Journal of Iraqi Al-Khwarizmi (JIKh) Volume:7 Issue:2 Year: 2023 pages: 56-67

Synthesis of gold nanoparticles and study their effect on optical properties of acridine orange dye

Authors Names

Asmahan Asaad Muhmood*[1], Liwaa Hussain Mahdi[2], Inass Abdulah Zgair[3], Shaymaa Issam Alawi[4] , Shymaa Awaad Kadhim[5]

[1,3,5] Kufa University, Faculty of science, Physics Department, Iraq

[2] Kufa University, Faculty of medicine, Iraq

[4] Kufa University, Faculty of Archaeology, Iraq

Key words: Acridine Orange, fluorinated dye, chemical reduction, linear optical properties

Published on: 25 /8 / 2023

ABSTRACT

In this work, a fluorinated Acridine Orange dye dissolved in distillate water at four different molar concentrations (0.5×10^{-6}, 1×10^{-6},0.5×10^{-5}, and 1×10^{-5}). Gold nanoparticles were prepared using the chemical reduction method using gold chloride at a concentration of (0.01 M) with sodium citrate. The reaction resulted in a red liquid containing gold nanoparticles. Using a particle size analyzer device, an analysis was carried out for the red liquid containing gold nanoparticles and the proportion of 45% of the liquid contained particles of (9-11 nm) size. The gold nanoparticles were added to the prepared dye samples with different volume concentrations (5,10, and 15) % for each prepared sample. The linear optical properties of the prepared samples before and after the addition were studied using a spectrophotometer within the range (200-800 nm). The optical parameters of all prepared samples were calculated (absorbance, transmittance, reflectivity, absorption coefficient, linear refractive index, extinction coefficient, optical conductivity), and the results showed the presence of a wide peak of absorption and an increase in the value of the optical parameters after adding gold nanoparticles and their increase with increasing the concentration of nanoparticles as well as movement of absorption peak towards longer wavelengths (red shift).

1. Introduction

Acridine orange is a fluorescent dye that has been used for more than 50 years and is still in use today. It has a molar mass of 265.35 g/mol and may be dissolved in water at a concentration of 28 g/L. Acridine orange has been used in DNA research for over 20 years as a (DNA) intercalator. It has a maximum absorption wavelength of 494 nm and a maximum emission wavelength of (525 nm). The absorption spectra, emission spectra, and fluorescence lifetimes of AO have all been shown to be significantly dependent on concentration. Aggregates develop in large concentrations, causing their characteristics to alter [1].

Due to their size and shape dependent surface (plasmon resonance) affinity with organic species, and high electrical conductivity properties, gold nanoparticles (Au NPs) are recognized as a potential candidate in many areas of science and engineering, including medical therapy, drug delivery, chemical sensing, catalysis, and electronic applications. [2].

The best application for adding nanoparticles to the acridine orange dye is to improve histological examinations, especially tissues affected by cancer, where the acridine dye is used in histological analyzes. As well as the dye prepared with nanoparticles can be used to prepare a laser medium used in the dye laser, where the nanoparticles work to shift the absorption peak to longer wavelength (red shift) to make the laser work at another wavelength.

2. Theoretical background

One of the most significant processes in light is photon absorption (matter interaction). The measurement of light extinction when a beam of light passes through a material is known as absorption. The intensity of the beam diminishes due to light absorption. The molecule may be thought of as an opaque disk with a cross. sectional area, an effective area visible to the photon of frequency (v). The cross-sectional area is greatest if the photon's frequency is near to a resonance frequency; otherwise, the cross–section is zero. Consider a slab of the sample (dz) with a total area of S [3].

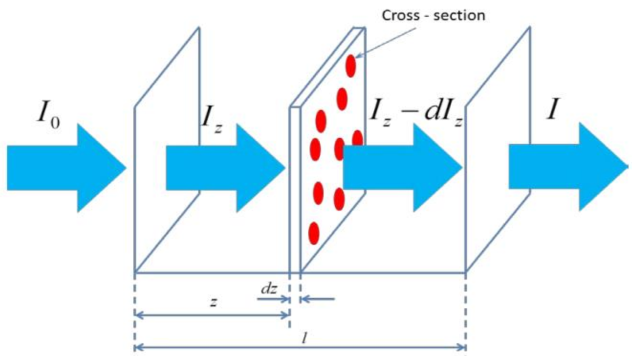


Figure (1): Light is absorbed by molecules with specified cross-sections [3].

The mutual impact of radiation and matter is one of the fundamental processes that underpins many of the universe's occurrences. The particles in any medium interact with the light waves that are sent through it. Interaction: can be described via several processes so called photophysical processes, in these processes the main route of energy relaxation of an excited dye molecule is either radiative or non-radiative transition [4]. The absorption process occurs when a photon collides with a dye molecule in a lower energy state, causing the dye to be excited. As a result, the photon is absorbed and its energy is used in the dye excitation. The process can occur (only if the incident photon energy equals the energy difference between the (two states) where the absorption occurs). The logarithmic relative reduction in intensity is termed as absorbance [5]:

$$A = log_{10}\left(\frac{I_0}{I}\right) \text{ ……………………….. (1)}$$

Transmittance is the ratio of transmitted light intensity to incident light intensity. Transmittance is computed by dividing the intensity value of the rays transmitting from the film (I) by the intensity of the initial incident rays (I_0), ($T=I/ I_0$) [6].

$$T = exp\ [-2.303A] \text{ ………………..…… (2)}$$

As illustrated in equation, the energy conservation law states that light beams are partly transmitted, absorbed, and reflected (3). The energy conservation rule [7] may be used to determine reflectance (R).

$$R + T + A = 1 \text{ …………………..… (3)}$$

The capability of a material for absorbing light with a specified wavelength, is the definition of absorption coefficient (α). According to equation (4), the optical absorbance (A) assisted in calculating the absorption coefficient [8].

$$\alpha = 2.303\,\frac{A}{d} \text{ ………………..…….. (4)}$$

One of the most significant optical constants is the refractive index (n), which changes with the wavelength of an electromagnetic wave. The electromagnetic wave loses some of its energy as it travels through a medium. The real component of the refractive index (n) is known as n, whereas the imaginary element of the extinction coefficient is known as K [9]. N = c / v. The refractive index of an optical or dielectric media (N) may be determined. Equation (5) is capable of calculating the refractive index (n) [10].

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - K^2} \quad \text{....... (5)}$$

The optical conductivity of a material is its frequency response when assaulted by light. To compute optical properties such as optical absorbance, reflectance, and absorption coefficient are employed (optical conductivity). Using the following relationship, the optical conductivity was calculated using the refractive index and absorption coefficient. [11]:

$$\sigma_{opt} = \frac{\alpha\, n\, c}{4\,\pi} \quad \text{.......................... (6)}$$

The Extinction coefficient was calculated for the samples by using the equation [10]:

$$K = \frac{\alpha\, \lambda}{4\,\pi} \quad \text{........................... (7)}$$

Because they are linked by a previous relationship, the extinction coefficient acts similarly to the absorption coefficient [12].

3. Experimental part:

In this part, equation (8) was used to prepare different concentration samples of Acridine Orange AO (0.5 x10^{-6}, 1x10^{-6}, 0.5x10^{-5}, and 1x10^{-5}) M. (3.1). [13]:

$$C = \frac{W \times 1000}{M_w \times V} \quad \text{............... (8)}$$

(C) Is the dye concentration (molL), W is the dye weight (g) determined using a sensitive weighted balance, M_w: dye's molecular weight (g/mol) and V is the solvent volume (ml).

After creating the basic concentration (1x10^{-4} M), the additional concentrations were prepared using the dilution equation (9) [14].

$$V_2 = \frac{C_1 \times V_1}{C_2} \text{........................ (9)}$$

By rearranging equation (9) we get:

$$C_1V_1 = C_2V_2 \quad \text{..................... (10)}$$

V_1: is the volume before dilution, C_1 is the primary concentration estimated from equation (8), V_2 is the volume after dilution, and C_2 is the new concentration, as shown in equation (9).

4. Preparing nanoscale gold

Gold nanoparticles were prepared by chemical reduction method using materials gold chloride ($HAuCl_4/H_2O$ and deionized water according to the following steps [15]:

- The gold chloride solution was diluted to reach a concentration of 0.005 M by dissolving it in non-ionic water according to the dilution formula ($C_1V_1 = C_2V_2$) and the solution is characterized by the following (HAuCl4 xH2O) gold chloride (III) hydrates with 99.995% purity and a molecular weight of Mw 339.79 g / mol. Presented by SIGMA "- Aldrich").

- A mixture consisting of the solution mentioned in paragraph (1) is placed in an amount of (5 milliliters) with the addition of (35 milliliters) deionized water on a magnetic apparatus and heated until it reaches a boiling point and leaves it to boil for (15-20) seconds.

- The concentration of sodium citrate ($Na_3C_6H_5O_7$) is prepared by taking one gram of it (powder) and dissolving it in 100 ml of deionized water).

- Sodium citrate prepared in paragraph (3) above, in an amount of (one milliliter), is added to the mixture in paragraph (2), then the heat is turned off and left on the magnetic stirrer device.

- Over time, the solution turns colorless and then turns dark red (violet), which is a sign of generating large nano-sized gold nanoparticles (40-100 nm) and then to bright red, which is a guide to reaching gold nanoparticles of size Smaller (less than 20 nm) as shown in Figure (2).

Figure (2): Stages of color formation for nano-gold.

$$4Ag^{*} + C_6H_5O_7\,Na_3 + 2H_2O \longrightarrow 4Ag^{0} + C_6H_5O_7H_3 + 3Na^{*} + H^{*} + O_2 \; \dots \; (11)$$

3. Results and Discussion

A. Gold Nanoparticles (GNPs) Synthesis

The chemical reduction approach was used to make gold nanoparticles. The resultant solution is a clear wine-red hue that is homogenous. The major benefit of chemical reduction is that it is characterized by great efficiency in synthesis. Moreover, the resultant nanoparticles have no inclination to clump together and are distributed at the nanoscale. The process's cheap cost of execution is also encouraging [16].

Surface plasmon resonance is a phase oscillation that occurs when light is absorbed by tiny metallic particles and is caused by a coherent and collective stimulation of the "free" (electrons in the conduction band) (SPR) [17].

Figure (3) shows the optical test performed on the (Au NPs) sample using a UV-VIS spectrophotometer in the range (200-800) nm.

The absorption spectra of Au NPs as a function of wavelength are shown in the figure, with the (SPR) appearing at 530 nm, which is consistent with the results. [16-18].

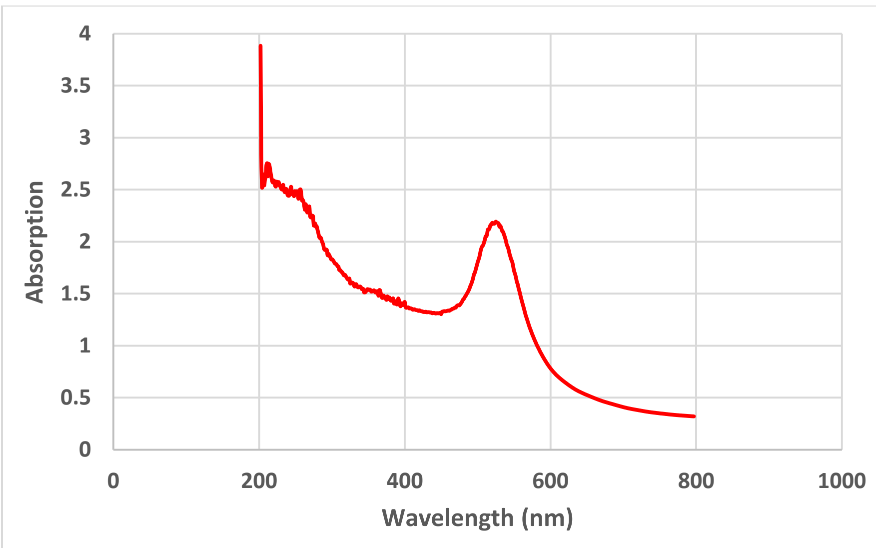
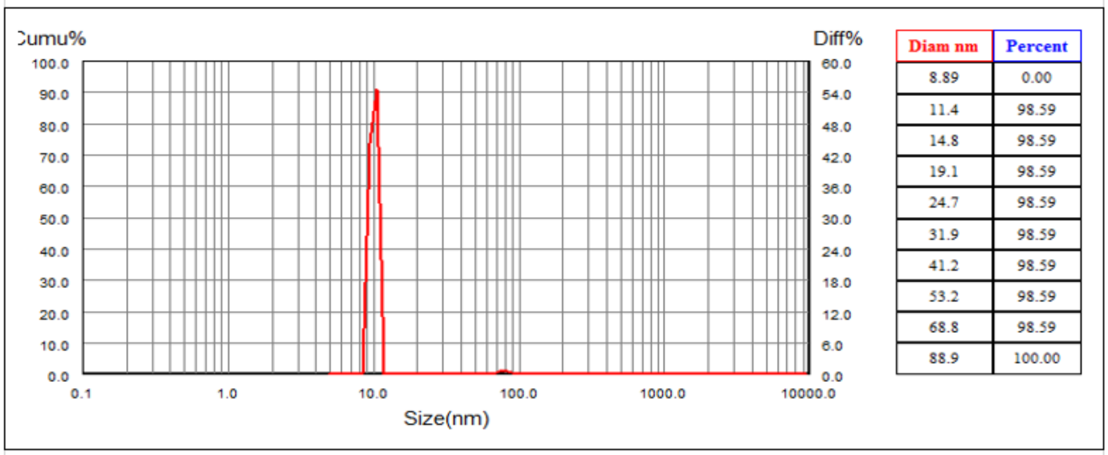


Figure (3): Absorption spectrum as function of wavelength for Au NPs.

Another evaluation termed particle size analyzer was performed at the Faculty of Pharmacy in order to acquire further information about the gold nanoparticles created utilizing the chemical reduction process. Figure (4) depicts the examination results.

Diam nm	Diff%	Cumu%	Diam nm	Diff%	Cumu%	Diam nm	Diff%	Cumu%
5.00-5.61	0	0	62.9-70.6	0	98.6	792-889	0	100
5.61-6.29	0	0	70.6-79.2	0.78	99.38	889-997	0	100
6.29-7.06	0	0	79.2-88.9	0.62	100	997-1119	0	100
7.06-7.92	0	0	88.9-99.7	0	100	1119-1255	0	100
7.92-8.89	0	0	99.7-111	0	100	1255-1409	0	100
8.89-9.97	44.14	44.14	111-125	0	100	1409-1581	0	100
9.97-11.1	54.46	98.6	125-140	0	100	1581-1774	0	100
11.1-12.5	0	98.6	140-158	0	100	1774-1990	0	100
12.5-14.0	0	98.6	158-177	0	100	1990-2233	0	100
14.0-15.8	0	98.6	177-199	0	100	2233-2505	0	100
15.8-17.7	0	98.6	199-223	0	100	2505-2811	0	100
17.7-19.9	0	98.6	223-250	0	100	2811-3154	0	100
19.9-22.3	0	98.6	250-281	0	100	3154-3539	0	100
22.3-25.0	0	98.6	281-315	0	100	3539-3971	0	100
25.0-28.1	0	98.6	315-353	0	100	3971-4456	0	100
28.1-31.5	0	98.6	353-397	0	100	4456-5000	0	100
31.5-35.3	0	98.6	397-445	0	100	5000-5610	0	100
35.3-39.7	0	98.6	445-500	0	100	5610-6295	0	100
39.7-44.5	0	98.6	500-561	0	100	6295-7063	0	100
44.5-50.0	0	98.6	561-629	0	100	7063-7924	0	100
50.0-56.1	0	98.6	629-706	0	100	7924-8891	0	100
56.1-62.9	0	98.6	706-792	0	100	8891-9500	0	100



Company:Angstrom Advanced Inc. Add:50 Braintree Hill Park, Ste 201, Braintree, MA 02184, USA Fax:1-781-519-4766

Figure (4): The nanoparticles number with nanoparticles size spectrum.

B. Linear Optical Properties of Acridine Orange dye

Figure (5) show the (absorption spectrum) of Acridine Orange (AO) as function of wavelength for the four concentrations samples obtained by UV-VIS spectrophotometer. By using equations (1-7), beside the spectrophotometer data, (reflectance, absorption coefficient, refractive index, optical conductivity, and extinction coefficient) respectively had been calculated as shown in table (1). The absorption increases with increasing dye molar concentration due to the greatest value of dye molecules in the energy ground state, which may absorb enough incoming photons, as seen in the figure. The absorption spectra peaks for the four samples were (435) nm.

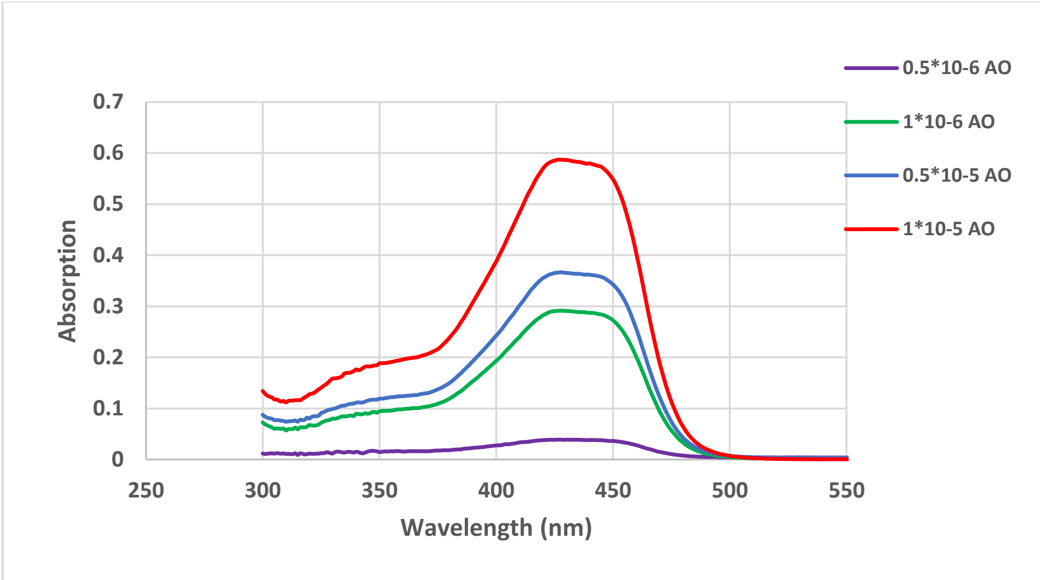


Figure (5): Absorption spectrum of Acridine Orange (AO) as function of wavelength.

Table (1): Optical parameters of Acridine Orange in four concentrations.

C Ml	A	T %	R	α cm $^{-1}$	σ_{opt} $*10^6$	n	K $\times10^{-8}$
$1*10^{-6}$	0.038	51.4	0.47	0.089	2.2	1.38	0.305
$0.5*10^{-6}$	0.289	26.14	0.708	0.664	16.98	1.7	2.3
$1*10^{-5}$	0.364	8.60	0.887	0.834	27.07	1.89	2.9
$0.5*10^{-5}$	0.584	0.93	0.976	1.34	38.82	1.95	4.6

Table (1) demonstrates that raising the dye concentration produces a rise in each of the following: (absorbance, refractive index, optical conductivity, reflectance, absorption coefficient, and extinction coefficient) and a decrease in each of transmittance and molar extinction coefficient.

The optical density of this medium is consolidated by the largest number of dye molecules in the ground state, allowing it to absorb more input photons and reflect less photons.

Because of the large disparity between the optical density values of the dye solution and those of air, the medium with a high optical density has a high refractive index. The loss of excited energy (as nonradiative transitions or collisions with adjacent molecules) is reduced when the absorbance increases at large molar concentrations. As seen in the table, this results in a lower molar extinction coefficient (1) [19].

The following figures (6,7,8,9) show the absorption spectrum as function of wavelength for four concentrations after adding Au NPs in (5, 10, and 15) % for each concentration.

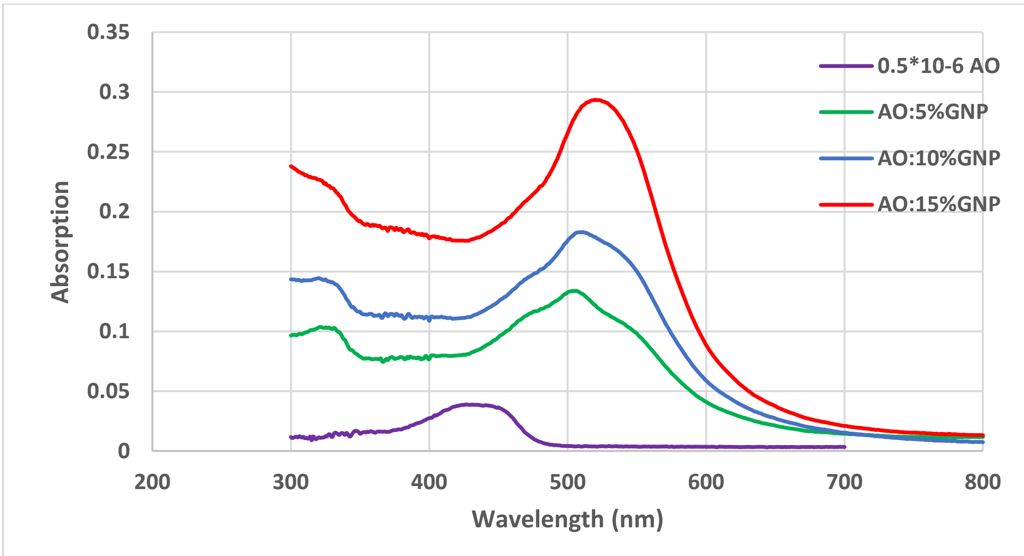


Figure (6): Absorption spectrum as function of wavelength for 0.5×10^{-6}AO: Au

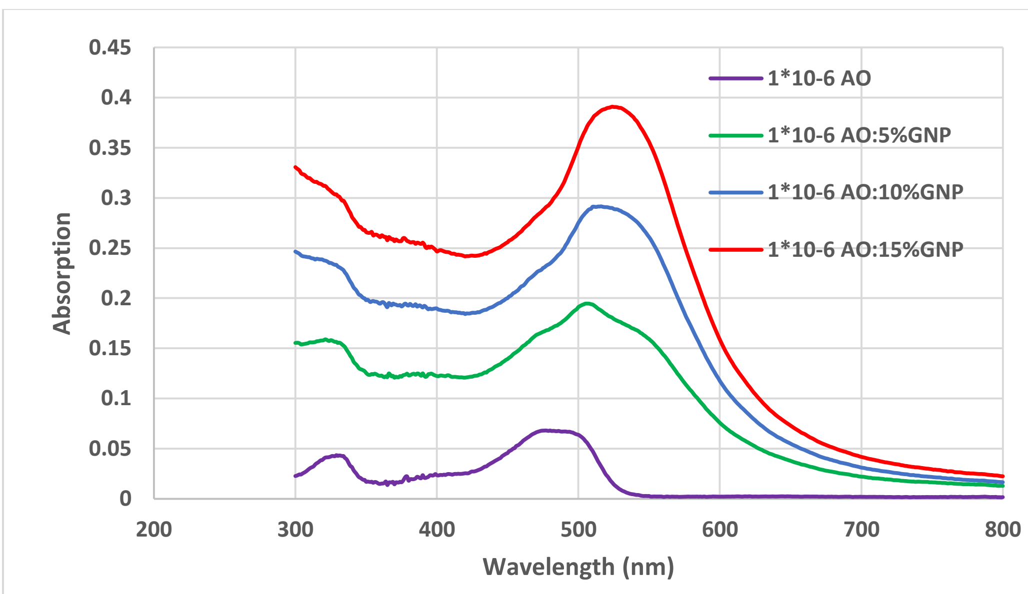


Figure (7): Absorption spectrum as function of wavelength for 1×10^{-6}AO: Au NPs.

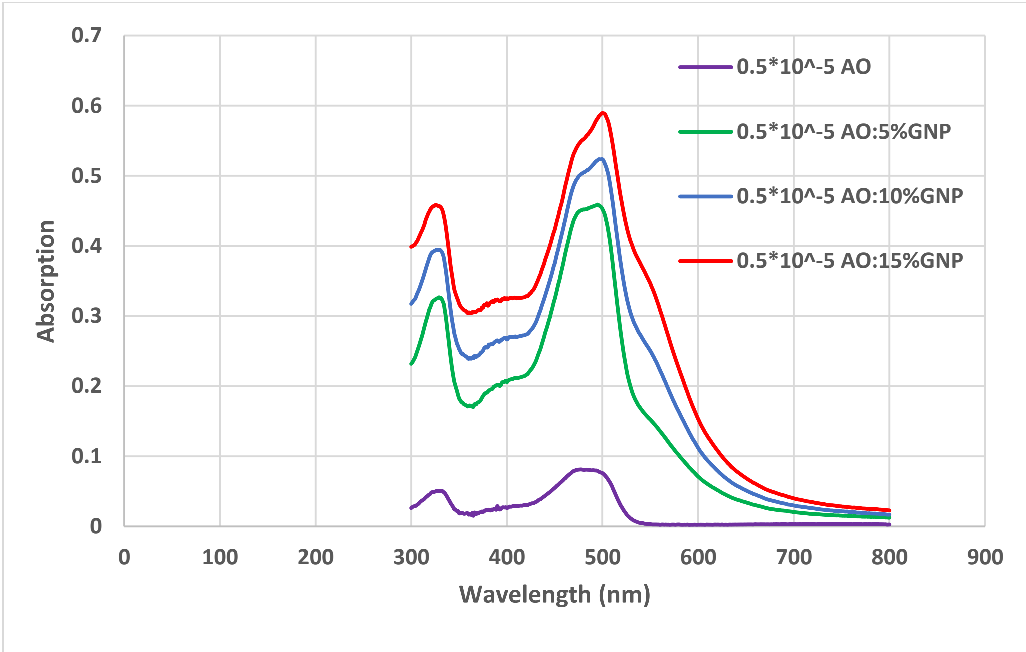


Figure (8): Absorption spectrum as function of wavelength for 0.5×10^{-5}AO: Au

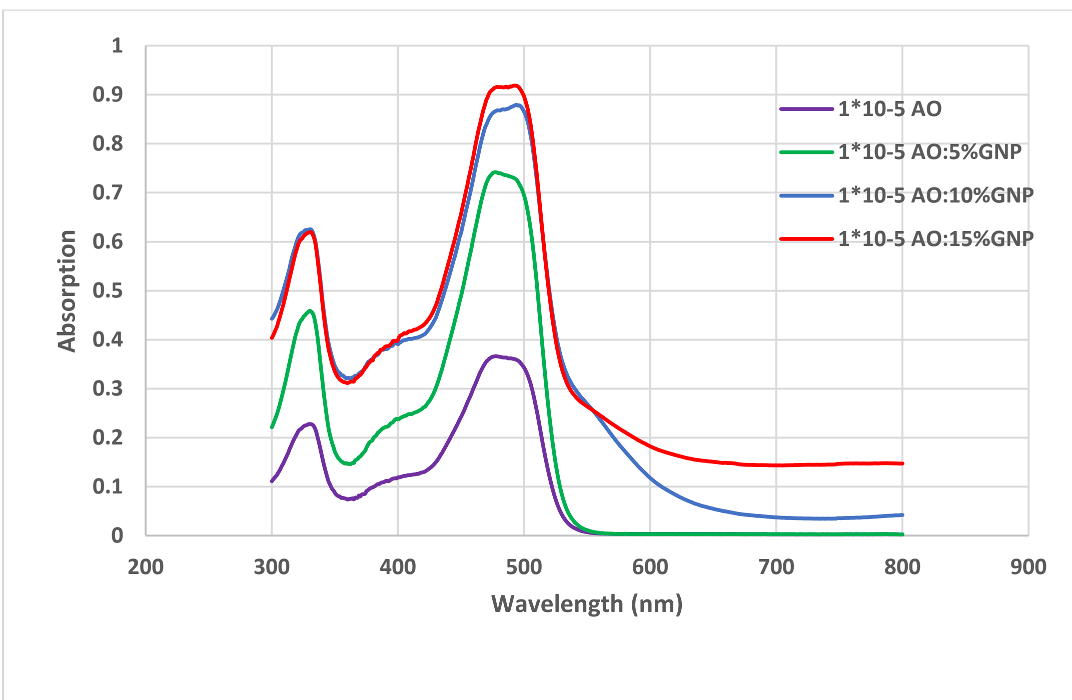


Figure (9): Absorption spectrum as function of wavelength for 1×10^{-5}AO: Au NPs.

Table (2): Optical parameters of Acridine Orange dye with and without Au NPs.

C	λ	A	T%	R	α cm^{-1}	n	σ	K	Δλ
$0.5*10^{-6}$ AO	440	0.038	91.46	0.078	0.087	1.73	0.26*10^7	0.308*10^-7	-
$0.5*10^{-6}$ AO:5% GNPs	507	0.13	65.22	0.234	0.307	2.57	1.78*10^7	1.23*10^-7	67
$0.5*10^{-6}$ AO:10% GNPs	510	0.182	50.9	0.315	0.42	3.04	2.94*10^7	1.71*10^-7	70
$0.5*10^{-6}$ AO:15% GNPs	523	0.293	40.17	0.318	0.67	3.06	4.78*10^7	2.81*10^-7	83
$1*10^{-6}$ AO	488	0.066	85.58	0.075	0.154	1.72	0.63*10^7	0.62*10^-7	-
$1*10^{-6}$ AO:5%GNPs	507	0.19	63.9	0.166	0.44	2.21	2.35*10^7	1.8*10^-7	19
$1*10^{-6}$ AO:10% GNPs	513	0.39	51.15	0.197	0.67	2.38	3.81*10^7	2.78*10^-7	25
$1*10^{-6}$ AO:15% GNPs	526	0.39	40.67	0.203	0.89	2.41	5.17*10^7	3.78*10^-7	38
$0.5*10^{-5}$ AO:	490	0.079	83.06	0.088	0.184	1.79	0.78*10^7	0.71*10^-6	-
$0.5*10^{-5}$ AO:5% GNPs	498	0.45	34.84	0.176	1.05	2.36	2.3*10^7	4.14*10^-6	8
$0.5*10^{-5}$ AO:15% GNPs	498	0.51	29.94	0.193	1.201	2.38	5.94*10^7	4.77*10^-6	8
$0.5*10^{-5}$ AO:15% GNPs	498	0.58	25.72	0.203	1.35	2.41	6.52*10^7	5.39*10^-6	8
$1*10^{-5}$ AO	480	0.741	18.17	0.073	1.705	2.42	7.1*10^7	6.5*10^-6	-
$1*10^{-5}$ AO:5%GNPs	496	0.816	13.28	0.057	1.88	2.6	7.6*10^7	7.3*10^-6	16
$1*10^{-5}$ AO:10% GNPs	498	0.873	7.02	0.052	2.01	2.7	8.3*10^7	8.09*10^-6	18
$1*10^{-5}$ AO:15% GNPs	498	0.919	3.36	0.047	2.11	3.02	8.8*10^7	8.36*10^-6	18

As seen from table (2) the increase of dye concentrations leads to change in the optical parameters of AO dye as well as the presence of Au NPs caused a change in the optical parameters.

The figures (6-9) and table (2) show in clear manner that the presence of gold nanoparticles with particle size (9-11) nm lead to enhancement in optical absorption and shifting the absorption peaks of the dye samples to longer wavelength (red shift) from 488 nm to 523 nm in $0.5*10^{-6}$ml. Not only the optical absorption enhanced but also the other optical parameters.

Increased concentration raises the intensity of absorption, which is related to a rise in the number of molecules, which increases the likelihood of absorption with the concentrations utilized, as stated by the Beer-Lambert law.

More n values with increased AuNPs resulted in increased absorbance and denser AO dye, which lowered light propagation velocity through them, leading in increased (n) values. While (n) denotes the ratio of light velocity in vacuum to light velocity in any medium. Then, As the material becomes more opaque to incoming light, the velocity of light slows, and n and k rise as a result [20].

4. Conclusions

Manufacture of nano-gold by chemical method is a successful method through which we obtained nano-gold with a size (9-11 nanometers) and it is characterized by its stability without the occurrence of large agglomeration. The optical properties of the medium changed after changing the concentrations, as it was found that increasing the concentration increased, the properties changed more. The properties of the medium changed after adding gold nanoparticles (optical and spectroscopic).

References

1- Mustafa ERSÖZ Dr. Arzum IŞITAN Meltem BALABAN, NANOTECHNOLOGY 1, 1st Edition – October 2018, Denizli.

2 - SYNTHESIS OF SILVER NANOPARTICLES BY CHEMICAL REDUCTION METHOD: EFFECT OF REDUCING AGENT AND SURFACTANT CONCENTRATION G. Suriati, M. Mariatti and A. Azizan, International Journal of Automotive and Mechanical Engineering (IJAME), Volume 10, pp. 1920-1927, July-December 2014

3 - A.E. Siegman, "Lasers", Mill Valley, Calif.: University Science Books, 1986.

4 - Yassin H.Khadim, Mithaq .M.Mehdy Al- Sultani, Study of the spectral characteristics for the Styryl 9M laser dye , International Journal of ChemTech Research , Vol.10 No.9, pp 646-653, 2017.

5- Alaa Jewad Kadham Algidsawi, Studying the Effect of Metal omplexes on the Optical, Electrical and Ultrasound Properties of PVA and PVAc ilms Prepared by Casting Method, University of Baghdad, Doctor of Philosophy Degree, July 2015 A.D.

6 - Asmahan A. Muhmood, Inass A.Zgair , Mushtaq A. Hussein , Liwaa H. Mahdi , Bashaer S.Jabbar ,Adel H. Omran Alkhayatt, Preparation and optical characterizations of PVA: Ag Nano composite, Journal of Physics: Conference Series 1879 (2021) 032083, IOP Publishing.

7 - Das, R. and Pandey, S. 2011. "Comparison of optical properties of bulk and nano crystalline thin films of CdS using different precursors", International Journal of Material Science, 1(1): pp. 35-40.

8 - Mahshad Ghanipour and Davoud Dorranian, Effect of Ag-Nanoparticles Doped in Polyvinyl Alcohol on the Structural and Optical Properties of PVA Films, Hindawi Publishing Corporation Journal of Nanomaterials Volume 2013.

9 - Diemiruaye, J. M. 2013., Int. J. Thin Film Sci. Tec., 2 (2):pp. 53-66.

10 - Huda Hasan Ridha, Improving the Solar Cell Efficiency by using Luminescent Solar Concentrators, MSc. Thesis, Kufa University, 2018.

11 - Suhad Heyawi Mohsen, Luminescent concentrators based on two organic dyes to increase the solar cell efficiency, MSc. thesis, Kufa University, 2017.

12 - Nguyen Ngoc Long, Le Van Vu, Chu Dinh Kiem, Sai Cong Doanh, Cao Thi Nguyet, Pham Thi Hang, Nguyen Duy Thien, Luu Manh Quynh, Synthesis and optical properties of colloidal gold nanoparticles, Journal of Physics: Conference Series 187 (2009)

13 - Francisco Javier Flórez -Barajas, Zayda Constanza Sánchez –Acevedo, Heriberto Peña - Pedraza, Synthesis and characterization of gold nanoparticles in solution using chitosan as reducing agent, Respuestas, 24 (2), May - August 2019, pp. 49-55.

14 - Marcin Banach, and Zygmunt Kowalski, Chemical Reduction as the Main Method for Obtaining Nanosilver, Journal of Computational and Theoretical Nanoscience Vol. 10, 1–9, 2013.

15 - Mustafa D. jaafer , Hussein H. Turnachy , Salah M. Saleh Al- Khazali , and Adel H. Omran Al-Khayatt , Comparative of silver and gold nanoparticles synthesized by the chemical reduction method for antimicrobial applications , Cite as : AIP conference proceedings 2290,050026. Puplished Online:04 December 2020

16 - Kelly, K.L., Eduardo Coronado, Lin Lin Zhao, and George C. Schat, The optical properties of metal nanoparticles: The influence of size, shape, and dielectric environment, Journal of Physical Chemistry B, 107, No. 3: p. 668-677, 2003.

17 - Nguyen HH, Park J, Kang S, Kim M., Surface plasmon resonance: a versatile technique for biosensor applications. Sensors (Basel). 2015 May 5;15(5).

18 - Lorean Madriz, Ronald Vargas, - Key aspects of surface plasmon resonance spectroscopy for analytical chemistry applications, Journal of Analytical & Pharmaceutical Research, Volume 7 Issue 4 – 2018.

19 - JassimM.Jassim1 *, Yassin H.Khadim, Mithaq .M.Mehdy Al- Sultani2, Study of the spectral characteristics for the Styryl 9M laser dye, International Journal of ChemTech Research, Vol.10 No.9, pp 646-653, 2017.

20 - J. R. Lakowicz, “Radiative decay engineering: Biophysical and biomedical applications,” Anal. Biochem., vol. 298, pp. 1–24, Oct. 2001.