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Analytical studies of synthesized silver nanoparticles and their applications in degradation of different pollutants

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Abstract: Silver nanoparticles have been synthesized by wet method using silver nitrate as a source of silver and glucose as reducing agent and trisodium citrate as a capping agent. The progress of the reaction was examined by observing change in cooler from colorless to yellow and finally to light brown color. The synthesized silver nanoparticles were confirmed using Uv-vis spectra the plasmon of silver nanoparticles at 400nm, SEM images shows the silver nanoparticles in the range (10-78 nm), and EDS –SEM zetasizer, zeta potential analysis showed the distribution of nanoparticles in nano range and zeta potential distribution of silver nanoparticles was a negative value (-46.3 Mv) prove to the presence of silver ions. Silver nanoparticles were applied for degradation of methylene blue from water and also for degradation of crude oil (Iraqi aliphatic crude oil in Basra). The gas chromatography-mass spectra (GC-MS) was used to examine the organic compounds before and after addition of silver nanoparticles on the crude oil.

Key words: Silver nanoparticles, Degradation, Uv-vis, SEM, Zeta (sizer and potential), GC-MASS.

1 INTRODUCTION

Nanotechnology is a rapidly progressing field. Advances will have great applications on fields such as electronics, materials and medicine[1]. The application of nano scale materials and structures is an emerging area of nano science and nanotechnology. Nano-sized metal particles have been used widely in various fields including bio field[2], catalysis and photonics[3]. The novel properties of nanomaterial's offer excessive promise to provide new technological breakthroughs. Nanotechnology has been explored for creating lighter and stronger materials, for cleaning contaminated ground water, for replacing toxic chemicals in many uses, for enhancing solar cell efficiency and for targeted cancer treatment [4]. Nanotechnology offers a lot of promise in the area of pollution sensing and prevention, by exploiting novel properties of nanomaterial's[5]. Organic pesticides and industrial pollutants can be degraded into harmless and often useful components, through a process called photocatalysis using metal oxide semiconductor nanostructures[6]. Over the last decades silver nanoparticles have found applications in catalysis, optics, electronics and other areas due to their unique size-dependent optical, electrical and magnetic properties[7] . The obtained nanoparticles were usually characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), dynamic light scattering (DLS), X-ray diffraction (XRD), and ultraviolet– visible (UV–Vis) absorption spectroscopy[8].

Silver nanoparticles have been synthesized by different physical and chemical methods based on the accessibility and achievability of rules to achieve the essential applications. The physical methods, which are also classified as "top-down approach," for the preparation of silver nanoparticles include ball milling, flame pyrolysis, electric arc discharge, and laser ablation These methods often require expensive instruments, high temperature, and pressure ,whereas the "bottom-up approach," which includes the chemical methods[9], involves the concepts of wet chemistry. In this research paper, the formation of Nanoparticles is carried out via the wet chemistry using chemical reductants, such as glucose. Dyes belong to the class of synthetic organic compounds and are widely used in the textile industry. The removal of these non-biodegradable organic chemicals from the environment is a crucial ecological problem. Many techniques, such as activated carbon sorption, flocculation, electro-coagulation, UV-light degradation, and redox treatments, are being routinely used for abating dyes.

Recently, metal nanoparticles were reported as effective photocatalysts for degrading chemical complexes, under ambient temperature with visible light illumination. Moreover, scientists have also shown considerable interest in using nanoparticles for the photocatalytic degradation of dyes[10]. Reducing the particle size of materials is an efficient and reliable tool for improving their biocompatibility. In fact, nanotechnology helps in overcoming the limitations of sizeand can change the outlook of the world regarding science[11,12,]. Currently most of the applications of silver nanoparticles are in antibacterial/antifungal agents in biotechnology and bioengineering, textile engineering, water treatment, and silver-based consumer products[7].

The efficiency of dye degradation was calculated using the following equation[13]

$$\% \text{ degradation} = (A_0 - A_t)/A_0 \times 100$$

where, A_0 = initial absorbance and A_t = absorbance at time 't'.

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2 EXPERIMENTAL

2.1 Synthesis of silver nanoparticles: Chemicals and solvents were purchased from Sigma-Aldrich. The UV-Vis spectra was accomplished by using UV-160v, Shimadzu spectrophotometer at the regions (400-700 nm). Field emission -Scanning electron microscopy (FE-SEM) images were taken by using a Zeiss instrument with an accelerating voltage of 200kv (Iraq/Basrah). Zeta sizer and potential from Malvern. The mixture of silver nitrate solution, glucose sugar and the capping agent of trisodium citrate were prepared at a concentration of (w/v). The mixture prepared by taking 0.1 g in 100 ml of each material in deionized water. Then Bakers contain the mix placed on a hot plate stirrer at 60° C. After 6 min, the color of the solution changed to yellow and after two hours it's changed to the brown color refers to formation of silver nanoparticles as can be seen in **Figure 1**. Leaser pointer was used as a tool for examined the nanoparticles as can be seen in **Figure 2**.

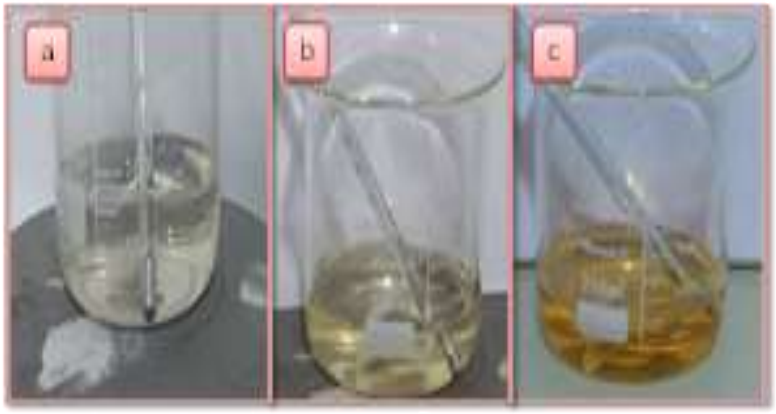

Fig. 1: the stages of changing color of silver nanoparticles during their synthesis**.**

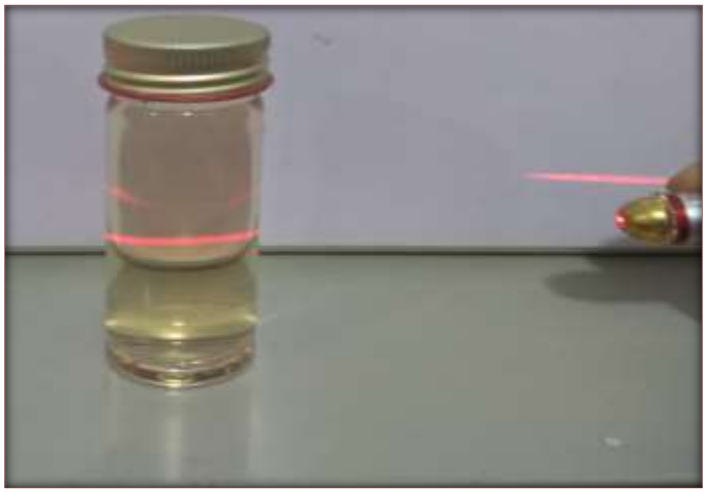

Fig. 2: Laser beam shows strait line when passing the solution of silver nanoparticles.

2.2 Degradation of organic pollutant using silver nanoparticles: The synthesized silver nanoparticles were used for degradation of methylene blue dye in water and for degradation of organic materials in Iraqi crude oil in Basrah. Methylene blue dye which used as a pollutant agents. The MB concentration is (5 ppm). The photocatalytic was done without use of any kind of stirring, using LED light (30 watt). (5ml) of synthesised silver nanoparticles were added to (20 ml) of (5 ppm) of methylene blue dye then the LED light (30 watt) was put on the top of methylene blue dye container. Finally (5 ml) from the mixed solution was examined by spectrophotometer at (663 nm) every (15 min). Moreover, silver nanoparticles were used for degradation of aliphatic crude oil. Firstly the crude was extracted using column chromatography provided with alumina and silica and hexane used as a solvent for the mobile phase. Secondly, the aliphatic hydrocarbons was extract and finally it's examined in GC-MASS spectra before and after addition of (0.5) g of silver nanoparticles for 3 hours under lighting by LED light (30 watt). The aliphatic hydrocarbon was extracted in hexane. (0.1) g from silver nanoparticles was collected from aqueous solution using centrifuge and its added to (0.05) g from aliphatic hydrocarbons for 3 hours using LED light (30 watt) for degradation. Silver nanoparticles was used for degradation of total hydrocarbon in Basrah crude oil (IRAQ). The degradation was managed using GC-MASS technique.

3. RESULTS AND DISCUSSION

3.1 UV-Vis Spectrometry: Silver nanoparticles solution, ware identical to the characteristics UV-metallic silver. The peak intensity **(Figure 3**) is mention to the coherent oscillation of electrons at the surface of silver nanoparticles. The nanoparticles which are smaller than the wavelength of light can produce a coherent resonance waves at a particular absorbance wavelength which is in the visible range for silver nanoparticles. The appearance of surface plasmon resonance peak (SPR) at (420) nm provides a convenient spectroscopic signature for the formation of silver nanoparticles.

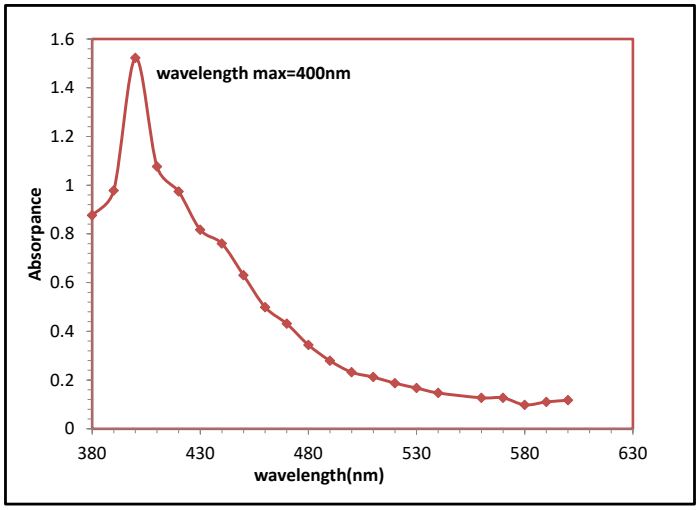

Fig 3: UV-Vis absorption spectra of silver nanoparticles provide the plasmon peak at 400 nm.

3.2 SEM analysis: Silver nanoparticles was imaged under SEM., as seen in **Figure (4).** The size and shape of the silver nanoparticles were examined clearly under scanning electron microscope. The particle size is between (10) nm to (78) nm. From the figure 4 it appears that silver nanoparticles in spherical shape. The image of the silver nanoparticles exhibited a clear separation however its appear like to parts with cut line in the middle of the nano sphere.

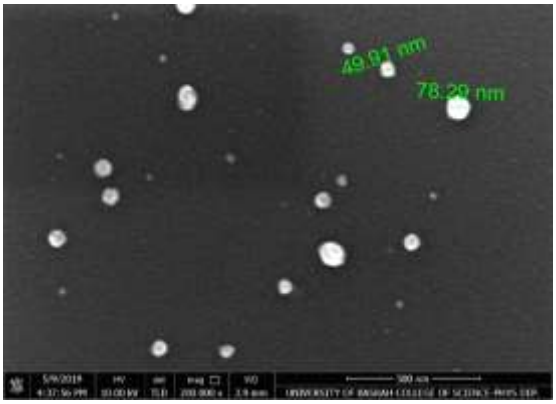

Fig. 4 : FE-SEM image of synthesized silver nanoparticles

Energy dispersive x-ray was used in order to examine the elements analysis on the surface. **Figure 5 and table 1** shows the percentage of silver is 57.23% which represent the maximum percentage of element in the prepared sample. However the percentage of other elements were registered as can be seen in table1.

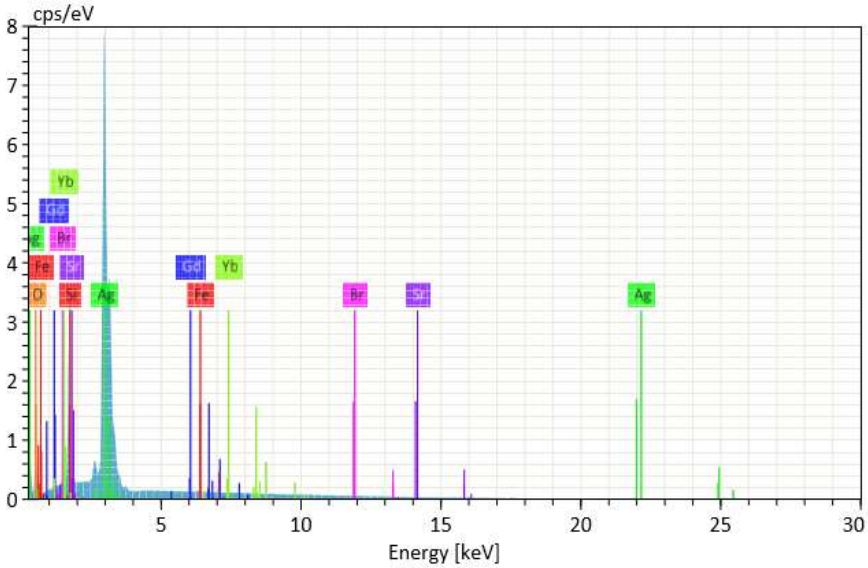

Fig.5: EDS spectra for silver nanoparticles

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Table 1: EDS-SEM analysis show the high percentage of silver nanoparticles

Element	Mass [%]	Atom. [%]
Oxygen	**18.89**	55.03
Silicon	**12.10**	20.07
Iron	**0.06**	0.05
Bromine	**0.06**	0.04
Strontium	**0.08**	0.04
Silver	**57.23**	24.73
Gadolinium	**0.06**	0.02
Ytterbium	**0.07**	0.02
Sum	**88.55**	100.00

3.3 Zeta sizer and zeta potential: Zeta sizer and zeta potential were used in order to scan the size of particles in prepared solution also the potential of solution. Figure 6 shows the distribution of silver ion. It clear that the size of nanoparticles was almost in the nano range. From figure7, Shows the zeta potential distribution of silver nanoparticles was a negative value (-46.3 Mv) permanent to the presence of silver ions.

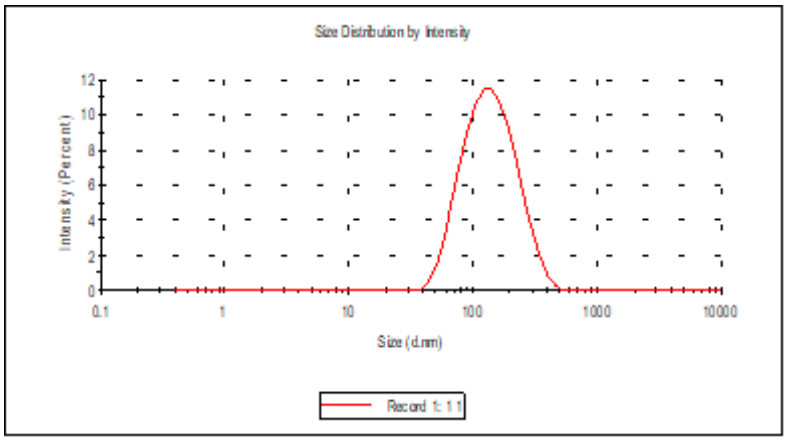

Fig. 6: shows zeta sizer analysis for synthesized silver nanoparticles

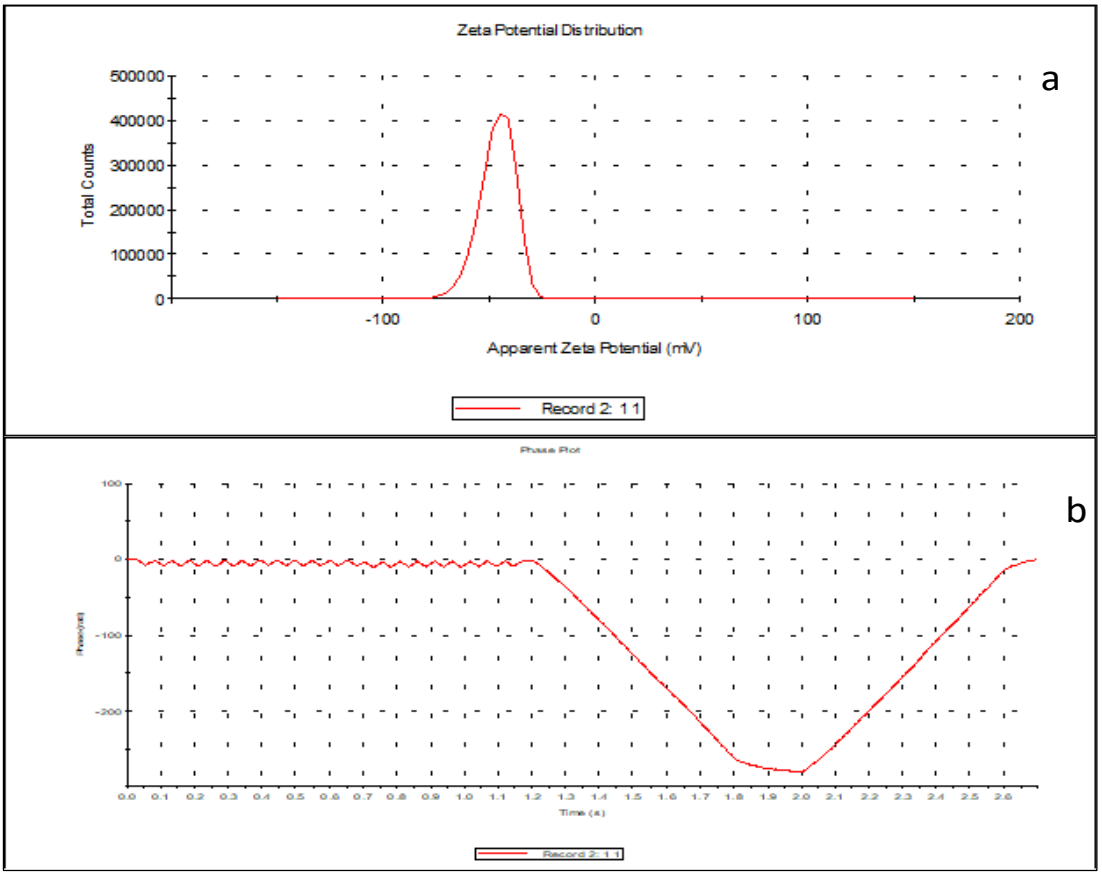

Fig. 7: Shows zeta potential analysis for synthesized silver nanoparticles provide the potential at (-46.3 Mv).

3.4 Study the optimum condition of the degradation: The optimum condition of the degradation using silver nanoparticles were studied such as effect of concertation of silver nanoparticles, effect of temperature, effect of volume of silver nanoparticles and effect of interferences. The degradation was done at the optimum parameters as following:

3.4.1 Effect of concertation of silver nanoparticles on degradation of MB: The concertation of silver nanoparticles at (0.1, 0.025 wt/v%) was studied using two solutions at the concentration(0.1g/100ml, and 0.025 /100ml), in presence and without light. The percentage of fracture of methylene blue with no silver nanoparticles solution is the slowest. Degradation of methylene blue dye using silver nanoparticles solution at the concentration (0.025gm / 100ml) give 24.4% of the dye was broken and at the same time, the prepared solution of silver nanoparticles at a concentration (0.1gm / 100ml) contributed to the cracking of (41.5 %) from methylene blue dye. Figure 8 and table2 shows these results.

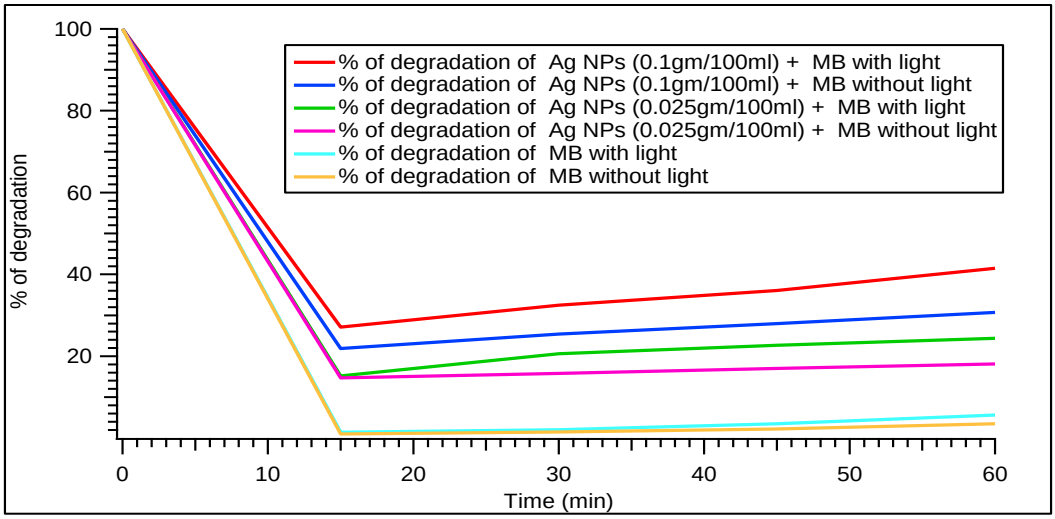

Fig. 8: Graph shows percentage of degradation of methylene blue using different concentrations of silver nanoparticles at one hour.

Table2: Shows % of degradation of methylene blue using different concentrations of silver nanoparticles at one hour.

Time(min)	% of degradation Ag nanoparticles (0.1) with light	% of degradation Ag nanoparticles (0.025) with light	% of degradation Ag nanoparticles (0.1) without light	% of degradation Ag nanoparticles (0.025) without light
0	100	100	100	100
15	27.1	15.2	21.9	14.7
30	32.5	20.6	25.4	15.8
45	36.1	22.7	28.0	17.0
60	41.5	24.4	30.7	18.1

3.4.2 Effect of temperature: The degradation of methylene blue at different temperature degrees shows at figure 9 and table3 these study shows that 45 °C is the best temperature degree for this synthesis which is provide metal Ag^0 without black Ag_2O precipitate. And also provide the fast degradation because the heat

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encourages collisions between the silver nanoparticles and methylene blue therefore the reaction for degradation become fast and the percentage of degradation become high.

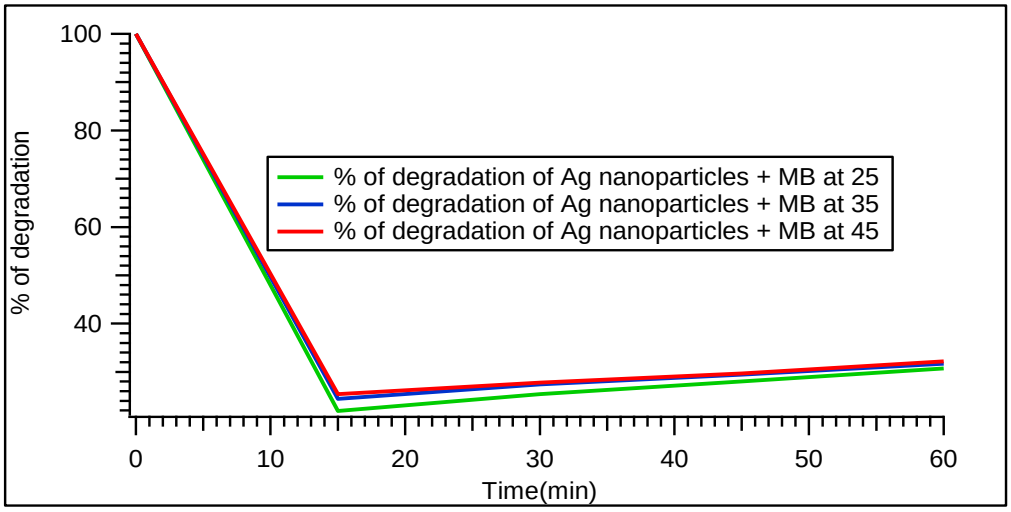

Fig.9: shows the percentage of degradation of methylene blue at different temperature degrees.

Table3: Shows percentage of degradation of methylene blue at different temperature degrees

Time(min)	% of degradation Ag nanoparticles at 25 °C	% of degradation Ag nanoparticles at 35 °C	% of degradation Ag nanoparticles at 45 °C
0	100	100	100
15	21.9	24.4	25.4
30	25.4	27.4	27.8
45	28.0	29.4	29.7
60	30.7	31.1	32.2

3.4.3 Effect of volume of silver nanoparticles on degradation of MB: Different volumes of silver nanoparticles solution was taken for degradation, figure 10 and table4 summarized these results

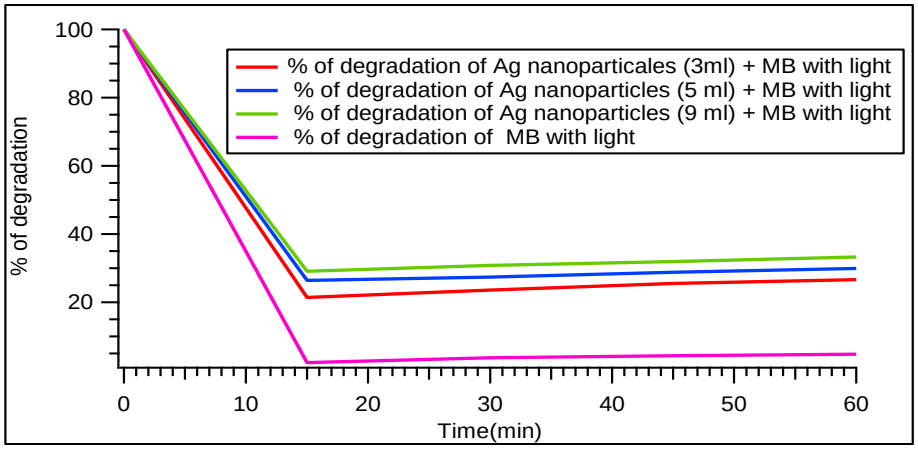

Fig. 10: Graph shows percentage of degradation of methylene blue using different volumes of silver nanoparticles**.**

Table 4: Shows percentage of degradation of methylene blue using different volumes of silver nanoparticles.

Time(min)	% of degradation Ag nanoparticles (3ml) with light	% of degradation Ag nanoparticles (5ml) with light	% of degradation Ag nanoparticles (9ml) with light	% of degradation MB with light
0	100	100	100	100
15	21.4	26.4	29.1	2.3
30	23.6	27.4	30.8	3.7
45	25.5	28.8	31.9	4.3
60	26.6	29.9	33.3	4.8

Its clear that using (9) ml is better for degradation from adding (3) ml from silver nanoparticles indicate for the big role of nanoparticles in degradation of methylene blue dye in water.

3.4.4 Effect of interferences: The study of the effect of different interferences is important to examine their effect on the degradation of methylene blue. Trisodium citrate was used as a capping agent and glucose was used as a reducing agent, therefore the effect of these materials in the solution was studied. **Figure 11**

and table 5 show these effects. From this figure it's clear that the % of degradation of silver nanoparticles 37.86% then trisodium citrate 26.93% then 18.04 % by glucose

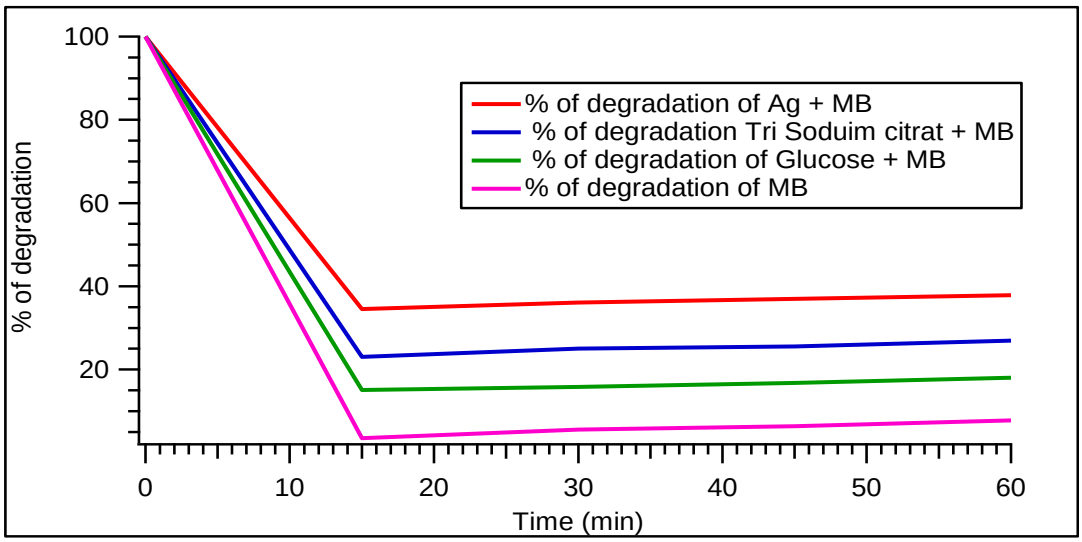

Figure 11: Graph shows the effect of the interferences on the degradation of silver nanoparticles at one hour.

Table 5: Shows the effect of the interferences on the degradation of silver nanoparticles at one hour.

Time(min)	% of degradation of silver nanoparticles	% of degradation Tri Sodium citrate	% of degradation Glucose	% of degradation Methylene blue
0	100	100	100	100
15	34.57	23.02	15.1	3.5
30	36.08	25.06	15.8	5.6
45	36.97	25.51	16.8	6.4
60	37.86	26.93	18.04	7.8

3.4.5 Degradation of methylene blue in water by using silver nanoparticles: After the studying of the optimum conditions of the nanoparticles the degradation process of synthesized silver nanoparticles were applied, **figure12** and **table 6** show the result at optimum conditions

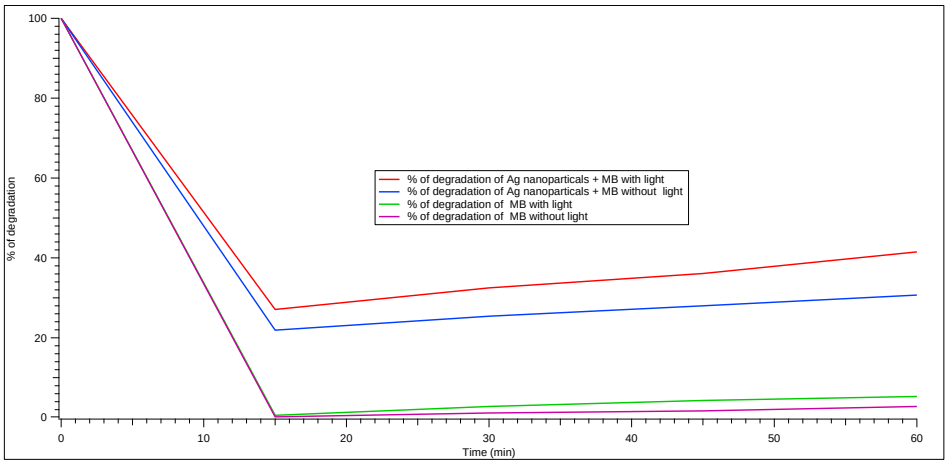

Figure 12: Degradation of methylene blue dye using silver nanoparticles at the condition (1 hour, at 30watt light, without light).

Table 6: Degradation of methylene blue dye using silver nanoparticles at the condition, (1 hour, at 15w light, without light)

Time (min)	% of degradation of Ag NP with light	% of degradation of Ag NP without light	% of degradation MB with light	% of degradation of MB without light
0	100	100	100	100
15	27.1	21.9	0.6	0.23
30	32.5	25.4	2.8	1.17
45	36.1	28.0	4.3	1.7
60	41.5	30.7	5.3	2.8

3.5 Gas- Chromatography-mass spectra technique: Gas- Chromatography-mass spectra technique used for analysis the crude oil before and after addition of silver nanoparticles from figure 13 represents the GC spectrum of aliphatic hydrocarbons separated from crude oil before and after the addition of nanoparticles. The spectrum represents the relationship between time (min) and abundance. From Figure 13(before addition of silver nanoparticles) we can see peaks at retention time: (1.3,1.46,1.52,1.67,1.88,8.8,10.4,11.57, 12.04,13.5,15.3,17.4, respectively). Figure 11after the addition of nanoparticles. Characterizes the GC spectrum of aliphatic hydrocarbons separated from Iraqi crude oil after the addition of silver nanoparticles.

We note from the figure the appearance of peaks at the time of retention: (1.3,2.14,2.97,6.66,9.8,16.8) respectively, and when compared with Figure 13 we note the disappearance of some peaks and the emergence of new peaks and less abundance, which means the breakage of some vehicles and the emergence of new organic molecules. **Table 7** and **table 8** list mass spectra analysis at the time of retention of the aliphatic hydrocarbons before and after degradation respectively.

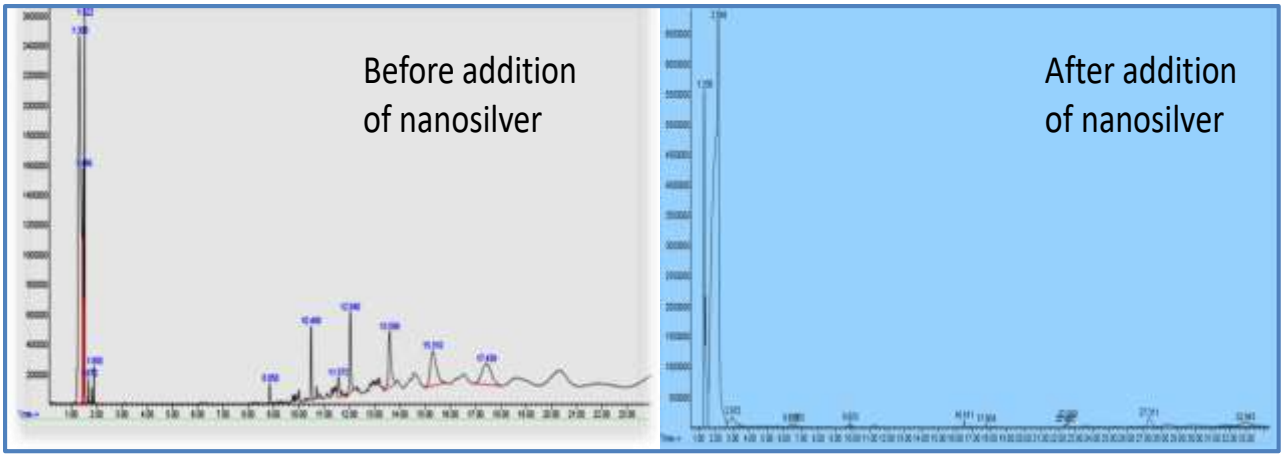

Figure 13: GC- Chromatogram spectra showing of the aliphatic hydrocarbons in Iraqi crude oi before and after addition of silver nanoparticles**.**

Table 7: Mass spectra of aliphatic crude oil before addition of silver 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**

Table 8: Mass spectra of aliphatic crude oil after addition of silver 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 hydroperoxide	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**

4. CONCLUSION

The appearance of surface plasmon resonance peak at (400nm) provides a convenient spectroscopic signature for the formation of silver nanoparticles. The present work demonstrates economic, simple and fast method for the preparation of silver nanoparticles. Analysis from SEM show silver nanoparticles in spherical shape the particle size is in the range from (10-78) nm. These new finding demonstrate that silver nanoparticles were effective for transfer the crud into simple hydrocarbons. The present work provides a promising method to release normal organic materials by silver nano product from water and sediment. The results of this work show the ability of silver nanoparticles to graft as a photo catalyst for degradation of methylene blue dye in water and degradation of aliphatic hydrocarbon in Iraqi crude oil. The total procedure of synthesis of silver nanoparticles by wet method and their applications in degradation of different hydrocarbons in the area of green chemistry with less pollutant at both the reaction and the product in the synthesis and in the applications.

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest.

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