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RESEARCH PAPER

Synthesis and Analytical Characterization of Gold Nanoparticles using Microwave-Assisted Extraction System and Study their Application in Degradation

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ABSTRACT

Preparation of gold nanoparticles (AuNPs) was done by the addition of tetrachloroaurate ($HAuCl_4$) *to dodonaea viscose (L.)* leaves watery extract. The procedure was performed in microwave-assisted extraction (MAE). *Dodonaea viscose (L.)* watery extract functions as a reducing and capping agent to synthesis AuNPs. The gold nanoparticles was identified by the changes in colour from yellow to red –purple, UV-vis spectroscopy, and surface plasmon band at (600 nm). (EDX -FESEM) and TEM instruments were used to investigate the element analysis, distribution of nanoparticles and to calculate their sizes and shapes. Energy dispersive X-ray spectra (EDX) was applied for characterization of gold nanoparticles, the detected percentage of gold nanoparticles was (0.52 wt/wt %). The result from TEM shows the nanoparticles with diameter (6-80 nm) and vary shapes. Furthermore, characterization of nanoparticles was performed before and after the formation of gold nanoparticles using FT-IR. The band appeared at 669 cm^{-1} indicated the gold nanoparticle formation. The synthesized gold nanoparticles have been used for degradation of 6.6 % methylene blue organic dye pollutant in aqueous solution, and also for degradation of aliphatic hydrocarbons in crude oil. The results of degradation were monitored by GC-MS. The breakage of some organic materials and the appearance of new organic materials with less molecular weight and less abundance were achieved. Through the use of gold nanoparticles, it has been observed that a large number of aliphatic compounds have disappeared, especially those with molecular weights 200-288, the loss in the molecular weight is about 40%.

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INTRODUCTION

Nanotechnology deals with particles less than the size of 100 nm which generate new properties and behaviour [1]. The particle sizes can allow for different behaviour to be observes such as electrical conduction, melting temperature, reactivity and mechanical properties [2]. Metal nanoparticles specifically gold nanoparticles have an essential role in the biotechnology and biomedicine applications, due to a large surface

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bio-conjugation with molecular probes. AuNPs also have many optical properties which are mainly associated with localized plasmon [3,4]. The performance of nanomaterials is different from its bulk, this is due to the dominance of interfacial phenomena, quantum effects, and size confinement [5].

Due to the structural stability of aromatic compounds; their removal by traditional techniques is challenging, these techniques include reverse osmosis, adsorption, coagulation, and filtration. A photocatalytic process is one of the promising methods which has been suggested by scientists in the recent years. This method is used in the detoxification of many hazardous and toxic pollutants as well as remedies of environment [6,7]. Different morphologies can be created for nanogold such as nanosphere, nanorods, nanoshell, nanocage, nanostar, and nanoprism [8]. Many methods were used by researchers for synthesis of nanomaterials such as physical [9], chemical [10], and green chemical methods [11]. Green synthetic method develops to be more suitable for the synthesis of metal oxide nanoparticles. Multiple advantages of this method include the following criteria: cheap, easy, eco-friendly, convenient single-step method, does not require high pressure, energy, and temperature or toxic chemicals for production [12].

Nowadays, MAE equipment is designed for lab purposes as a safe and fast method to perform. It offers the user several ways to regulate the extraction procedure. MAE equipment offers advantages of fast, simple operation that is free of organic solvents. Compounds can be extracted more selectively with comparable or enhanced recoveries in comparison with conventional extraction processes. MAE is used for extraction of natural compounds from plants, and the reduction of the extraction time, solvent consumption, and high efficiency are now well known. Therefore, MAE is considered as a green extraction system with increasing attention [13-15].

In this study, gold nanoparticles were synthesized in green chemical method using plant watery extract, and it was applied in degradation of organic dyes such as methylene blue. Methylene blue dye was used as a model for dye organic pollutant. Moreover, gold nanoparticles were applied for degradation of aliphatic hydrocarbons in Iraqi crude oil. The novelty of this study includes the removal of various environmental pollutants. This is the first time in which gold nanoparticles utilized for degradation of aliphatic hydrocarbons using LED light.

MATERIALS AND METHODS

Apparatuses

The production of specific size and morphology of nanoparticles as well as various functional groups was confirmed by using several techniques. The UV-Vis spectrum was performed by using UV-160v, Shimadzu spectrophotometer at the regions (400-700 nm). Energy Dispersive X-ray (EDX instruments) of gold nanoparticles was carried out by using field emission scanning electron microscopy (FESEM). Images were taken by using TEM instrument (University of Tehran, Iran) with an accelerating voltage of 200kv. FTIR spectra were recorded on Shimadzu FTIR-8300 infrared spectrophotometer (University of Basrah, Iraq), and the absorbance was taken between 3600-600 cm^{-1}. Finally, GC-MS instrument was used for analysis of degradation of different organic pollutants by gold nanoparticles.

Preparation of water extract of *Dodonaea viscose*

The dried leaves of *dodonaea viscose (L*.) were crunched and grinded to get a powder crude about 500 g. For the first time, we used microwave-assisted extraction homemade for preparing watery extract from *dodonaea viscose.* 1 mg of *dodonaea viscose (L*.) crude was mixed with 100 ml of distilled water in a round bottle flask (250 ml), then it was placed inside MAE, conditions of extraction was 50 °C for 1 min, and cooled at room temperature. After that, centrifuge was used for 4000 rpm and 10 min. Finally, the solution was filtered for getting the watery extract of *dodonaea viscose*. The watery extract was stored at 4 °C till it use.

Synthesis and stabilizing of gold nanoparticles using dodonaea viscose (L.) extract

Colloidal gold nanoparticles were prepared by addition of 1000 ppm of tetrachloroaurate as a reducing agent to 1000 ppm of *dodonaea viscose (L*.) watery extract. The mixture was heated in MAE for 1 min, the colour changes from yellow to red-purple colour indicated the formation of gold nanoparticles. Laser beam was used to approve the gold nanoparticles formation, Fig. 1. The goal of using laser beam that the linear laser peam indicating for tyndall effect which is the scattering

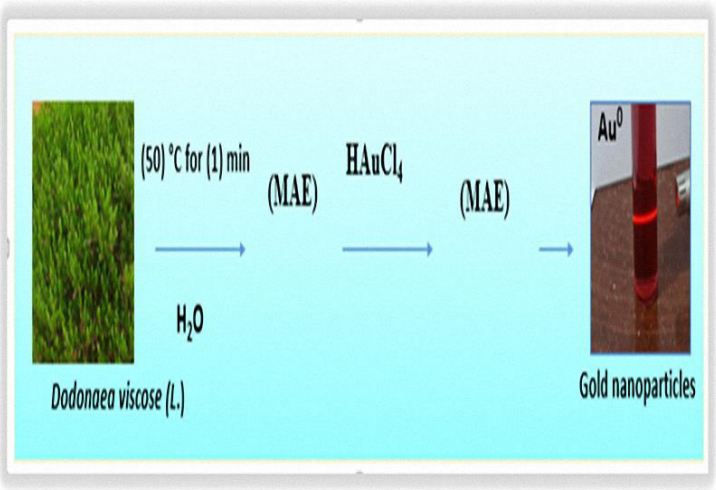

Fig. 1. Schematic diagram shows the procedure of synthesis of gold nanoparticles

of light happened in the nanoparticles diameters.

Degradation of organic pollutant using gold nanoparticles (AuNPs)

The photocatalytic degradation of methylene blue dye was done without use of any kind of stirring, using LED light (30 watt). Then 5 ml of synthesized AuNPs were added to 20 ml of 5 ppm of methylene blue dye, the LED light (30 watt) was put on the top of methylene blue dye container. Finally 3 ml from the mixed solution was examined by spectrophotometer at maximum wavelength 663 nm every 15 min. Moreover, AuNPs were used for degradation of total aliphatic hydrocarbons in Basrah crude oil, Iraq. Firstly, the crude was extracted using column chromatography provided with alumina and silica as a (stationary phase) and hexane solvent used as a (mobile phase). Secondly, the aliphatic hydrocarbons was extract in hexane and 0.1 g from AuNPs was collected from their aqueous solution using centrifuge, and its added to 0.05 g aliphatic hydrocarbons for 3 h, using LED light (30 watt) for degradation. Finally, the total aliphatic hydrocarbons was examined in GC-MS spectra before and after addition of AuNPs.

RESULTS AND DISCUSSION

Characterization of gold nanoparticles

UV–Vis spectroscopy

The Au^{+1} ions to Au^0 reduction was examined by the UV-Vis spectroscopy, the sample aliquots 1.0 ml solution of AuNPs, which was diluted to 3.0 ml using deionised water. The analysis of UV–Vis was done at the range of 300-600 nm, and absorption peaks were observed at 400-600 nm regions due to the excitation of surface plasmon vibrations in the AuNPs solution, which are identical to the characteristics UV- Vis spectrum of metallic gold. The peak intensity in Fig. 2 demonstrated the coherent oscillation of electrons at the surface of AuNPs. The nanoparticles which are smaller than the wavelength of light can produce a coherent resonance waves at a specific absorbance wavelength which is in the visible range for AuNPs. The surface plasmon resonance peak (SPR) at 600 nm offered a convenient spectroscopic signature for the creation of AuNPs.

FT-IR spectra

FT-IR results evidenced the presence of functional groups responsible for effective reduction (Au^{3+} to Au^0). FT-IR result for the leaf extract shows in Fig. 3 (curve 1). The intense broad absorbance at 3390 cm^{-1} is the characteristic of the hydroxyl functional group in alcohols and phenolic compounds or watery extract. The band at 2927 cm^{-1} can be assigned to secondary amines. The band at 1643 cm^{-1} can be assigned to the amide or to C=C in aromatic rings. The band at 1047 cm^{-1} corresponds to the C–N stretching vibration of aliphatic amines or to alcohols/ phenols or both of them. The FTIR spectrum of the gold nanoparticles Fig. 3 (curve 2) showed bands at 2974 cm^{-1} and 2924 cm^{-1} along with other small bands these are due to hydrogen bonding. The bands at 2356 to 2400 for C-O, 1653 cm^{-1} for C=C stretching, 1100

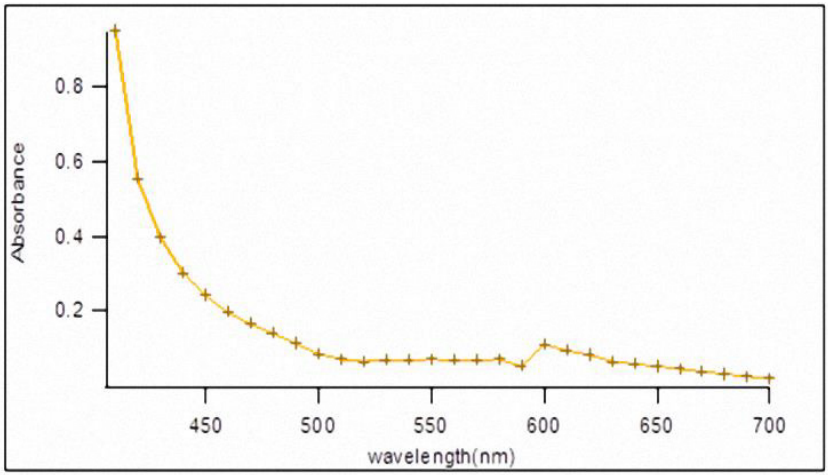

Fig. 2. UV-Vis absorption spectrum of gold nanoparticles shows plasmon spectra at 600nm

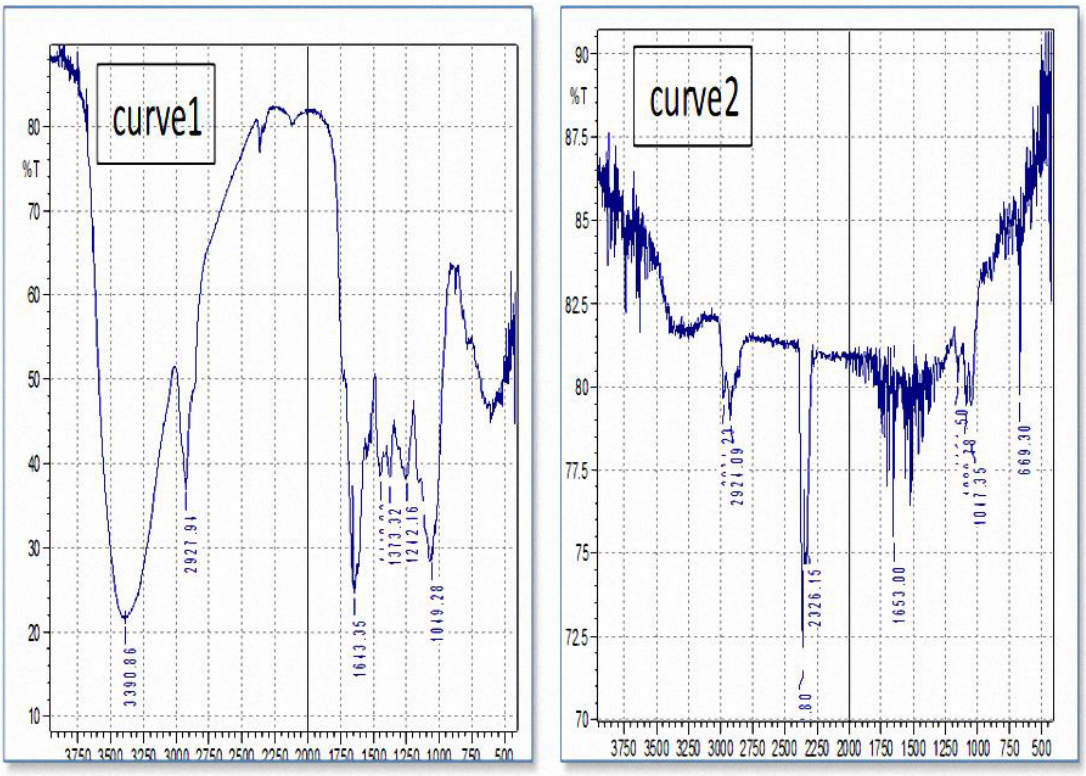

Fig. 3. FTIR analysis was used for the characterization: (Curve 1) water leave extract, (Curve 2) gold nanoparticles.

cm^{-1}, 1089 cm^{-1}, 1047 cm^{-1} for C-O stretching, for the secondary alcohol. From Fig. 3 can be seen that the intense broad absorbance at 3390 cm^{-1} is the characteristic of the hydroxyl functional group in alcohols and phenolic compounds or watery extract become smaller indicating for reduction of gold to AuNPs and also the new band in (curve 2) at 669 cm^{-1} indicates for the metal formation.

(EDX-FESEM) Analysis

The present method for AuNPs is simple, appropriate, allows monocrystalline-line gold particles, almost narrows size, and the distribution of nanoparticles can be easily examined by EDX as

Table 1. Shows elements analysis values of formed gold nanoparticles by EDX-FESEM

Element	Series	unn. [wt.%]	C norm. [wt.%]	C Atom [at%]	C (3 Sigma) [wt.%]
Carbon	K-series	72.54	72.54	78.75	24.04
Oxygen	K-series	25.15	25.15	20.50	9.44
Chlorine	K-series	1.46	1.46	0.54	0.24
Sodium	K-series	0.33	0.33	0.19	0.15
Gold	M-series	0.52	0.52	0.03	0.16

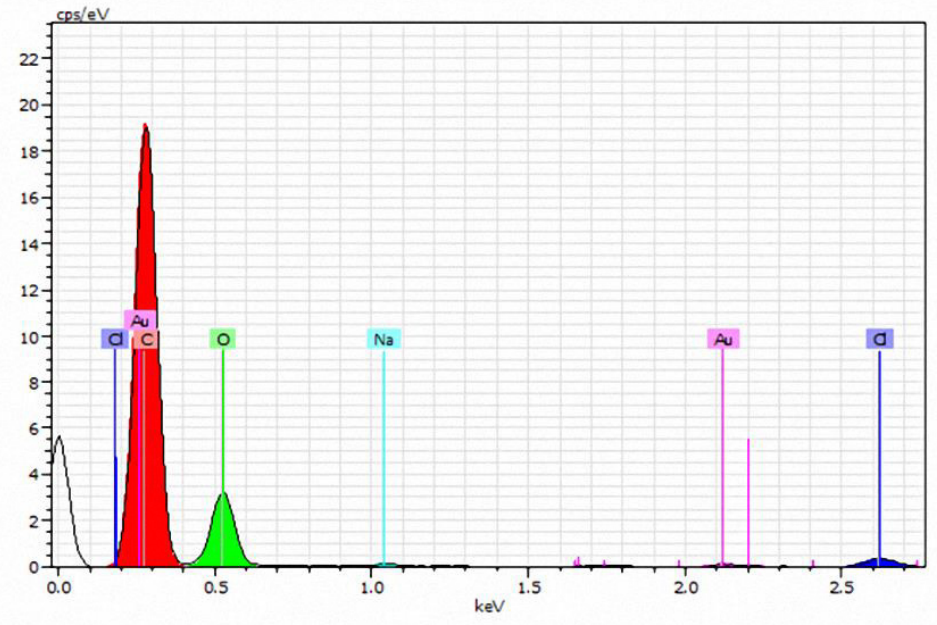

Fig. 4. EDX Spectra shows the presence of gold nanoparticles in the thin film of gold nanoparticles.

can be seen in Table 1 and Fig.4. The droplets of prepared solution on carbon layer shows very good element analysis. Fig. 4 shows the percentage of AuNPs (0.52 wt.%), which presented with some another elements from the prepared solution. The elemental analysis of AuNPs was evaluated using EDX. Fig. 4 showed the silver peak appeared at 0.3 Kev .

TEM analysis

TEM results revealed their distinct size in the range 6-80 nm, and morphology of AuNPs seems to be vary in their shapes (spherical particles, irregularly shaped particles and cylindrical particles, Fig. 5. Furthermore, AuNPs distribution was very good and single nanoparticle can be seen alone, that point toward using good capping agent in this study which was *Dodonaea viscose (L.)*.

Degradation of organic pollutants

There are two parts of application of AuNPs were used, the first is degradation of methylene blue, and the second is degradation of crude oil.

Degradation of methylene blue dye in water

Gold nanoparticles have attracted a lot of attention for the photocatalytic removal of organic pollutants. A number of studies showed that the morphology plays an important role in the photocatalytic activity used as a photo catalysis of degradation of organic compounds. In this study, the methylene blue (MB) was used as an model of water dye pollutant. Fig. 6, illustrates the degradation of MB with and without AuNPs under lighting (LED 30 watt). The rate of degradation was more when using AuNPs. Maybe the reason

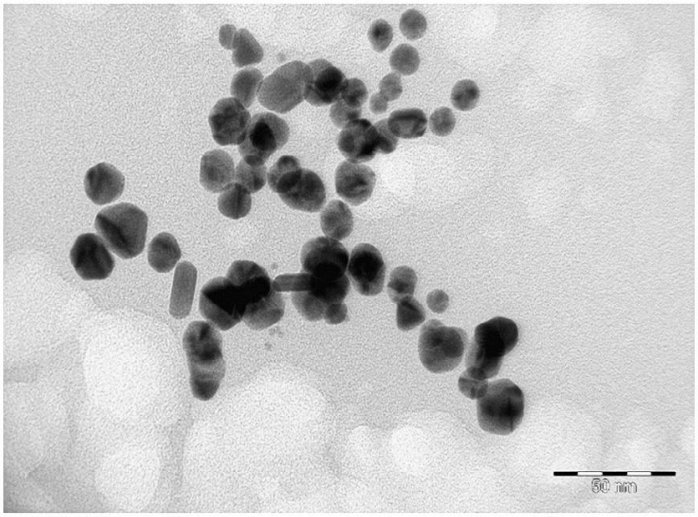

Fig. 5. TEM image of gold nanoparticles.

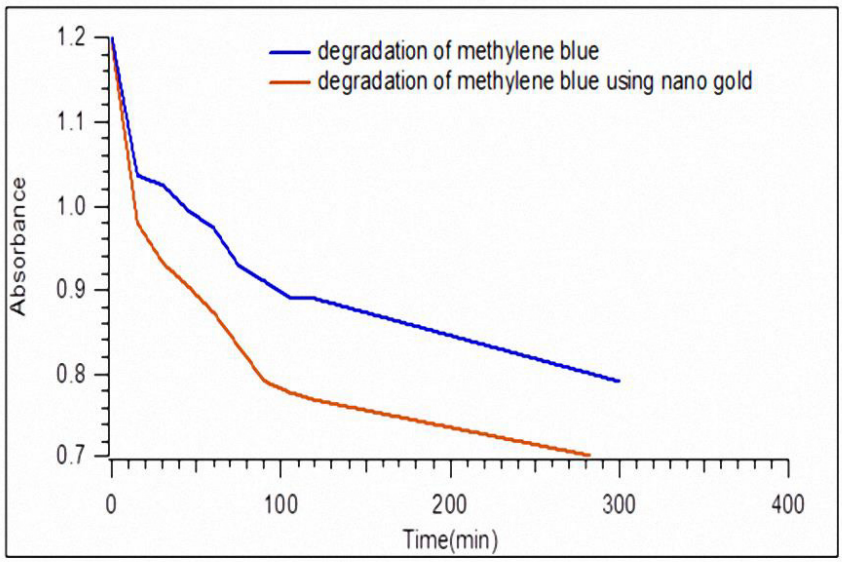

Fig. 6. Degradation of MB using gold nanoparticles.

is that using AuNPs with high surface area to volume ratio enhances the surface of degradation. Therefore, AuNPs function in a favourable role as a photo catalyst. The efficiency of dye degradation was calculated using the following equation:

$$\%Degradation = \frac{(A_\circ - A_t)}{A_\circ} * 100 \quad (1)$$

Where: $A_\circ$ = initial absorbance; A_t = absorbance at time

From Fig 6, the percentage of degradation of methylene blue using AuNPs was 41.66%, while the percentage of methylene blue alone was 35%. Therefore, 6.6% of degradation of methylene blue dye was reached by using gold nanoparticles.

Degradation of crude oil

Gas-Chromatography-mass spectra technique used for analysis the Iraqi crude oil before and after addition of gold nanoparticles. Characterizes the GC spectrum of aliphatic hydrocarbons separated from Iraqi crude oil after the addition of gold nanoparticles. We observed the disappearance of

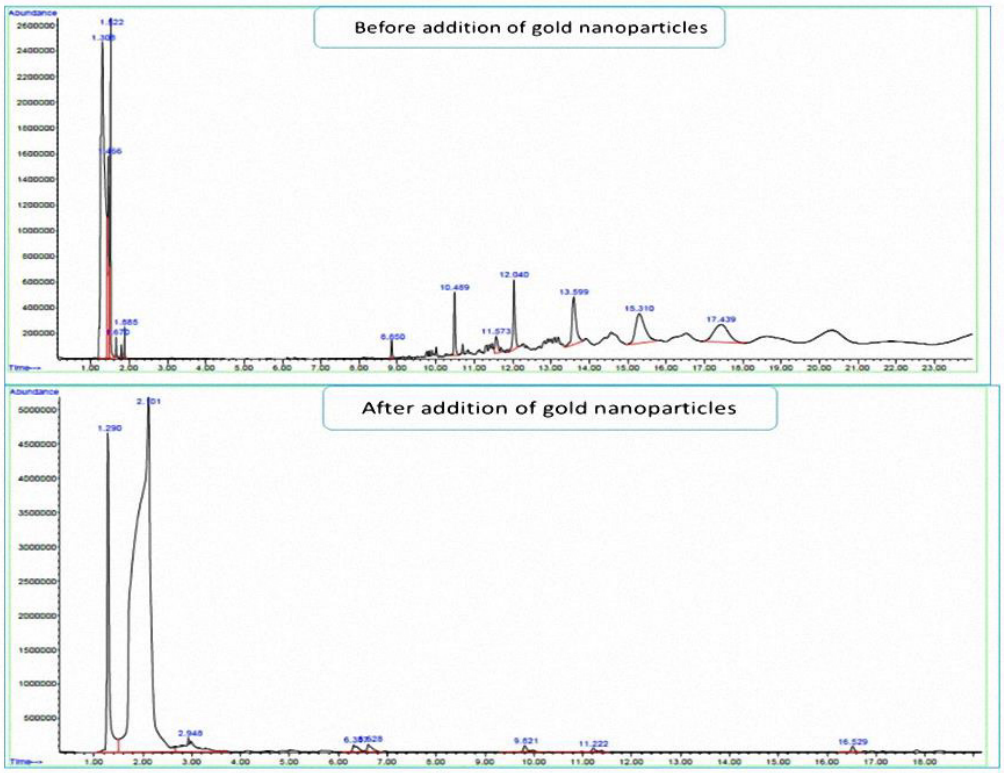

Fig. 7. Shows two graphs of GC-MASS spectra before and after addition of gold nanoparticles.

Table 2. Shows GC-MASS Results of aliphatic hydrocarbons of Iraqi crude oil before addition of gold nanoparticles

Peak no.	Organic compounds	%	M/Z	Base peak	RT (min)
1	3-methyl- pentane	13.2	86	57	1.3
2	2-methyl butane	25.8	72	43	1.46
3	Pentane	2.47	72	43	1.46
4	Methyl - cyclo Pentane	42.2	84	56	1.52
5	Ethyl cyclobutane	21.7	84	56	1.52
6	Cyclohexane	32.4	84	56	1.67
7	2-methyl 1-pentene	7.26	84	56	1.67
8	Heptane	47.5	100	43	1.88
9	3-methyl hexane	32.6	100	43	1.88
10	Undecane	25.1	156	57	8.8
11	Dodecane	7.12	170	57	8.8
12	Tetradecane	21.2	198	57	10.4
13	1-octadecane sulphonyl chloride	7.24	352	57	11.57
14	6-methyl octadecane	7.26	268	57	12.04
15	Nonadecane	4.18	268	57	12.04
16	2,6,10-trimethyl tetradecane	19.4	212	57	13.5
17	Heptadecane	3.66	240	57	13.5
18	10-methyl- eicosane	3.66	296	57	15.3
19	di-tert-dodecyl disulfide	3.01	402	57	15.3
20	1-chloro –octadecane	7.18	288	57	17.4

some peaks and the emergence of new peaks and a smaller amount abundance, which means the breakage of some vehicles.

From Fig. 7 and Table 2, peaks at retention time: (1.3, 2.14, 2.97, 6.66, 9.8, and 16.8 min) was appeared respectively. After addition of AuNPs many peaks were disappeared. Thus, AuNPs capable for degradation the aliphatic hydrocarbons

Table 3. Shows GC-MASS spectra of aliphatic hydrocarbons of Iraqi crude oil after addition of gold nanoparticles

Peak no.	Organic compounds	%	M/Z	Base peak	RT(min)
1	2,4-dimethyl pentane	43.0	100	43	1.3
2	2-methyl hexane	11.0	100	43	1.3
3	3-methyl pentane	7.99	86	57	2.14
4	2-methyl butane	1.91	72	43	2.14
5	2,4- dimethyl hexane	12.6	114	43	2.97
6	Octane	11.6	114	43	2.97
7	1-ethyl butyl hydroperoxid	76.5	118	43	6.66
8	3-methyl 3-pentathiol	2.90	118	43	6.66
9	Undecane	5.52	156	57	9.8
10	Dodecane	4.89	170	57	9.8
11	3-ethyl 3-methyl heptane	2.42	142	57	16.8

in the crude oil. However, new hydrocarbons peaks appeared with less abundance due to degradation of large hydrocarbon materials to small hydrocarbons, Table 3 and Fig. 7.

CONCLUSION

Herein, we fabricated gold nanoparticles using *Dodonaea viscose (L.)* as reducing agent in MAE technique. Gold nanoparticles can be used for removal of both methylene blue dye pollutant from contaminated water as well as it used for degradation of aliphatic hydrocarbons in Iraqi crude oil from polluted area. The surface plasmon resonance peak at (600) nm is clarified a convenient spectroscopic signature for the creation of AuNPs. Analysis from EDX-FESEM and TEM show AuNPs spherical in shape and are well dispersed in their solution. The particle size is in the range of nanometer from (6 - 80 (nm. The results of this work show the ability of gold nanoparticles to function as a photocatalyst for degradation. The whole process of synthesis of gold nanoparticles from the plant and their applications in degradation of different hydrocarbons is considered an application in the field of green chemistry. Thus, the promising experimental data is encouraging scientists for removal of different kinds of pollutant on a large scale. Gold nanoparticles are promising material for the elimination of different pollutants from the environment because the procedure of application and synthesis of AuNPs is considered simple, quick, economic, and high efficiency.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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