscus plant leaves. The influence of gamma radiation on the size, distribution, and shape of the prepared AuNPs was monitored.

2. Materials and methods

2.1 Material

Chloroauric acid (HAuCl4.3H2O) was obtained from MERCK Company-Germany. leafs of hibiscus plant was purchased from local market.

2.2 Methods

2.2.1 Gold nanoparticles synthesis using hibiscus plant extract

Hibiscus sabdariffa (Roselle in English) as illustrated in Figure 1a is a medicinal plant used for its health advantages. It possesses antibacterial, antioxidant, and anti-inflammatory qualities, as well as being reasonably safe and non-toxic. Hibiscus leaves include phenolic acids, organic acids, flavonoids, and anthocyanins, which may contribute to the plant's medicinal effects. It can also be utilized as a reducing agent in nanotechnology applications [19].

A volumetric flask (500 mL) was used to dissolve one gram of $HAuCl_4.3H_2O$ in 100 mL of distilled water, which was then placed on a magnetic stirrer until completely homogenized. After that, the plant extract was made by adding 2 gram of hibiscus plant to 100 mL of distilled water and heating it to 50^oC for 30 minutes after which it was filtered, as shown in Figure1b. The $HAuCl_4.3H_2O$ solution was placed on a stirring hotplate, at a temperature of $50\text{-}70^oC$, with a magnetic bar, the hibiscus extract solution was added until the color changed to bright red, indicating the acquisition of gold nanoparticles.

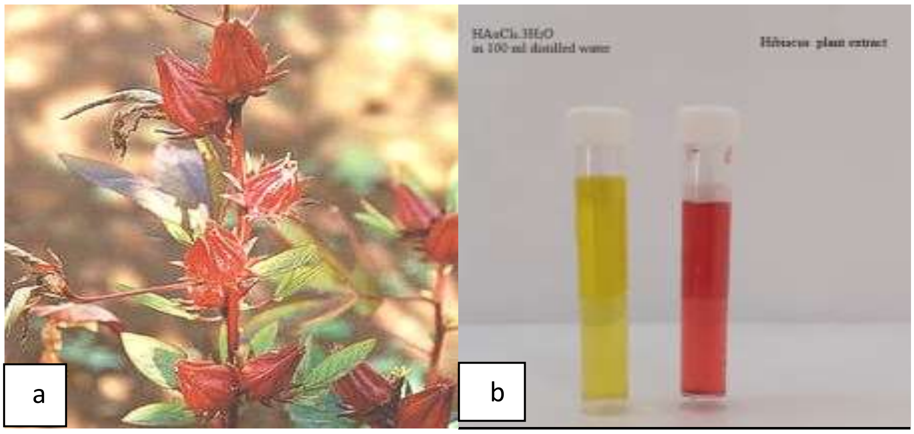

Figure 1: a. Hibiscus sabdariffa plant. b. the prepared solutions

2.2.2 Gold nanoparticles characterization:

UV-Visible spectrometer: The absorbance spectra of the synthesized AuNPs were obtained using UV-Vis spectroscopy (Shimadzu, Japan).

Atomic force microscope (AFM): Allows you to see three-dimensional objects. Shape, size, surface texture, and roughness, among other physical properties were described quantitatively and qualitatively using an AFM (SPM AA 3000, USA).

Fourier transform infrared spectroscopy (FTIR): FTIR was utilized to confirm functional bio-molecules linked with gold nanoparticles, which are involved in the reduction of gold ions into AuNPs. The infrared spectra of nanoparticle absorption and emission were determined using the FTIR method. An FTIR spectrometer(Shimadzu-8400) was used to examine the absorption spectra between 4000 and 400 cm^{-1} for the extraction of the herbals plant at room temperature.

X-ray diffraction Analysis(XRD): The molecular and atomic structure of a crystal are determined using the X-ray diffraction technique (in which the crystalline structure causes a beam of incident X-rays to diffract in several precise directions).

Scanning Electron Microscopy (SEM): SEM handles electrons to record high-resolution images of structures and metal layers so as to give a measure with quality and uniformity of process. It is used to identify surface morphology and particle size**.**

2.2.3 Irradiation process

A gamma cell with Co-60 was used as gamma ray source in this study, with a dosage rate of 16Gy/hr. The gold nanoparticle samples were placed in the gamma cell with the identical gamma dose applied to all of them. The samples were exposed to different irradiation doses of (5,6,10) kGy.

3. Results and discussion

The development of nanoparticles synthesis with optoelectronic and excellent physico-chemical characteristics is the core of nano science. a green synthesis procedure was used that lowers aqueous $HAuCl_4.3H_2O$ and the pharmacologically important of hibiscus plant extract, gold ions (Au^{+3}) are changed to gold nanoparticles.

Characterizations of gold nanoparticles

The solution's color change from yellow to red, with the appearance of the usual peak of plasmon resonance at about 560 nm, indicates the formation of AuNPs. This is compatible with the results of a previous work [13]. Figure 2a shows the UV–Visible absorption spectrum of AuNPs prepared by the green method with hibiscus plant as the reducing agent, which revealed a surface plasmon resonance absorption peak centered at 543 nm. Figure 2b shows the the influence of gamma irradiation on AuNPs spectra. A wide absorption band in the visible range at 543 nm is seen in the optical spectrum of conventional biosynthesized gold nanoparticles. The SPR peak location wass changed from 543 to 525 nm when a sample of gold nanoparticles was irradiated with a 10kGy gamma ray dose, indicating the creation of smaller particles [20].The irradiation process is very dependent and progressive on the growth of AuNPs produced by the reduction of Au ion to Au atom [21]. For high dose rate of γ -irradiation, the nucleation behavior that leads to the development of smaller particles increases, and the reduction process takes over, allowing for the formation of new clusters and smaller nanoparticles [20].

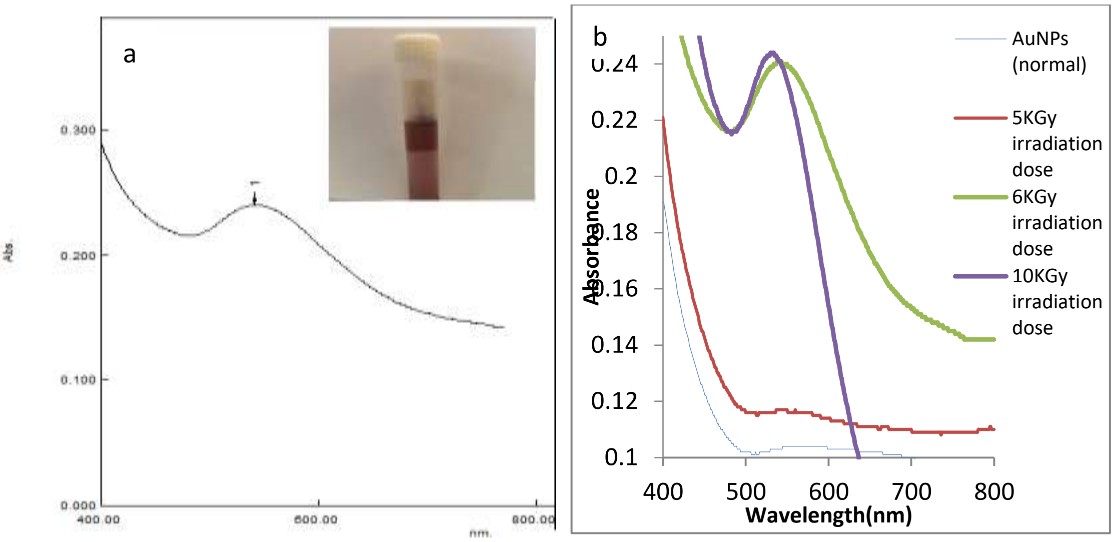

Figure 2: a. UV-Vis. spectra of gold NPs synthesized by hibiscus plant as reducing agent and b. the spectra of the the irradiated gold nanoparticles with different γ- radiation doses.

AFM analysis is used to assess the presence of synthesized AuNPs, and to give quantitative and qualitative information on many physical characteristics, such as morphology, size, roughness, and the texture of surface. AFM examination produced two and three-dimensional pictures of AuNPs, which were found to have a consistent distribution, spherical form, and nanosized particles (Figure 3). The particle size of the synthesized gold nanoparticles from Hibiscus plant as the reducing agent was (48 nm), as shown in Figure 3a. For 10 kGy γ-irradiation dose, the particle size was reduced to (30 nm). This drop corresponds to the normal sample's shift in SPR peak position in the UV/Vis study. It was noted that the particle size decreased as the dosage rate of γ-radiation was increased. The aggregation of AuNPs was limited by gamma irradiation, resulting in the development of mono dispersity (Figure 3b).

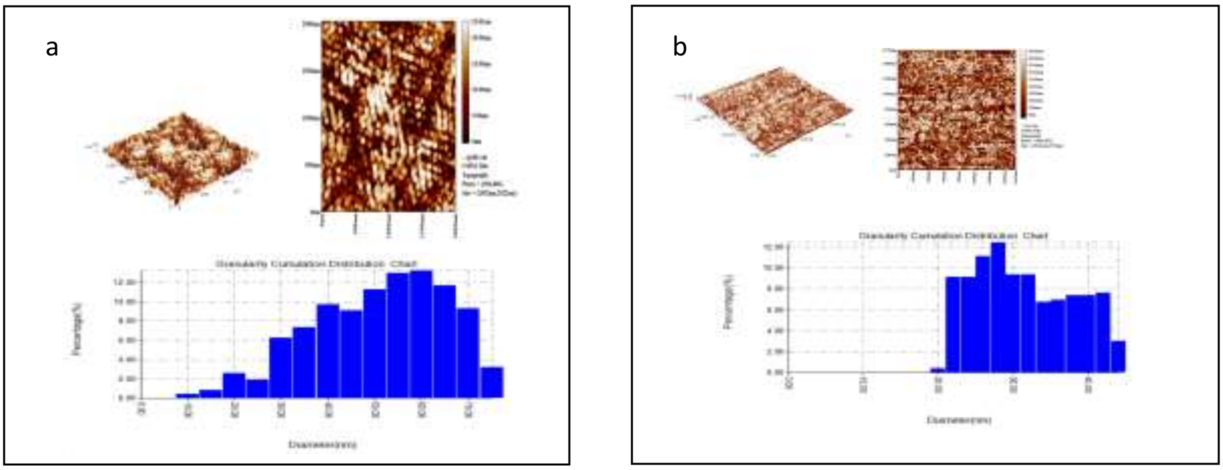

Figure 3: FAM images of synthesized gold nanoparticles and corresponding histograms of particle size distribution before(a) and after(b) irradiation process.

The extract was subjected to FTIR analysis to determine the various functional groups present so as to differentiate the putative bio-molecules which are responsible for the reduction of gold ion to AuNPs. Figure 4 shows the FTIR spectrum of synthesized AuNPs. The aromatic alcoholic and phenolic chemicals are indicated by a wide maximum peak that extended from 1000 to 3500 cm^{-1} and was recorded at 3442 cm^{-1}, the amide groups are at

1631 cm^{-1}, polysaccharides and pectin are combined in the 1623 cm^{-1} band, the water molecule is represented by the 2256 cm^{-1} band, the band at 2042 cm^{-1} corresponds to lipids and fatty acids, whereas the 3442 cm^{-1} band corresponds to the bond OH, and the NH amide is at 3249 cm^{-1}. As a result of these findings, phenolic, alcoholic chemicals were assumed to be responsible for AuNPs reduction and stability [15]. The AuO functional group resonance is associated with the 631 cm^{-1} absorption band. This demonstrates that the nanocomposite contains nanosized Au particles.

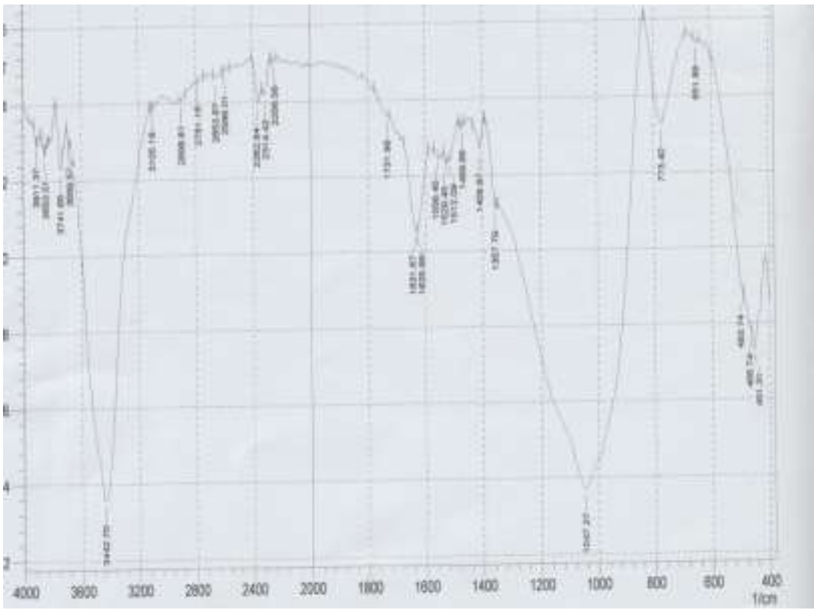

Figure 4: FTIR spectrum of AuNPs synthesized by hibiscus leaf extract.

Figure 5 shows the X-ray diffraction pattern of nano-gold crystalline phases. As demonstrated in the figure, the Bragg reflection patterns at 2θ = 38^{o} (111), 44^{o} (200), 64^{o} (220), and 77^{o} (3 1 1) are realized for the face-centered cubic (FCC) structure of AuNPs [22]. The data on the standard card are used to locate these reflection patterns (JCPDS file No. 04-0784). The findings revealed that the sample was composed of gold with a crystalline structure.

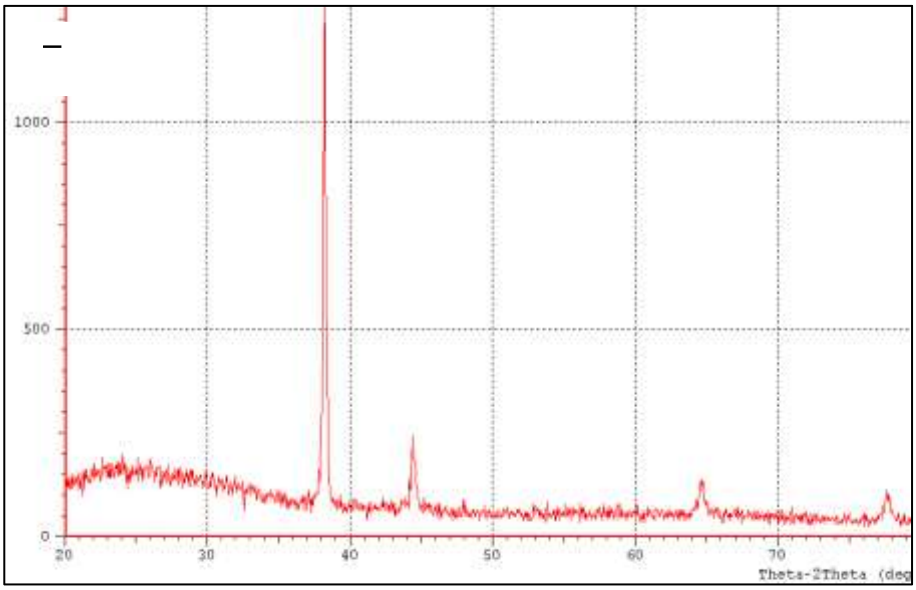

Figure 5: X-ray diffraction pattern for gold nanoparticles.

SEM analysis was employed to find the size and style of gold nanoparticles prepared from hibiscus plant extract. Figure 6a represents the SEM images recorded from drop casting method on glass substrate. The images, with a magnification of (10kx) and(50kx), showed that the nanoparticles size were in the range (25.61 - 48.36) nm and most of the particles inside the nanoscale appeared with spherical and semi-spherical shapes with clear agglomeration. While, the size of the gold nanoparticles after irradiation is within the range (18.16-36.16) nm, which were of spherical or semi-spherical shapes and more contiguous, as shown in Figure 6b.

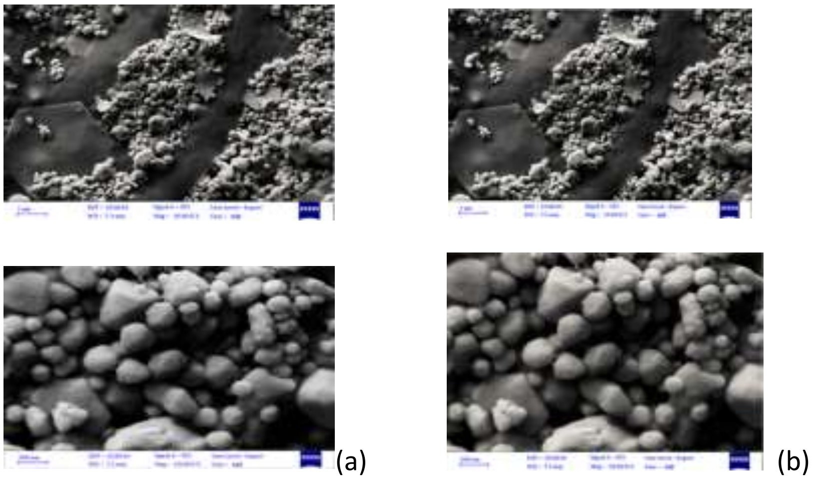

Figure 6: SEM images of synthesized AuNPs by hibiscus extract plant as reducing agent with magnification (10kx) and (50kx). a. before irradiation , b. after irradiated with 10k Gy γ-radiation dose.

Irradiation was performed out in an aqueous media since gamma rays would interact with AuNPs and induce ionization. Because photoelectrons are energetic, and gold has a greater photoelectric cross section than water, a dosage augmentation might theoretically occur in a variety of ways. Increased photoelectric absorption is the most intriguing approach because it is more effective and can create a dosage augmentation [23]. Furthermore, metal ions can be reduced to zero-valent metal particles utilizing hydrated electrons generated by gamma radiolysis of aqueous solutions, eliminating the need for another reducing agents and the associated side reactions. The quantity of zero-valent nuclei can also be changed by modification the dose of irradiation [24].

4. Conclusion

Leaf hibiscus plant was used as a reducing agent in this investigation to prepare AuNPs. The formation of AuNP was confirmed by UV-Vis absorbance spectrum, AFM, FTIR, and XRD examinations. The green synthesis of gold nanoparticles is a fast, effective and easy technology, as evidenced by the previous results. The surface plasmon resonance peak was qualifier by the red colour formation and UV-Vis analysis at 543 nm. The fine dispersion, nanosized, and spherical form of gold nanoparticles were also determined by the AFM study. The –COOH groups of phenolics and flavonoids in the hibiscus leaves are the main reason for the reduction process of gold ions, while, the C- groups contributed in stabilizing gold nanoparticles.

UV-Vis spectra and AFM analysis showed that using a gamma-irradiation-based approach to generate massive gold NPs with a limited size distribution offers considerable advantages.

The X-ray diffraction pattern confirmed the formation of the AuNPs. And this confirmed the SEM results with the nanoscale and spherical or semi-spherical shapes and are more contiguous.

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