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SYNTHESIS OF GOLD NANOPARTICLES FROM *DIOSCOREA HAMILTONII* TUBER EXTRACT AND INVESTIGATION TO CATALYZE THE DECOMPOSITION OF COLORED ORGANIC DYES

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Abstract – *This research introduced the process of gold nanoparticles (DH-AuNPs) synthesized from Dioscorea hamiltonii tuber extract and $HAuCl_4.3H_2O$ by green chemistry methods. DH-AuNPs were synthesized under optimal conditions with a reaction temperature of 90°C, using 3.0 mM $HAuCl_4.3H_2O$ and a ratio of $HAuCl_4.3H_2O$ to DH of 1:1 (v/v) within 60 minutes. The morphology, structure, and content of DH-AuNPs were determined by SEM, DLS, EDX, FT-IR, UV-Vis, and TGA measurement methods. As a result, DH-AuNPs had an average particle size of 201 nm and 70.68% of the formed nanoparticles in the product. The catalytic activity of DH-AuNPs was investigated by monitoring the decrease in absorbance during the degradation of various colored organic dyes, such as EY, MO, RhB, and Rh6G. In the presence of the DH-AuNPs catalyst, the reaction between $NaBH_4$ and the colored compounds proceeded rapidly, reaching completion within 14 minutes.*

Keywords: Dioscorea hamiltonii, gold nanoparticles, green synthesis.

I. INTRODUCTION

Today, there is a growing recognition of the imperative for long-term sustainable development and addressing the environmental challenges stemming from industrialization and modernization processes. In response, there's a paradigm shift towards seeking clean energy, environmentally friendly materials, and high-quality compounds. The shift aiming to mitigate adverse impacts on the environment, human health, and biodiversity has garnered significant attention and interest worldwide. Therefore, applying green technology in different fields is necessary and urgent. Scientists are constantly exploring new directions to create environmentally friendly products with good quality, simple techniques, and low fees. Green synthesis methods are the best choice for synthesizing metal nanoparticles in general and gold nanoparticles (AuNPs) in particular. Meanwhile, gold nanoparticles synthesized from plant extracts are receiving widespread attention and research from domestic and foreign scientists due to the use of environmentally friendly compounds in the reaction. In addition, AuNPs also have specific applications such as cancer treatment, drug delivery, sensors, and catalysts. *Dioscorea hamiltonii* is a wild tuber, a climbing vine with a smooth stem, which is found in the North Central provinces of Vietnam. The tuber penetrates deep into the ground, has a brownish-yellow color, and smooth surface, and breaks into ivory-white when snapped, without fibers. The chemical composition of *Dioscorea hamiltonii* tuber includes proteins, carbohydrates, mucilage, lipids, choline, allantoin, and others. These components play the role of stabilizers in reducing Au^{3+} to Au^0 and creating a linking environment during the synthesis of AuNPs.

Therefore, the synthesis of AuNP nanoparticles from *Dioscorea hamiltonii* tuber extract and $HAuCl_4.3H_2O$ represents a new and practical approach in the field of green technology. These AuNPs exhibit promising potential as catalysts for the degradation of organic dyes in water, indicating their possible applications in environ-

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mental pollution remediation and efforts toward sustainable development.

II. RESEARCH OVERVIEW

Doan Van Hong Thien et al. synthesized gold nanoparticles (AuNPs) from lemon extract using polyvinylpyrrolidone (PVP) as a stabilizing agent. The reaction was carried out under optimal conditions with an Au^{3+} to lemon extract ratio of 1:1 (v/v), at 65^oC for 45 minutes. The average particle size of AuNPs was determined to be 12-16 nm using modern analytical techniques such as UV-Vis, FT-IR, and TEM [1].

Lim et al. [2]. conducted a study on the synthesis of gold nanoparticles (AuPNs) using the extract of *Punica granatum* peels. Besides, the study assessed the catalytic activity of AuNPs through the reduction of the 4-NP compound. The study employed various analytical methods such as UV-Vis, FT-IR, TEM, HR-XRD, and DLS to determine the structure, morphology, and size of the AuNPs. The results revealed that the AuNPs exhibited a spherical shape with sizes ranging from 21-38 nm.

Nguyen Ngoc Khanh Anh et al. [3] utilized tea leaf extract to synthesize AuNPs from a HAuCl4 solution. The analytical methods utilized in this study included UV-Vis spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD). The results yielded spherical AuNPs with an average size of 10-15 nm. Furthermore, the incorporation of these AuNPs into a base cream showed non-reactivity on the skin, with the gold concentration in the cream measured at 7.55 ppm.

Dudhane et al [4]. synthesized AuNPs from flower extracts of the *Combretum quadrangulare* and used them for antibacterial purposes. Analytical methods such as UV-Vis spectroscopy and transmission electron microscopy (TEM) demonstrate that the gold nanoparticles (AuNPs) have sizes ranging from 15 to 30 nm. The antibacterial effect of AuNPs is notable against *S. aureus*, *Pseudomonas aeruginosa*, and *Salmonella typhimurium*.

Nguyen Thi My Thao et al. [5] investigated the preparation of silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) using passion fruit peel extract (PEP) as both a reducing and stabilizing agent. PEP-AgNPs and PEP-AuNPs exhibited spherical shapes with average sizes of 25 nm and 7 nm, respectively. PEP-AgNPs demonstrated strong antibacterial activity against *Escherichia coli*, *Bacillus subtilis*, and *Staphylococcus aureus*. The catalytic activity of PEP-AgNPs and PEP-AuNPs was confirmed by reducing the concentration of nitrophenol and decolorizing a dye, as demonstrated in kinetic reaction studies.

III. RESEARCH METHODS

Materials: $HAuCl_4.3H_2O$, $NaBH_4$, methyl orange (MO), rhodamine B (RB), rhodamine 6G (R6G), eosin Y (EY) were purchased from Acros, and *Dioscorea hamiltonii* tubers (DH).

The synthesis process of gold nanoparticles (DH-AuNPs) included the following stages. First, the reflux method was used to extract *Dioscorea hamiltonii* tubers (DH) by adding 10 g of *Dioscorea hamiltonii* tubers to 100 mL of distilled water, heating for an hour, the mixture is filtered to obtain the extract (DH), and storing the DH in the refrigerator (4^oC). Second, the green chemistry method was employed to synthesize DH-AuNPs by mixing $HAuCl_4.3H_2O$ solution with extract (DH). The reaction was investigated under different conditions, including changes in $HAuCl_4.3H_2O$ concentration, the volume ratio of $HAuCl_4.3H_2O$ and DH solution (v/v), temperature, and time. Third, the study detected the formation of DH-AuNPs using a UV-Vis spectrophotometer within the wavelength range of 520 to 540 nm. Next, at the completion of the reaction, the DH-AuNPs product was centrifuged to isolate solid DH-AuNPs. Then, the solid DH-AuNPs were washed with distilled water and ethanol to eliminate impurities. The synthesis process ended by drying the solid DH-AuNPs at 60^oC.

The physicochemical properties of gold nanoparticles (DH-AuNPs) in the product are evaluated using contemporary analytical techniques including UV-Vis spectroscopy, FT-IR spectroscopy, Scanning electron microscope,

determination of particle size distribution, and zeta potential, energy dispersive spectroscopy (EDX), and thermogravimetric analysis (TGA).

Investigation of the catalytic ability of gold nanoparticles (DH-AuNPs) involved evaluating their effectiveness by the decomposition reaction of colored compounds such as methyl orange (MO), rhodamine B (RB), rhodamine 6G (R6G), and eosin Y (EY). For example, the reaction decomposed methyl orange (MO) by $NaBH_4$ with catalytic DH-AuNPs at room temperature. This reaction was performed in a cuvette by mixing 0.5 mL $NaBH_4$ (0.1 M) with 2.5 mL EY (0.1 mM), adding 25 mL of DH-AuNPs catalyst. To monitor the absorbance of EY at its characteristic wavelength of 515 nm over time, a UV-Vis spectrophotometer was utilized to conduct scans within the wavelength range from 300 to 800 nm. Similarly, the reactions were performed with compounds MO, RB, and R6G under the same conditions. Simultaneously, the absorbance of MO, RB, and R6G at their respective characteristic wavelengths (515 nm for MO, 464 nm for RB, 554 nm for R6G) was monitored using UV-Vis spectroscopy over time (525 nm for R6G).

IV. RESULTS AND DISCUSSION

A. Synthesis of DH-AuNPs from Dioscorea hamiltonii tuber extract

The process for synthesizing DH-AuNPs involves mixing 4 mL of DH with 1 mL of $HAuCl_4.3H_2O$ solution (1 mM), followed by calcination at 90^{o}C for 20 minutes. The presence of DH-AuNP was confirmed by the change in color of the solution and emerging the photometric peak of UV-Vis at a wavelength from 520 to 540 nm. Then, the product was centrifuged to obtain solid DH-AuNPs (Figure 1).

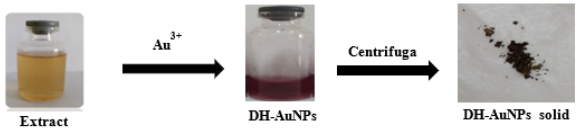


Fig. 1: Synthesis of DH-AuNPs using *Dioscorea hamiltonii* tuber extract (DH)

B. Investigation of factors affecting the synthesis of DH-AuNPs

Synthesis of DH-AuNPs was carried out under different reaction conditions, which were monitored using a UV-Vis photometer between 520 and 540 nm to determine the absorbance of the surface plasmon band (SPR) towards gold nanoparticles. To investigate the reduction of Au^{3+} to Au^0 using DH extract, we systematically vary four parameters: the concentration of $HAuCl_4.3H_2O$, the volume ratio of $HAuCl_4.3H_2O$ to DH (v/v), the temperature, and the reaction time.

The reaction between DH and $HAuCl_4.3H_2O$ at different concentrations ranging from 2.0 to 4.0 mM: The formation of DH-AuNPs was determined using UV-Vis spectroscopy, specifically measuring the absorbance at a wavelength of 538.5 nm (Figure 2). The results show that, at low concentrations (2.0 – 2.5 mM), the SPR bands of DH-AuNPs appear weak, indicating no reduction of Au^{3+} ions to Au^0. At a concentration of 3.0 mM, the absorbance reached 0.631, proving the presence of DH-AuNPs in the product. Conversely, at concentrations greater than 3.0 mM, a decrease in absorbance was observed. This decrease can be attributed to the fact that the amount of reducing agent (DH) becomes insufficient compared to the $HAuCl_4.3H_2O$ concentration, resulting in reduced reduction of DH. In conclusion, the optimal $HAuCl_4.3H_2O$ concentration was determined to be 3.0 mM.

The investigation into the effect of the volume ratio of $HAuCl_4.3H_2O$ (3.0 mM) to DH in the range of 1:1; 1:2; 1:3; 3:1; 2:1 (v/v): The results showed that an increase in the volume of $HAuCl_4.3H_2O$ produced an increase in the absorbance of the product (Figure 3). During the biosynthesis of DH-AuNPs, the SPR band did not appear at a high rate and vice versa. In particular, the highest absorbance of 0.489 at the wavelength of 538.5 nm was observed when the ratio was 1:1 (v/v).

The investigation into the reaction temperature

was conducted within the range of 60-100^{o}C (Figure 4): The results show that DH-AuNPs are only formed after 60^{o}C. Notably, DH-AuNPs were formed at 90^{o}C, with an absorbance value of 0.783 at a wavelength of 538.5 nm. Higher temperatures caused aggregation of DH-AuNPs from colloidal solutions as noted by a decrease in absorbance in UV-Vis spectroscopy. The results show that the synthesis efficiency of DH-AuNPs depends mainly on the reaction temperature.

The effect of reaction time on the biosynthesis of DH-AuNPs was recorded by UV-Vis spectrum from 10 to 90 minutes (Figure 5): The increased absorbance value at the characteristic wavelength confirmed that DH-AuNPs were produced in high concentrations with a longer reaction time. The results of DH-AuNPs synthesis show that the concentration of AuNPs gradually increases when the solution is stirred in the first 40 minutes and the reduction process is completed after 60 minutes.

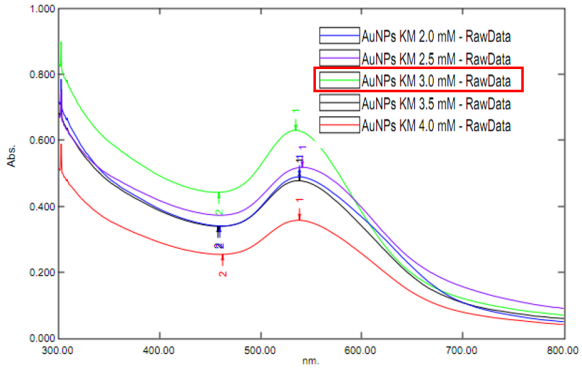


Fig. 2: The effect of $HAuCl_4.3H_2O$ concentration on DH-AuNPs formation described by UV-Vis spectrum

Based on the results obtained from various surveys, the optimal conditions for synthesizing DH-AuNPs particles are as follows: reaction temperature (90^{o}C), concentration of $HAuCl_4.3H_2O$ (3.0 mM), volume ratio of $HAuCl_4.3H_2O$ to DH (1:1 (v/v)), reaction duration (60 minutes). These conditions have been found to yield DH-AuNPs

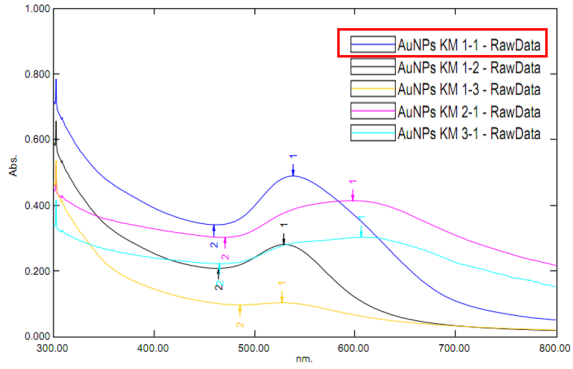


Fig. 3: The effect of the volume ratio of $HAuCl_4.3H_2O$ to DH extract (v/v) on DH-AuNPs formation described by UV-Vis spectrum

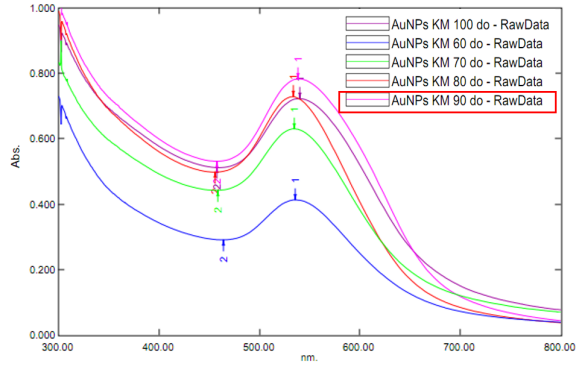


Fig. 4: The effect of temperature on DH-AuNPs formation described by UV-Vis spectrum

with desirable properties, including appropriate particle size, distribution, and stability. Therefore, these parameters can be considered suitable for the synthesis of DH-AuNPs.

Infrared spectroscopy analysis was performed to identify possible functional groups in the DH sample and DH-AuNPs (Figures 6(A), 6(B)). The FT-IR spectrum of the DH sample shows main bands, including 3551, 2929, 1750, 1619, 1234, and 1182 cm^{-1}. These bands move to new

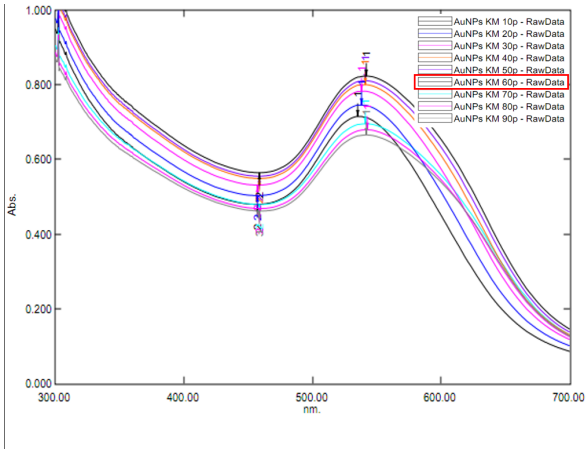
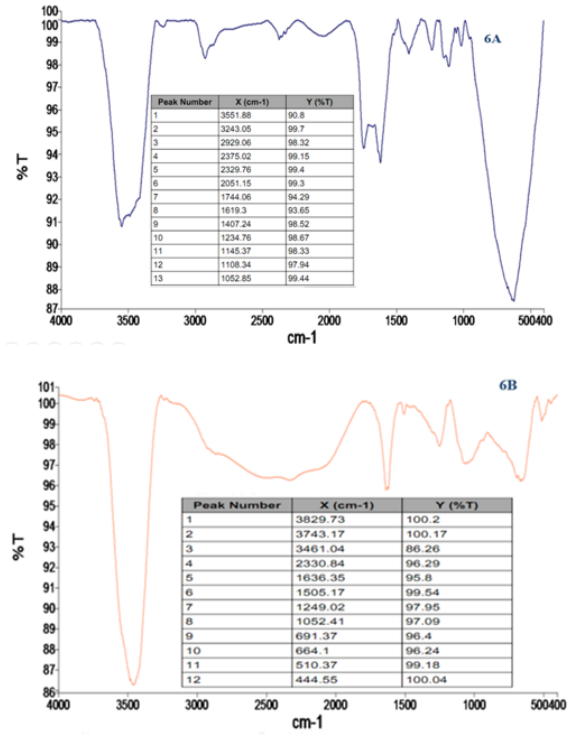


Fig. 5: The effect of time on DH-AuNPs formation described by UV-Vis spectrum

positions in the spectrum of the DH-AuNPs sample, demonstrating that the chemical components in DH, including proteins, glucose, mucus, and lipids decreased in the FT-IR spectrum of DH-AuNPs with main peaks at 3461, 2330, 1636 and 1249 cm^{-1}. It is indicated that the absorption bands of DH-AuNPs are similar to DH. This means that the compounds contained in DH are reducing agents and stabilizers in the DH-AuNPs product.

The analytical results obtained from scanning electron microscope (SEM) images of DH-AuNPs reveal spherical-shaped nanoparticles with particle sizes ranging from 100 to 250 nm. This size range is larger than what is observed in dynamic light scattering (DLS) images, where the average size is determined to be 201 nm with a polydispersity index (PI = 1.936). Additionally, the stability of the DH-AuNPs is assessed through zeta potential measurements, and elemental composition is determined using energy-dispersive X-ray spectroscopy (EDX). These analyses are depicted in Figures 7(A), 7(B), 7(C), and 7(D). This difference is due to agglomeration during centrifugation because the SEM image was taken on a solid sample. Besides, the zeta potential analysis results have a negative potential value (Zeta = -10.4 mV), inferring that the DH-AuNPs sample has high stability in the product. Through



Peak Number	X (cm-1)	Y (%T)
1	3551.88	90.8
2	3243.05	99.7
3	2929.06	98.32
4	2375.02	99.15
5	2329.76	99.4
6	2051.15	99.3
7	1744.06	94.29
8	1619.3	93.65
9	1407.24	98.52
10	1234.76	98.67
11	1145.37	98.33
12	1108.34	97.94
13	1052.85	99.44

Peak Number	X (cm-1)	Y (%T)
1	3829.73	100.2
2	3743.17	100.17
3	3461.04	86.26
4	2330.84	96.29
5	1636.35	95.8
6	1505.17	99.54
7	1249.02	97.95
8	1052.41	97.09
9	691.37	96.4
10	664.1	96.24
11	510.37	99.18
12	444.55	100.04

Fig. 6: Infrared spectrum (FT-IR) of DH sample (6A) and DH-AuNPs (6B)

SEM results, DLS and Zate confirmed that DH-AuNPs are in nano size, homogeneous, and very stable in synthetic environments.

EDX analysis results show a strong peak at 2.2 keV, confirming the element Gold's presence in the sample. The average content of the element Gold is estimated to be 70.68% (w/w).

TGA was performed at a heating rate of 10^oC/1 min in a gas flow of 20 mL. The results show that in the temperature range below 250^oC, there is a weight loss of 2.8%, which represents the evaporation of water and volatile compounds in the DH-AuNPs sample (17% for the DH extract). The DH-AuNPs sample lost 12.6% of its weight while the DH extract lost 57.73% of its weight in the temperature range of 250 – 750^oC. This result shows that the DH sample and DH-AuNPs sample have similar chemical compositions. Particularly, there is no weight loss in the thermal region from 450^oC to 745^oC, proving that the

oxidation of organic compounds has occurred on the AuNPs nanoparticles and there is only the presence of AuNPs in the product in that condition. (Figure 8(A), 8(B)).

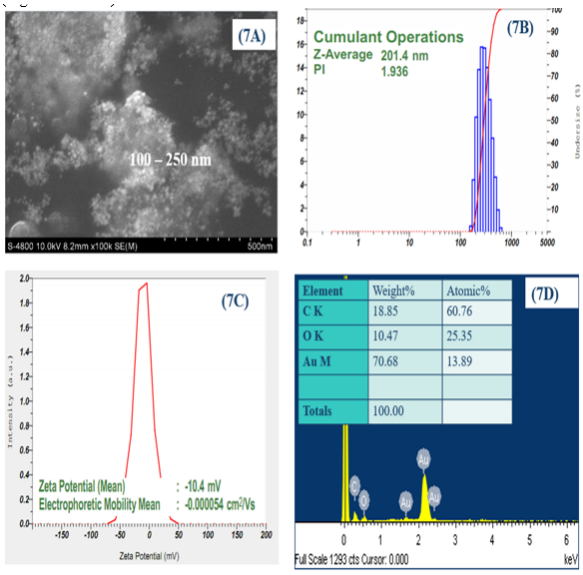


Fig. 7: SEM (7A), DLS (7B), Zeta (7C), and EDX (7D) of DH-AuNPs

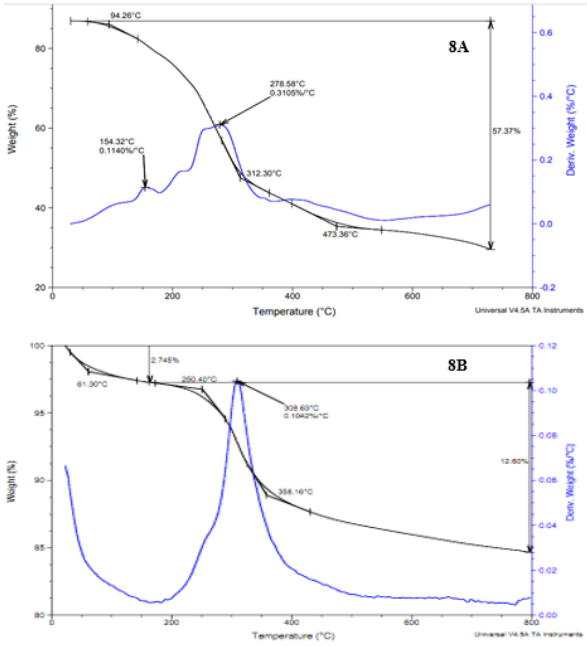


Fig. 8: TGA of DH (8A) and DH-AuNPs (8B)

C. Investigate the catalytic ability of DH-AuNPs on the decomposition reaction of color compounds

Utilizing DH-AuNPs as a heterogeneous catalyst for the oxidation-reduction reaction, with $NaBH_4$ as a hydrogenation agent, can facilitate the decomposition of colored organic substances. The decomposition reactions of color compounds, such as EY, MO, RhB, and Rh6G with $NaBH_4$, can be compared both in the absence of a catalyst and in the presence of DH-AuNPs as a catalyst. This comparison would provide insights into the effectiveness of DH-AuNPs in accelerating the decomposition process and potentially reducing the required reaction time or enhancing the extent of decomposition. There was a slow reaction catalyst (Figure 9 (A, B, C, D) consistent with published research [5]. The introduction of DH-AuNPs catalyst into the mixture significantly accelerated the decomposition reaction. This can be observed by the loss of color and decrease in absorbance recorded on the UV-Vis spectrum at the characteristic wavelength of the color compounds EY (515 nm), MO (464 nm), RB (554 nm), and R6G (525 nm). UV-Vis spectra were recorded throughout the reaction (Figure 10 (A, B, C and D)). The DH-AuNPs catalyst has decreased the reaction time between $NaBH_4$ and the corresponding color compounds to 14 minutes for EY, MO, and RB and 16 minutes for R6G.

The results confirm that DH-AuNPs synthesized from *Dioscorea hamiltonii* tubers extract act as a heterogeneous catalyst, for the decomposition reactions between $NaBH_4$ and color compounds in organic dyes. In addition, the catalytic activity of synthesized DH-AuNPs in this work shows similar effectiveness compared to studies around the world [4, 5].

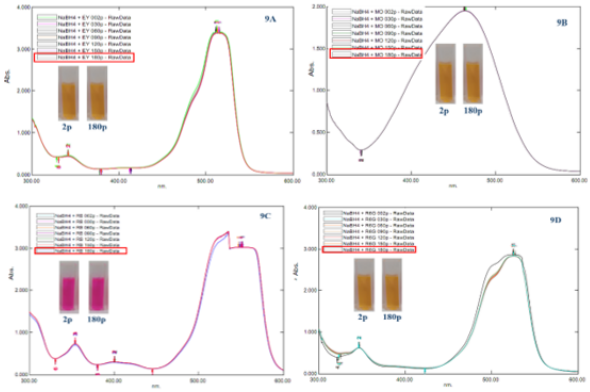


Fig. 9: UV-Vis spectrum investigating the reaction between the color compounds EY (9A), MO (9B), RB (9C), and R6G (9D) with $NaBH_4$ with DH-AuNPs catalyst

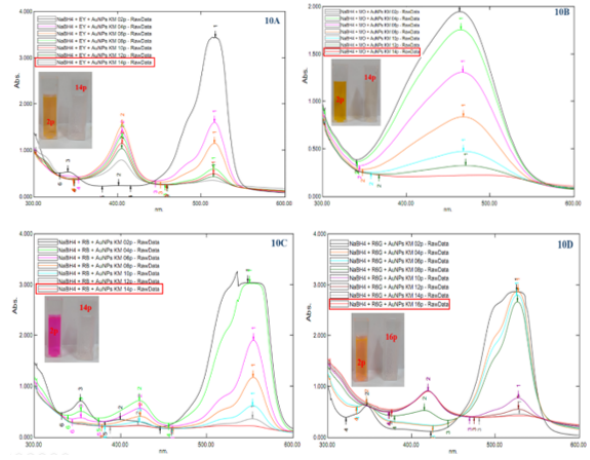


Fig. 10: UV-Vis spectrum investigating the reaction between the color compounds EY (9A), MO (9B), RB (9C), and R6G (9D) with $NaBH_4$ without DH-AuNPs catalyst

V. CONCLUSION

This study provides a green method to synthesize gold nanoparticles and investigate its applications in the environmental field. Obtained DH-AuNPs were in a spherical shape with an average size of 210 nm. The catalytic ability of DH-AuNPs nanoparticles was evaluated through the decomposition reaction between color compounds in dyes with the reducing agent $NaBH_4$. When the DH-AuNPs catalyst is present, the reaction occurs quickly. Indeed, the reaction between $NaBH_4$ and colored compounds including EY, MO, RhB, and Rh6G occurred completely after 14 min. This is the scientific background in studying the catalytic ability of DH-AuNPs for other reactions. In the future, the *Dioscorea hamiltonii* tuber extract, an excellent agricultural source, maybe a potential candidate for the green synthesis of other metal nanoparticles with many applications.

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