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Research Article

Biosynthesis of Gold Nanoparticles (AuNPs) with Dimrit Raisin Extract and Their Degradation Activity for Water Contaminants

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ABSTRACT

AuNPs are being conventionally synthesized by traditional methods (physical and/or chemical) with preferred and well-defined morphology, size and shape. On the other hand, it has been reported that these methods involve difficult reaction conditions and/or toxic chemicals. In this study, an easy, cost effective and more environmentally and biological-friendly method was described for the synthesis of gold nanoparticles with Dimrit raisin extract for the first time. The effects of some experimental parameters, such as concentrations of both raisin extracts and Au solutions, synthesis time and synthesis temperature were investigated for the synthesis of AuNPs. The synthesized AuNPs were extensively characterized by UV-Visible spectrometer, Transmission electron microscopy (TEM), X-ray diffraction patterns (XRD) and Fourier transform–infrared spectroscopy (FTIR). TEM results show spherical along with triangular and hexagonal shaped nanoparticles with an average size of 15 nm. Large amounts of toxic dyes are used in the different industrial area and dyes posed a threat for water sources. Therefore, it has become imperative to develop inexpensive and environmentally friendly methods to remove dyes from water. In recent years, degradation using green synthesized nanoparticles has become an efficient method to remove dyes from the water sources. In this study, the catalytic activity of the AuNPs for the degradation of both methylene blue (MB) and methyl orange (MO) dyes were also studied and AuNPs behaved as effective catalysts for both degradations of MB and MO dyes in terms of percentage removal and kinetics. The experiment results showed that AuNPs can be employed as strong candidate in wastewater treatment studies.

Anahtar Kelimeler: *Dimrit raisin, AuNPs, Optimization effect, Dye degradation*

Altın Nanopartiküllerin (AuNP) Dimrit Kuru Üzüm Özütü İle Biyosentezi ve Su Kirleticileri İçin Bozunma Aktiviteleri

ÖZ

İstenilen morfoloji, boyut ve şekle sahip AuNP'ler, geleneksel olarak fiziksel ve/veya kimyasal yöntemler kullanılarak sentezlenmektedir. Fakat, bu yöntemlerin toksik kimyasal kullanımı, pahalı olması ve zorlu reaksiyon koşullarını içerdiği de bilinmektedir. Bu çalışmada Dimrit kuru üzüm özütü ile altın nanopartiküllerin sentezlenmesi için ilk defa kolay, uygun maliyetli, daha çevreci ve biyolojik bir yöntem tarif edilmiştir. AuNP'lerin sentez çalışmalarında hem özüt hem de Au çözeltisinin derişimi, sentez süresi ve sentez sıcaklığı gibi bazı deneysel parametrelerin etkileri araştırılmıştır. Sentezlenen AuNP'ler, UV-Vis spektrometresi, Transmisyon elektron mikroskobu (TEM), X-ışını kırınım difraktometresi (XRD) ve Fourier dönüşümü-kızılötesi spektroskopi (FTIR) ile karakterize edilmiştir. TEM sonuçları, 15 nm ortalama boyuta sahip AuNP'lerin üçgen ve altıgen

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şekiller ile birlikte nanopartiküllerin genellikle küresel şekilde olduğunu göstermiştir. Farklı endüstriyel alanlarda büyük miktarlarda toksik boyalar kullanılmaktadır ve boyalar su kaynakları için tehdit oluşturmaktadır. Bu nedenle, boyaları sudan gidermek için ucuz ve çevre dostu yöntemler geliştirmek zorunlu hale gelmiştir. Son zamanlarda, yeşil sentez ile elde edilmiş nanopartiküller kullanılarak gerçekleştirlen bozunma işlemleri, boyaların su kaynaklarından uzaklaştırılması için etkili bir yöntem haline gelmiştir. Bu çalışmada, ayrıca AuNP'lerin hem metilen mavisi (MB) hem de metil turuncu (MO) boyalarının bozunumu için çalışmalar gerçekleştirilmiştir. AuNP'ler, yüzde uzaklaştırma ve kinetik sonuçları değerlendirildiğinde hem MB hem de MO boyalarının bozunumu için etkili bir katalizör olarak görev almıştır. Ayrıca deney sonuçları, AuNP'lerin atık su arıtma çalışmalarında başarılı bir şekilde kullanılabileceğini göstermiştir.

Keywords: *Dimrit kuru üzümü, AuNPs, Optimizasyon etkisi, Boya bozunumu*

I. INTRODUCTION

Nanotechnology is one of the most hopefully fields of study in modern nanoscience and technology, as it interacts with many different sciences such as chemistry, biology, physics and materials science [1,2]. Due to very high surface/volume ratio, their significantly small size and showing superior physicochemical properties, metal nanoparticles play a significant role in different applications such as optical, catalytic activity, magnetic, electronic, and antibacterial properties [3].

There is a broad variety of methods for producing nanoparticles, including chemical reduction [4, 5], photochemical reduction [6,7], electrochemical reduction [8] and laser ablation [9]. When the encountered environmental risks in traditional synthesis methods of metal nanoparticles were evaluated, the researchers have started to prefer in the synthesis of facile, non-toxic, environmentally-friendly green synthesis of metal nanoparticles using plants [10,11], fruits [12] and biological organisms, such as fungus [13], and bacteria extracts [14], playing both reducing and stabilizing agents [15,16]. Among them, green synthesis with plant and fruit extracts is the most profitable method to eliminate the cost and time loss that occurred during the selection and planting of microorganisms [17].

Owing to their stability, less toxicity, and biocompatibility, AuNPs have been found to have applications in sensors [18], biomedical application [19], catalytic reduction [20], antimicrobials [21] and cancer therapy [22] depending on their sizes, shapes and crystal structures in a variety of fields, such as chemistry, biology, physics, and material science.

The organic dyes are used in different industries fields, such as paper, textiles, plastics, tanneries cosmetics, food, and pharmaceuticals [23]. Accumulation of dyes in the environment poses a risk for living creatures and ecosystem [24]. Some significant disorders may be occurred with exposure to dyes, such as liver illness, skin cancer, kidney damage, and central nervous system poisoning [25]. Different methods, including oxidation, adsorption, coagulation, membrane separation, photocatalytic degradation, and reduction degradation, are successfully used to remove dyes from the environment [3]. Recently, degradation with nanoparticles has attracted attention among other methods as it has important advantages such as rapid, low cost and high catalytic efficiency [26].

In this study, we have presented our new methodology on green synthesis of Dimrit raisin mediated AuNPs, their optimizations and characterizations. The concentrations of both Dimrit raisin extracts and Au solutions, synthesis time and synthesis temperature were investigated in detail for the formation of well-defined small and stable nanoparticles. Consequently, our new methodology has also provided guidance for the synthesis of other metal nanoparticles using different biological sources. Furthermore, synthesized AuNPs using Dimrit raisin extract were tested for their ability to degrade MB and MO dyes. Experimental results showed that AuNPs were very efficient for degradation of MB and MO dyes. As far as we can ascertain, this would be the first report using Dimrit raisin fabricated AuNPs and their catalytic activity for degradation of MB and MO dyes.

II. MATERIALS AND METHODS

A. MATERIALS AND REAGENTS

The ultrapure water (18 MΩ.cm) produced using PURIS purification system (Model: Expe-UP Series) was used to prepare all aqueous solutions employed during the synthesis procedures.

The gold salt ($AuCl_4Na \cdot 2H_2O$) was supplied from Sigma-Aldrich. MB and MO dyes were obtained from Merck and Aldrich, respectively. 0.2 M $NaBH_4$ solution was prepared from $NaBH_4$ salt (Fluka) by necessary dilution with ultrapure water.

The Dimrit raisins used for the synthesis of AuNPs were obtained from the local bazaar in Burdur City at Turkey. The obtained samples were cleaned thoroughly with 18 MΩ.cm ultrapure water. Then, raisins were dried in shade under the room temperature for one week. Afterwards, the samples were transferred into polyethylene bottles and stored at 4°C for until use.

B. SYNTHESIS OF GOLD NANOPARTICLES

To obtain the aqueous Dimrit raisin extract, 20 g of raisins were boiled in 1000 mL ultrapure water by reflux condenser at 100 °C for 5 minutes (min) and then cooled to ambient atmosphere. The obtained extract was then filtered with Whatman paper No.1 and the supernatant was used as reducing/stabilizing agents for the synthesis of AuNPs. Afterwards, 100 mL of 2.5×10^{-3} M $AuCl_4Na \cdot 2H_2O$ solution was added into 1000 mL of 2% extract and they were mixed for 120 min at room temperature for the synthesis of AuNPs. After the synthesis, a drop of the synthesized aqueous AuNPs was deposited in TEM copper grids covered with carbon, allowed to evaporate at room temperature. Furthermore, the aqueous AuNPs were centrifuged at 4500 rpm for 30 min and kept overnight in an oven at 35 °C and the dried AuNPs were used for XRD. For FTIR analysis, an evaporator (Heidolph Laborota 4000) was used to remove all water from the both Dimrit raisin extract and AuNPs solutions at 25 °C. FTIR analysis was performed for both extract and AuNPs.

C. CHARACTERIZATION METHODS

Surface plasmon resonance (SPR) band of AuNPs was obtained by UV-Visible spectroscopy (PG Instruments TG 60). The morphology of the AuNPs was performed with Transmission Electronic Microscopy (TEM) analysis (Zeiss Leo 906E). The crystalline size and structural properties of the AuNPs were determined by XRD (Bruker D8 Advance) with Cu Ka radiation. Moreover, the surface capping of AuNPs was investigated by FTIR (Perkin Elmer Fronter).

D. DEGRADATION STUDIES OF MB AND MO DYES

We investigated the degradation of both MB and MO dyes by AuNPs used as catalyst in the presence of $NaBH_4$. The catalytic studies were performed in aqueous media at room temperature under neutral pH. In the degradation procedure, 1 mL of $NaBH_4$ (0.2 M) was added separately to 1 mL of MB or MO dyes (1×10^{-4} M) followed by the addition of 0.1 mL AuNPs and 0.9 mL ultrapure water. Then, the spectrums of MB and MO dyes were monitored separately by using UV–Visible spectrometer at different times. Moreover, the control experiments were also performed in the presence of dyes and $NaBH_4$ solution together without adding AuNPs. The degradation efficiencies of both MB and MO dyes by AuNPs were calculated by the following equation;

$$\text{Percentage of degradation} = \frac{A_0 - A_t}{A_0} \text{x} 100 \text{ ,}$$

where A_0 is the initial absorbance and A_t is the absorbance at t time [27].

Furthermore, the kinetics of the degradation of both MB and MO dyes using AuNPs were expressed as a pseudo first-order reaction by the following equation;

$$In\left(\frac{A_t}{A_0}\right) = -kt,$$

where k is pseudo first-order rate constant, A_0 is initial absorbance and A_t is the absorbance at t time [28].

III. RESULTS AND DISCUSSIONS

A. OPTIMIZATION STUDIES FOR GOLD NANOPARTICLES

In this study, it was aimed to synthesize AuNPs with small size and high stability. Therefore, some important parameters were optimized such as extract concentration, metal salt concentration, synthesis time and synthesis temperature. Furthermore, optimum synthesis conditions were determined by evaluating the SPR bands obtained by UV-Vis spectrometer. The narrow of the SPR bands and the blue shift of the SPR bands are two important factors when evaluating SPR bands. While the narrow SPR band indicates that the nanoparticles formed are homogeneous, the wide SPR band shows the multiple distribution of the particles [29]. In addition, while the blue shift of the SPR bands indicates that the particle size of the nanoparticles is small size, the red shift of the SPR band indicates that the nanoparticles are large size [30].

Different concentrations of Dimrit raisin (0.5%; 1.0%; 1.5%; 2.0% and 2.5%) and Au solutions (10^{-1} M, 10^{-2} M, 10^{-3} M, 10^{-4} M, 10^{-5} M and 10^{-6} M) were prepared and Au solutions were added onto the Dimrit raisin extract as the ratio of 1:10 (v/v). The synthesis studies of AuNPs were carried out in the dark medium at room temperature. UV-Visible spectroscopy was used to observe the plasmon bands of AuNPs. The obtained SPR bands are shown in Figure 1a. When Figure 1a is evaluated, the narrowest and blue shifted band was obtained at 2% of extract concentration. Therefore, 2% was chosen as the optimum extract concentration. In addition, SPR bands of AuNP were obtained in the case of both 10^{-2} M and 10^{-3} M Au solutions and the SPR band was not observed at other concentrations. (10^{-1} M, 10^{-4} M, 10^{-5} M and 10^{-6} M). Therefore, it was decided that the concentration range of 10^{-2} M and 10^{-3} M should be optimized in more detail.

The effects of different concentration of gold solutions varied from 10^{-3} M to 10^{-1} M (1.0×10^{-3} M, 2.5×10^{-3} M, 5.0×10^{-3} M, 7.5×10^{-3} M, 1.0×10^{-2} M, 2.5×10^{-2} M, 5.0×10^{-2} M, 7.5×10^{-2} M, 1.0×10^{-1} M) for the synthesis of AuNPs by using 2% Dimrit raisin extract were investigated again in detail at room temperature after 24 h synthesis time to decrease the particle size and to enhance the intensity of SPR. Compared to other concentrations, 2.5×10^{-3} M Au was chosen as the optimum Au concentration based on peak height and shape corresponding to higher and sharper peak (Figure 1b).

During the synthesis of metal nanoparticles, the optimum synthesis time should be also determined to complete nucleation and obtain stable nanoparticles. For this, the experiments were carried out between 0 h and 240 min (Figure 1b). As can be seen from Figure 1c, the formation of AuNPs was started within 4 min and the significant increase was not observed in the absorbance value after 120 min. Since 120 min would be sufficient for the formation of stable AuNPs, it was chosen as the optimum synthesis time.

So as to investigate the effect of temperature, the synthesis for 120 min synthesis time using both 2% Dimrit raisin extract and $2.5x10^{-3}$ M Au solution was conducted at 4°C, 25°C 35°C, 40°C, 45°C and 55°C, respectively (Figure 1d). When the obtained SPR bands in Figure 1d were evaluated in detail, it

was determined that nanoparticle formation was low at +4 °C and almost same formations were obtained at other temperatures. Since high temperature have not a significant effect on the formation of AuNPs, 25 °C was chosen as the optimum synthesis temperature.

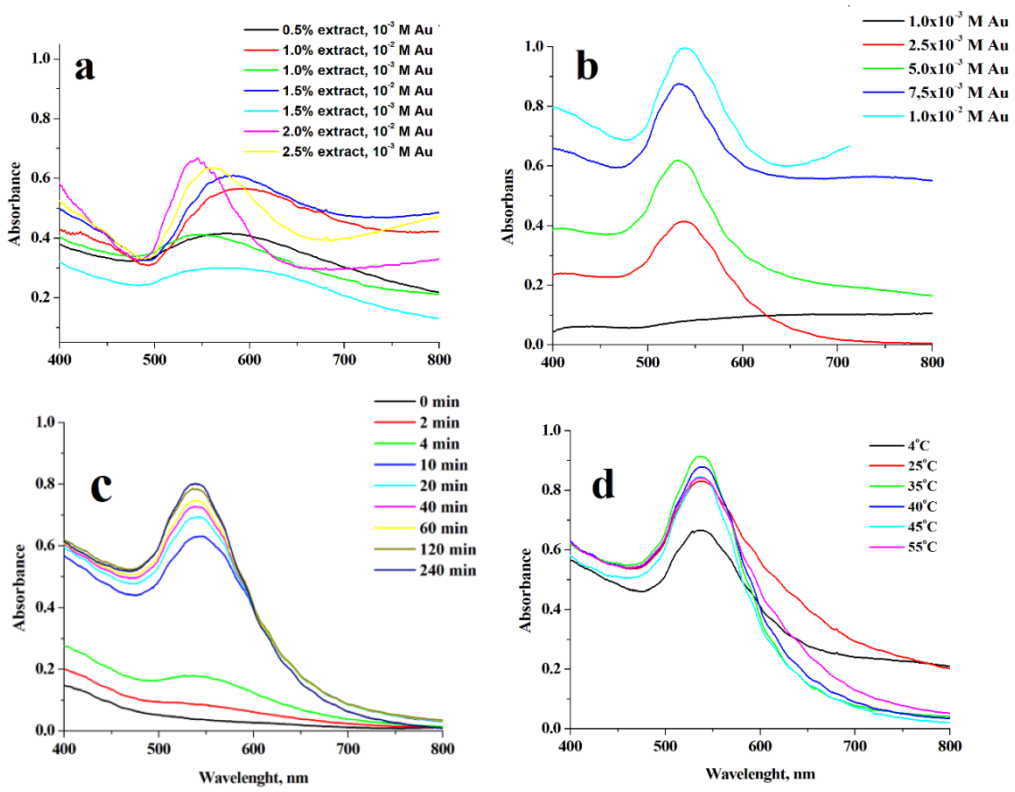

Figure 1. *The optimum* ***(a)*** *Dimrit raisin extract concentration,* ***(b)*** *Au concentration for the synthesis of AuNPs,* ***(c)*** *synthesis time for AuNPs,* ***(d)*** *synthesis temperature for AuNPs.*

The stability of AuNPs were also investigated by UV Visible spectroscopy at different synthesis time shown in Figure 2. The results showed that SPR bands were not shifted and the signals were not significantly changed with an increase of synthesis time. This result implied that the AuNPs were very stable without any aggregation.

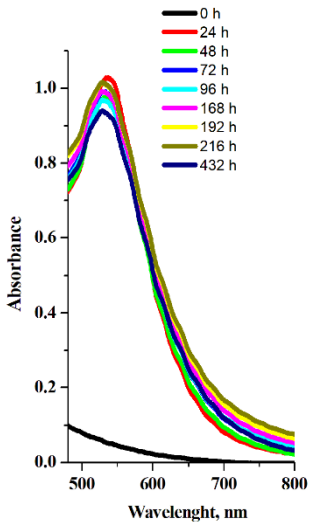

Figure 2. *Stability study of AuNPs*

B. CHARACTERIZATION STUDIES OF THE GOLD NANOPATICLES

The several methods were used to determine the size, morphology and crystallinity of the synthesized AuNPs. The first observation for the formation of metal nanoparticle was the colour change of the synthesis medium. The instant colour change was observed from pale yellow to violet during the formation of AuNPs. The characteristic signal of AuNPs in UV-Visible spectroscopy was observed at 538 nm while Dimrit raisin extract itself did not present any signals close to the SPR band of the AuNPs. Moreover, the structures and sizes of the AuNPs were identified by TEM analysis and the Image-Pro Plus program was used to determine the dimensions of the obtained AuNPs. TEM results revealed spherical along with triangular and hexagonal shaped nanoparticles with an average size of 15 nm corresponding to optimum synthesized conditions shown in Figure 3a. The TEM image showed that the synthesized AuNPs were separated from each other by a homogenous separation. Moreover, it showed that some organic molecules in Dimrit raisin capped the AuNPs.

Additionally, the XRD analysis was also performed to verify the crystal structure of synthesized AuNPs. Figure 3b showed the XRD pattern of AuNPs prepared at optimum conditions. The characteristic peaks at 2Θ corresponding to approximately 38.1°, 44.4°, 64.6° and 77.8 which can be indexed to planes (111), (200), (220) and (311) indicating the cubic crystal structure centered on the faces (FCC) of the Au (0) (PDF 00-004-0784).

FTIR measurements were also performed to identify the main functional groups on the Dimrit raisin, which played important role in reducing and capping AuNPs. Two FTIR spectra were shown in Figure 3c: Dimrit raisin and AuNPs, respectively. A broad band corresponding to the –OH group was appeared at 3310 cm^{-1} for Dimrit raisin. This band was slightly shifted to 3300 cm^{-1} for AuNPs. The presence of bands for Dimrit raisin at 2939 cm^{-1} and 1639 cm^{-1} could be related to stretching of C–H and C=C groups, respectively. After the synthesis, these bands were appeared at 2935 cm^{-1} and 1633 cm^{-1} for AuNPs. The observed band at 1418 cm^{-1} was due to C-C group for Dimrit raisin and this band was appeared at 1419 cm^{-1} for AuNPs. The bands at 1359 cm^{-1} and 1261 cm^{-1} were due to C-N group for Dimrit raisin. These bands were appeared at 1356 cm^{-1} and 1260 cm^{-1} for AuNPs. The band at 1030 cm^{-1} was attributed to C-N group for Dimrit raisin and this band was appeared at 1026 cm^{-1} for AuNPs. The main bands existing in FTIR spectrum of the extract were also present in FTIR spectrum of the synthesized AuNPs with lower intensities and slightly shifted. This is evident that the Dimrit raisin acts not only as reducing agent, but stabilizers too during the synthesis of AuNPs.

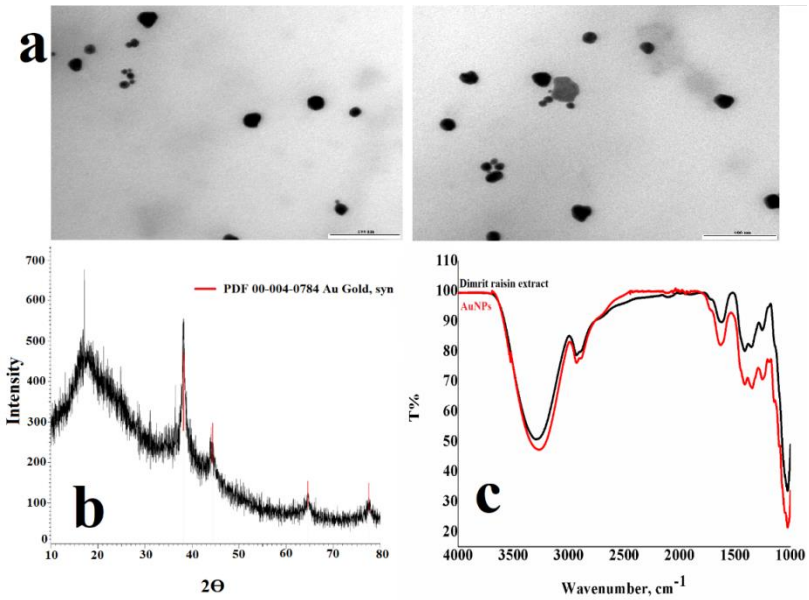

Figure 3. (a) *TEM images of AuNPs,* ***(b)*** *XRD patterns of AuNPs* ***(c)*** *FTIR spectra of Dimrit raisin extract and AuNPs.*

C. CATALYTIC ACTIVITY OF MB AND MO DYES

After the optimization studies of AuNPs were carried out, the catalytic activities of AuNPs were investigated for the colour removal of both MM and MO dyes which are frequently used in the textile industry and likely to be in wastewater. Both MB and MO dyes show maximum absorption peaks in UV-Visible spectrometer at 665 nm [31] and 465 nm [32], respectively. The catalytic activities of the obtained AuNPs were studied for the degradation of both MB and MO dyes with $NaBH_4$ used as reducing agent. Moreover, the degradations of both MB and MO dyes based on reduction were examined by evaluating the absorbance values at these wavelengths in the certain time intervals. The UV-Visible spectrums of both MB and MO dyes with only presence of $NaBH_4$ were shown in Figure 4a and 4b, respectively. As shown in both Figures, the absorption peaks of both dyes were slowly decreased with time. It was determined that the degradation reactions of MO and MB dyes were proceeded very slowly when $NaBH_4$ was only used. Then, the usability of AuNPs were investigated to accelerate this reaction as catalysts. In the degradation of dyes, $NaBH_4$ is acted as both electron donor and hydrogen donor, and nanoparticles are played a role as electron transfer mediator. Nanoparticles with a high surface-to-volume ratio are provided more catalytic sites and lower the activation energy. Therefore, nanoparticles catalyse the degradation of dyes [33]. The activities of AuNPs as catalysts were given in Figure 4c and Figure 4d. As illustrated in Figure 4c and Figure 4d, degradation rates based on the degradation of MB and MO by $NaBH_4$ of both dyes were also accelerated with the presence of AuNPs. The maximum degradation for the absorption intensity of MB and MO dyes was obtained with the presence of both AuNPs and $NaBH_4$ solution at 7 min and 11 min, respectively (Figure 4c and Figure 4d).

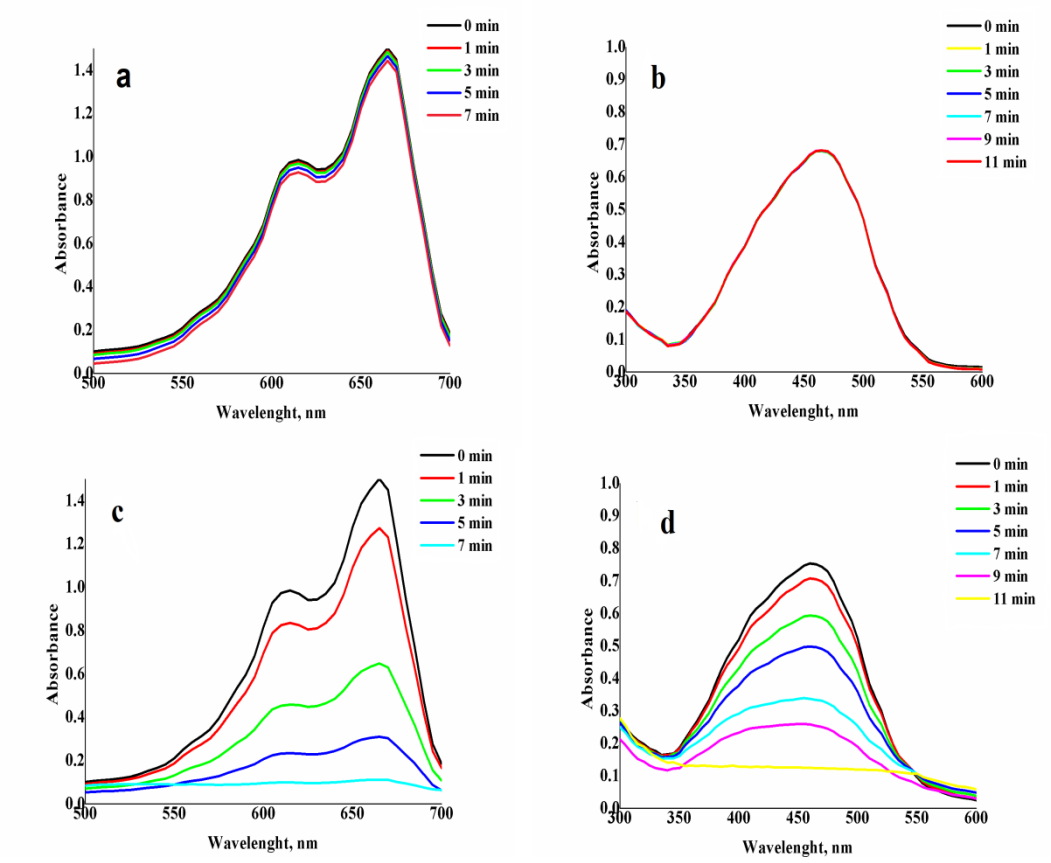

Figure 4. *UV–Vis absorption spectra of* ***(a)*** *MB in the presence of only $NaBH_4$ at time course intervals* ***(b)*** *MO in the presence of only $NaBH_4$ at time course intervals* ***(c)*** *MB in the presence of both $NaBH_4$ and AuNPs at time course intervals* ***(d)*** *MO in the presence of both $NaBH_4$ and AuNPs at time course intervals.*

At that times, the dye degradation percentage of MB and MO dyes were found to be 93% and 83%, respectively (Figure 5a). Furthermore, the degradation kinetics of MB and MO dyes were also obtained by plotting the ln (A_t/A_o) versus time shown in Figure 5b. The kinetic reaction rate constants determined from the degradation of MB and MO dyes were found to be 0.403 min^{-1} (R^2= 0.9904), and 0,166 min^{-1} (R^2= 0.934), respectively. The experimental results showed that the presence of AuNPs even at small volumes of 0.1 mL showed effective catalytic activity for the degradation of MB and MO dyes.

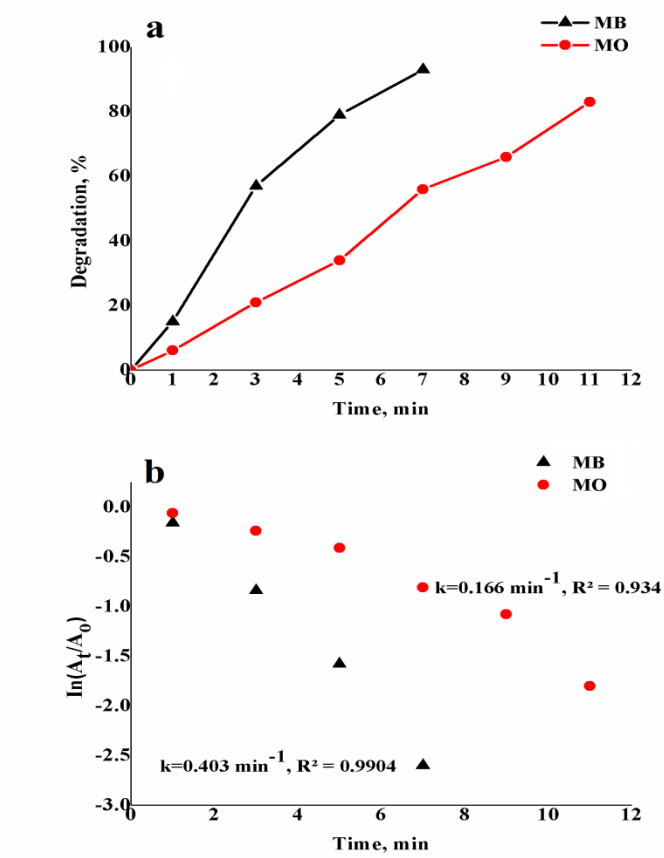

Figure 5. (a) *The change of degradation efficiency for MB and MO* ***(b)*** *Plot of ln (A_t/A_0) versus time for the catalytic degradation of MB and MO by AuNPs.*

IV. CONCLUSION

A facile, simple, and green method for the synthesis of AuNPs were successfully developed using Dimrit raisin. The effect of various experimental parameters, such as concentrations of Dimrit raisin extract and Au solutions, synthesis time and synthesis temperature were investigated in detail, respectively. The optimization study was found to be very crucial because AuNPs occurred immediately after mixing 2% extract with 2.5x10^{-3} M Au based on changing the coloration from pale yellow to violet but higher SPR band and lower size of AuNPs received for 120 min synthesis time and that was not changed for further values. Additionally, synthesized AuNPs were still stable and no precipitation occurred up to 432 h. The average size of the spherical shaped AuNPs was found to be 15 nm using optimum synthesis conditions. Furthermore, the catalytic activity of AuNPs was tested for the degradation of MB and MO dyes based on the reduction by $NaBH_4$. The obtained results showed that the presence of AuNPs even at small volumes of 0.1 mL showed effective catalytic activity for the degradation of MB and MO dyes. As a result, the obtained AuNPs using Dimrit raisin can be efficiently used in dye treatment and water purification systems.

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