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Reducing the Purification Period of Congo Red Dye Solution By Using Co-Exposure to Ultraviolet and Green Laser as A Photocatalyst Source

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Abstract

Attempts were made over the years to achieve economic and easy methods for water purification. This could well save time, cost, and earn a good process quality for many countries. This study aims to enhance the purification process parameters for Congo red dye polluted water and introduce a developed methodology with an impact on many associated parameters such as the time for water purification process. The research proposes a method to achieve this time reduction by mixing gold nanoparticle (AuNPs) (prepared by chemical reduction method) with Titanium dioxide nanoparticles (TiO₂NPs) (prepared by sol-gel techniques). The resulting mixture is incorporated into PVA host to synthesize a hard disk used as a purification disk to treat the pollutant water. The pollutant solution was exposed to different light sources to complete the photocatalyst process. In this respect, sunlight, UV light, green laser, blue laser, and combined UV light and green laser were used as a photocatalysis sources. Experimental work was conducted to adjust the right mixture and the right combination of light sources. Results were recorded accordingly and showed a significant reduction in the purification time with less than half the standard period when the conventional purification process is used.

Keywords: Water Purification, Congo Red Dye, Gold Nanoparticle, (AuNP) and Titanium Dioxide (TiO₂).

تقليل فترة تنقية محلول صبغة الكونغو الحمراء باستخدام التشعيع المشترك للأشعة فوق البنفسجية والليزر الأخضر

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الخلاصة

بذلت محاولات على مر السنين لتحقيق طرق اقتصادية وسهلة لتنقية المياه يمكن أن توفر الوقت والتكلفة ويحقق جودة عملية جيدة للعديد من البلدان. تهدف هذه الدراسة إلى تحسين معايير عملية التنقية للمياه الملوثة من صبغة الكونغو الحمراء وإدخال منهجية مطورة لها تأثير على العديد من العوامل المرتبطة مثل وقت عملية تنقية المياه. يقترح البحث طريقة لتحقيق هذا عن طريق خلط جزيئات الذهب النانوي (AuNP) (المحضرة بطريقة الاختزال الكيميائي)، مع جزيئات ثاني أكسيد التيتانيوم النانوية (TiO₂) (المحضرة بتقنيات سول-جل). يتم دمج الخليط الناتج في مضيف PVA لتكوين قرص صلب يمكن استخدامه كقرص تنقية لمعالجة المياه الملوثة و تعريض المحلول الملوث لمصادر ضوء مختلفة لإكمال عملية التحفيز الضوئي. يستخدم ضوء الشمس، الأشعة فوق البنفسجية، الليزر الأخضر، الليزر الأزرق، والمصدر المشترك لمصباح

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الأشعة فوق البنفسجية والليزر الأخضر كمصدر للتحفيز الضوئي. تم إجراء التجارب لضبط الميزج الصحيح والجمع الصحيح لمصادر الضوء. تم تسجيل النتائج وفقًا لذلك وأظهرت انخفاضًا كبيرًا في وقت التنقية بأقل من نصف الفترة القياسية عند استخدام عملية التنقية التقليدية.

1. Introduction

Semiconductor photocatalysis has been under extensive investigations for the photodegeneration of organic pollutants such as congo red dye which are one of the causes of water pollution i.e. semiconductor photocatalysis is used for the purification of water. The acceleration of a photoreaction in the presence of a catalyst is known as photocatalysis [1]. This photocatalysis process is based on the irradiation by photons of energy equal to or greater than their bandgap energy of semiconductor particles, that transmits the electron from the valence band (VB) to the conduction band (CB), thus creating an electron-hole pair [2]. When photons with energy ($h\nu$) equal to or greater than the semiconductor with (E_g) are incident, electron-hole pairs are created in the conduction band and valence band [3], as shown in Figure 1, which could be summarized in three main steps:

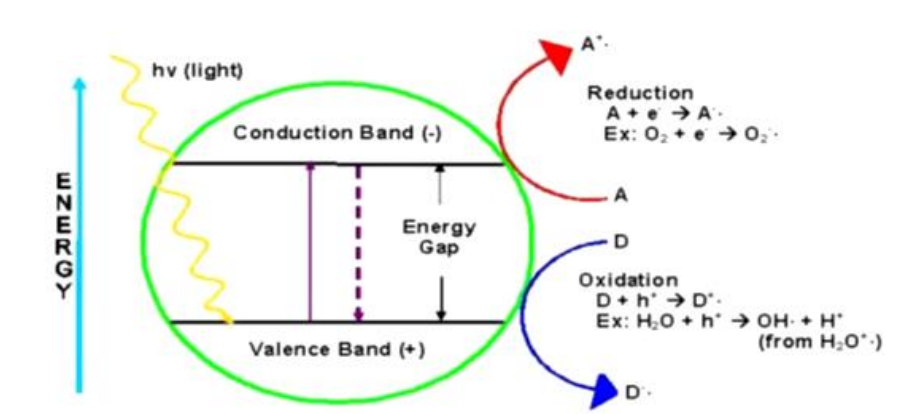


Figure 1-The photocatalyst process

(1) photons with sufficient energy are absorbed by a semiconductor; (2) the absorbed photons with energy greater than the bandgap energy (E_g) of semiconductors lead to the formation of electrons in the CB, and corresponding holes in the VB; (3) the separated electrons and holes are consequently involved in the redox reactions for the purification of the environment and energy production [4]. TiO_2NPS are an efficient photocatalyst, due to its high photocatalytic activity, that can be used to initiate the photodegeneration process for the purification of water

Materials in the nanoscale got the attention of many researchers. It has been involved in wide applications as a result of fabricating stronger materials [5,6]. For a material to be "nano scale", it must be on the nanometer scale of 100 nm or less [7]. Materials in the nanoscale have different properties from those of the bulk material. Nanoparticles properties depends on the shape and size of the nanoparticles, making them radically different from the bulk material. Bulk materials have fixed properties regardless of size, but nanoparticles are totally different [8, 9]. Nanoparticles have a high surface area to volume ratio which improves particles chemical and physical interaction with the surrounding environment, which can be liquid, solid, or even a polymeric matrix. Furthermore, the number of atoms inside a bulk material is comparable with the number of atoms on its surface, while the numbers of atoms inside nanoparticles are negligible in comparison with the number of surface atoms of nanoparticles. The huge nanoparticles surface area gives them unique properties such as surface plasmon resonance and optical properties.

Titanium dioxide nanoparticles, in this work, were prepared by sol-gel technique, where sol-gel is a simple method that produces ceramics and glasses with better purity than high-temperature conventional processes. Prepared materials have high homogeneity, small particle size and high surface area. In addition, this method is low-temperature treatment and low cost.

In the present work, Congo red dye: a sodium salt with a chemical formula of (C₃₂H₂₂N₆Na₂O₆S₂) and molecular weight of (696.66 g/mole) was used as a pollutant agent. It is highly soluble in water resulting in a colloidal solution, and it absorbs the electromagnetic spectrum at $\lambda_{\max}=497\text{nm}$ [10].

One method of preparing gold nanoparticles is the chemical reduction method, which was used in this work. The chemical reduction method consists of the following steps: The reduction of metal salts, electrochemical routes, or controlled decomposition of metastable organometallic compounds is used in the "bottom-up" technique of wet-chemical nanoparticle synthesis [11]. Large variations in particle shape and size distributions can be predicted when different reagents and conditions are used for synthesis [12,13-16]. However, it is possible to obtain comparable reaction rates and particle sizes by adjusting the temperatures for the reactions.

This article aims to enhance the purification process parameters for pollutant water polluted by Congo red dye and introduce a developed methodology with an impact on many associated parameters such as the time for water purification process. Many researchers have worked in this field.

2. Experimental Work:-

Gold nanoparticles were prepared by the chemical reduction method. The process starts with preparing a solution by mixing 0.1699 g HAuCl₄ (~5.0 x 10⁻³M) in 100mL deionized H₂O & been diluted. 5% sodium citrate solution was prepared by dissolving (0.25g sodium citrate in 50 mL H₂O). To synthesis gold nanoparticles, the diluted solution of HAuCl₄ was heated until it began to boil, at this point 1mL of 0.5% sodium citrate solution was added dropwise with continued heating until the solution changes its color to pale purple which is the first indication of gold NPs creation. After 8 minutes after the boiling point the solution, heating was stopped, and the solution was stirred to cool it to room temperature.

On another hand, TiO₂ nanoparticles were prepared by sol-gel technique with two solutions; The first solution consists of (1.25:1.25) ml of Titanium Isopropoxide (TTIP) (which is the main donor material) and Isopropanol. The second solution consists of 50 ml distilled water with a pH \cong 3, which can be obtained by adding a proper amount of HNO₃. The first solution was mixed with the second solution with a stirrer until the color of the solution changed to white. This color changing is the first indication of the creation of TiO₂NPs. The next step was adding 2.5 ml of AuNPs to TiO₂NPs solution with continuous mixing with a stirrer for 2 hours. Then 2.5ml of the final mixture was added to 7.5 PVA and was dried at a temperature of 70 °C to form a hard disk (Purification Disk), It can be used at once.

Congo red dye was dissolved in distilled water at high concentrations of 10⁻² M and the dye solution was diluted to 10⁻⁵M; this solution was taken up as the polluted water. The purification disk was immersed inside the Congo red dye solution. The resultant dye solution mixture was afterwards exposed to different light rays (sunlight, UV light, green laser, blue laser, combined UV light and green laser) to enable the purification process. To complete the purification process, the pollutant water was exposed to sunlight for 180 minutes, during this stage the absorption spectrum was examined for different samples with a time intervals for each sample (30, 60, 90, 120, 150, and 180 minutes). The same procedure was repeated using green and blue laser the same with exposure period. The same procedure has also followed co-exposure source using UV lamp and green laser with exposure period about 70 minutes (10, 20, 30, 40, 50, 60 and 70 minute).

Figure 2 shows the flowchart for the steps of the experimental work.

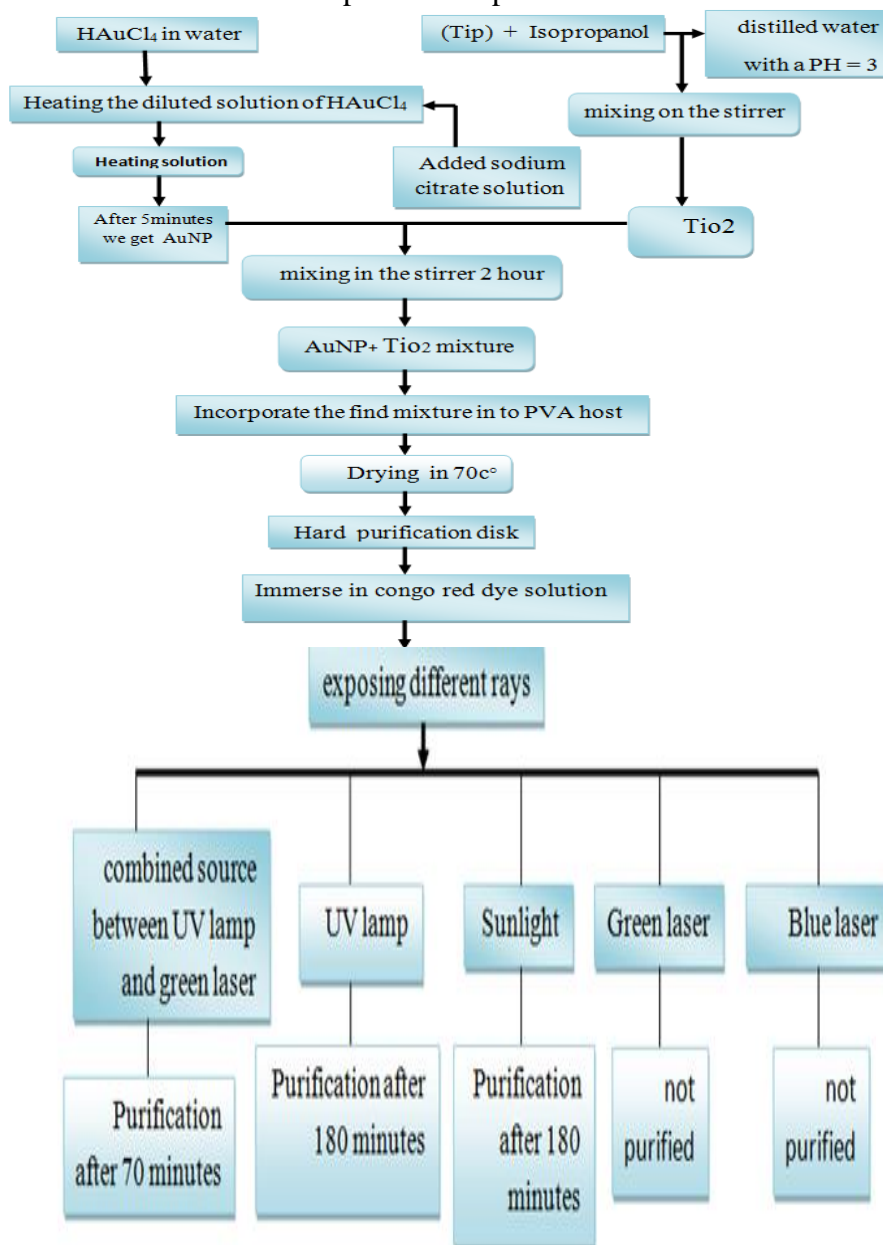


Figure 2- Flowchart for the experimental work

The (UV-laser.Camber) was used during the experiments to provide an irradiation source for the photocatalytic activity.

This UV-laser. camber is shown in Figure 3, consists of a black opaque box(height 60cm , width 30 cm) with a UV lamp fitted at the top inner side of the box. A laser source is inserted from the top of the box through a hole to provide the irradiation source. The sample is placed as shown at the bottom of the box.

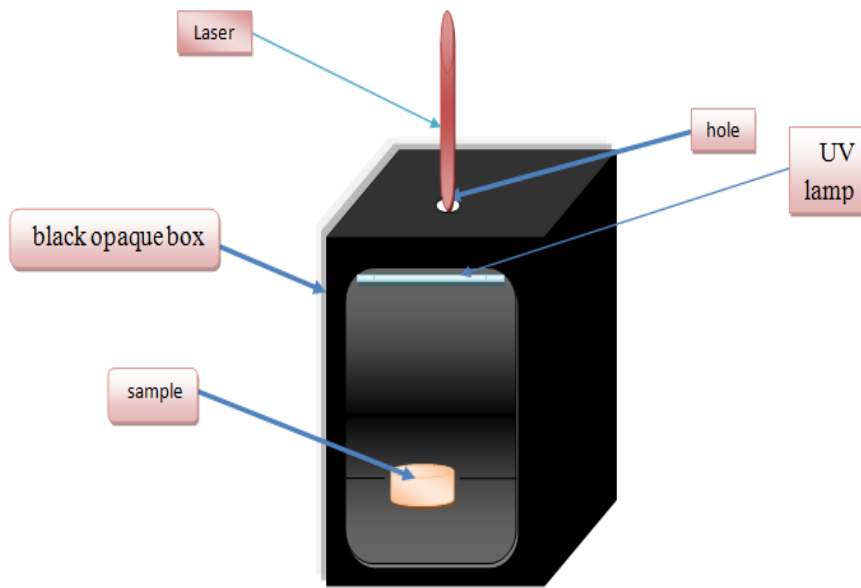


Figure 3-UV-laser. Chamber

3. Results and Discussions

Figure 4 shows the EDX spectrum of the (Au+TiO₂)NPs mixture. From the spectrum, the existence of gold with 26.88% percentage is clearly seen as well as the presence of TiO₂ with 0.53% percentage, in addition to 72.59% oxygen and 0.53 % Titanium(Figure 4 and Table 1).

Table 1-Percentages of each element as recorded by the EDX

Element	Line	Int	W%	A%
O	ka	132.3	72.59	96.85
Ti	ka	1.6	0.53	0.24
Au	ka	1.3	26.88	2.91

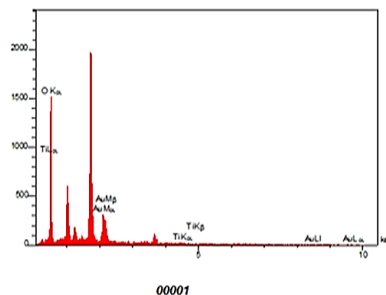


Figure 4-The EDX spectrum of AuNPs+TiO₂NPs

Figure 5 shows the XRD patterns for Au/TiO₂ samples, which were prepared by the chemical reduction method and the sol-gel technique. According to the standard, all the major peaks are well indexed to the anatase phase (JCPDS card No. 21-1272). No extra peaks, representing impurities, were observed, which indicates the pure nature of the desired product. In Figure 5, the reflections in the diffraction pattern can be indexed to the face-centered cubic Au (JCPDS card No. 002-1095) and anatase TiO₂ (JCPDS card No 21-1272). The diffraction peaks at 2θ

values of 44.41, 64.61 and 77.91 can be indexed to the (200), (220), and (311) planes of the Au nanoparticles, respectively, indicating the successful decoration/ formation of metallic Au NPs on the surface of TiO₂ microspheres.

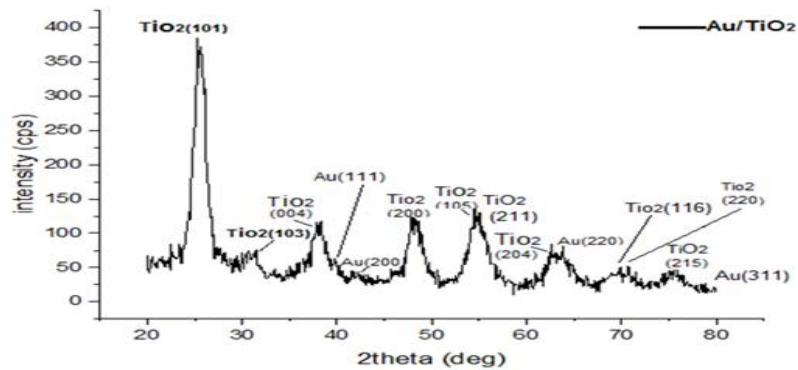


Figure 5: The X-ray diffraction spectrum of AuNPs+TiO₂NPs prepared by hot reduction method

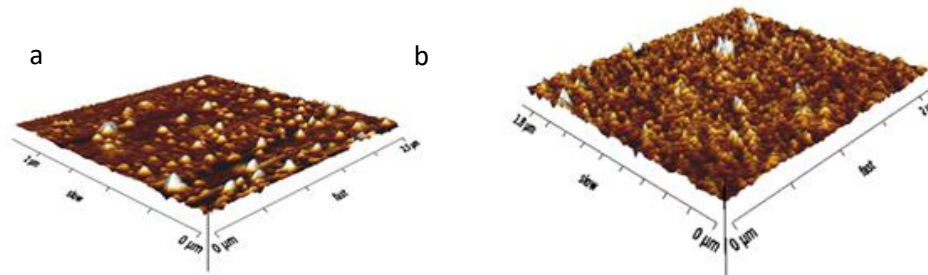


Figure 6-(a) AFM image of (Au+TiO₂)NPs.(b) AFM image of AuNPs.grain size determination was carried out with AFM test.

Figure 7(a) shows the SEM image of AuNPs prepared by the chemical reduction method. It can be observed that the particle size is 19.004nm while that of (AuNPs/TiO₂)NPs prepared by the sol-gel technique is about 33.791 nm (Figure 6(b)).

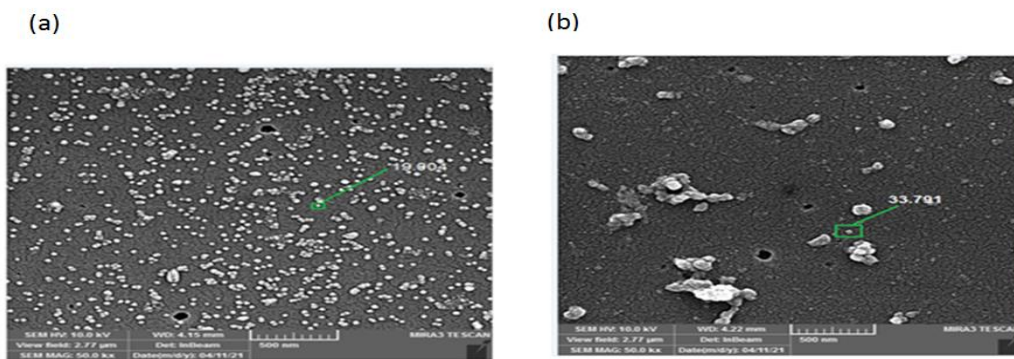


Figure 7- (a) the SEM image of AuNPs prepared by chemical reduction method. (b) the SEM image of (Au/TiO₂NPs)prepared by chemical reduction method and sol-gel techniques.

In Figure 8(a) the absorption spectrum for (Au +TiO₂) nanoparticles prepared by chemical reduction method and sol- gel technique shows that the maximum absorbance peak occurred at 361nm. Figure 8(b) shows the absorption spectrum for TiO₂ nanoparticles prepared by the sol- gel technique where the maximum absorbance peak occurred at 329 nm.

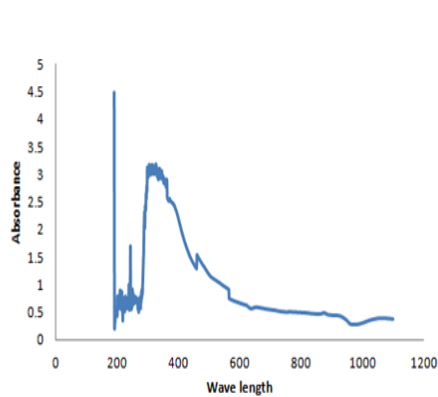


Figure 8- (a) The peak absorbance intensity of (Au +TiO₂)NPs prepared by hot reduction method and sol-gel techniques

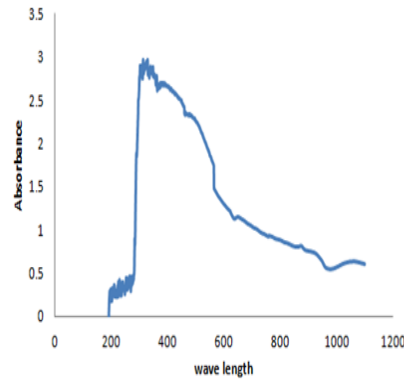


Figure 8-(b) The peak absorbance intensity of TiO₂NPs prepared by sol-gel technique

While Figure 9 shows the absorption spectrum for Au nanoparticles which were prepared by the hot chemical reduction method; the maximum absorbance peak occurred at 520 nm. The shift in the absorbance peak position for the Au/TiO₂ mixture indicates modulation in energy band gap.

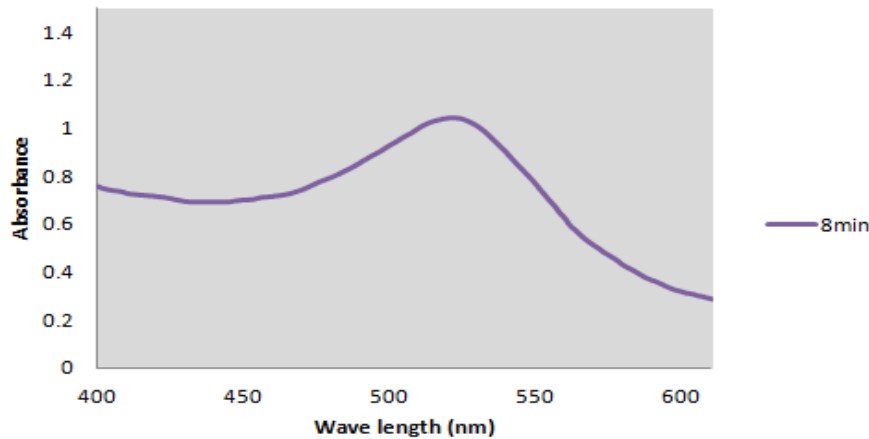


Figure 9- The peak absorbance intensity of AuNPs prepared by the hot reduction method.

The (Au/TiO₂)NPs in the PVA disk (the purification disc) was immersed inside the diluted Congo red dye solution and it was exposed to different light rays such as sun light, UV light, green laser, blue laser and combined UV light and green laser. For all the used sources, its absorption spectra were examined at time intervals of (30,60,90,120,150, and 180) minutes except at the case of combined source the absorption spectrum was examined at time intervals of (10,20,30,40,50,60 and 70) minutes. The polluted water was purified after 180 minutes at the case of sunlight and UV light while it was after 70 minutes at the case of combined UV light and green laser. This is the main result of our work where the purification period was reduced from 180 to 70 minutes. It was noted that there was no purification when using a single photocatalyst source such as sunlight, UV source or green or blue laser.

An explanation of the purification method carried out in this work is that the increase in the intensity of the incident light (through the use of the combined source) led to the acceleration of the purification process of the Congo dye. The increase in the light intensity increases the number of incident photons on the photocatalyst valence band. It promotes more electrons to the conduction band, which increases the number of released hydroxyl radicals. Then, the reaction rates will be increased. In addition to that, using a combined source lead to the precipitation of both the TiO₂NPs and the AuNPs in purification process because the UV light has a resonance absorption band gap with TiO₂NP and the green laser has a resonance band gap with AuNPs. Absorption spectra of Congo red dye with different light source .

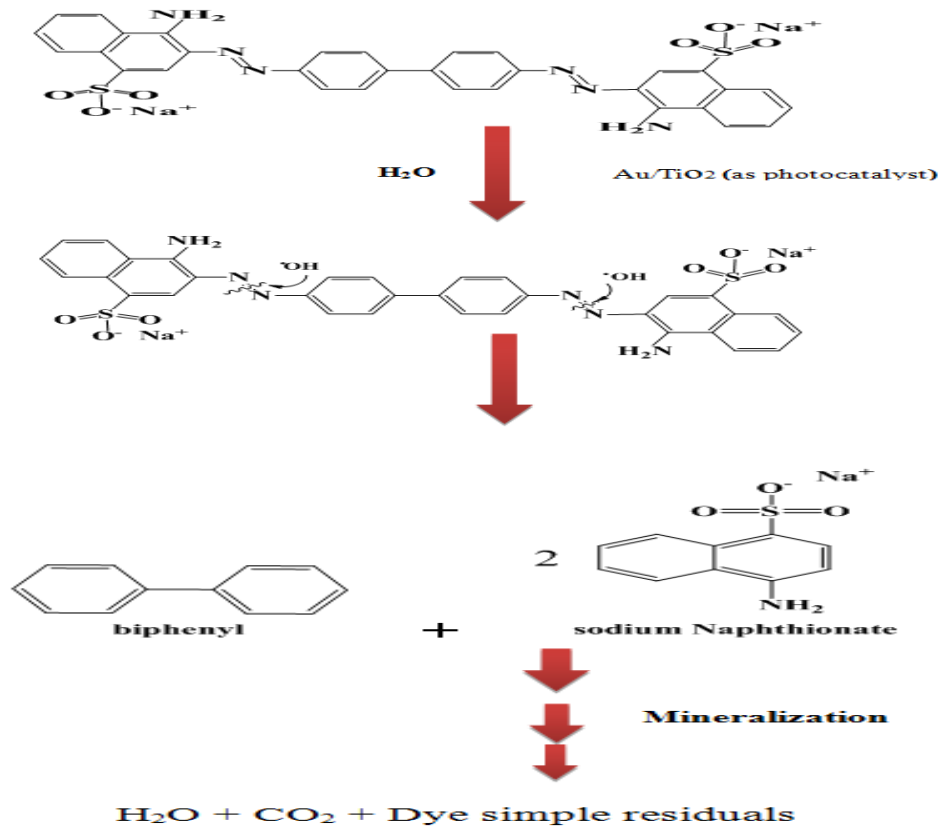


Figure 10- Degradation mechanism of Congo red dye.

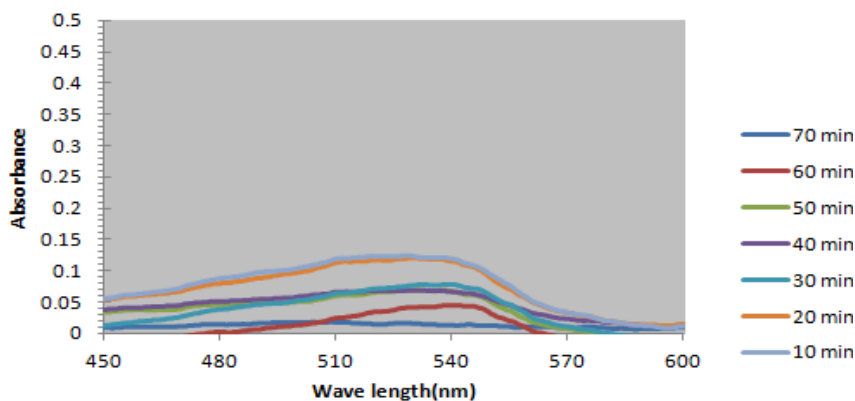


Figure 11-The peak absorbance of Congo red dye when exposed to UV light and green laser from a combined source.

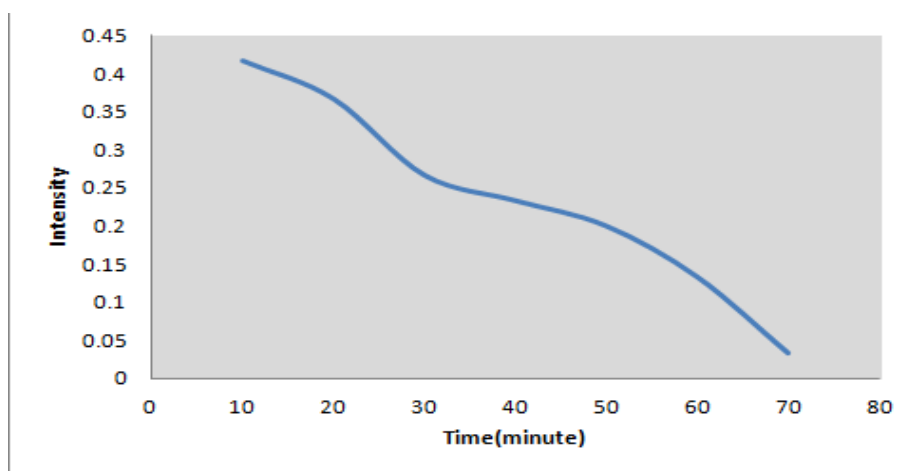


Figure 12- The peak intensity of when exposed to UV light and green laser from a combined source

Table 2-Absorbance and intensity peaks at different exposure times to UV light and green laser from the combined source.

Time (min)	Absorbance	Intensity
0	0.3	1
10	0.125	0.41
20	0.11	0.36
30	0.08	0.26
40	0.07	0.23
50	0.06	0.2
60	0.04	0.13
70	0.01	0.03



Figure 13-The shape of the dye during the purification stage using the combined source of UV light and green laser.

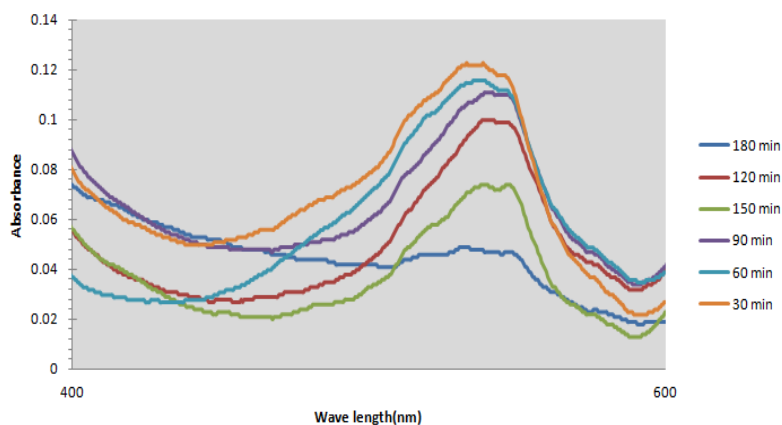


Figure 14- The peak absorbance of sunlight source

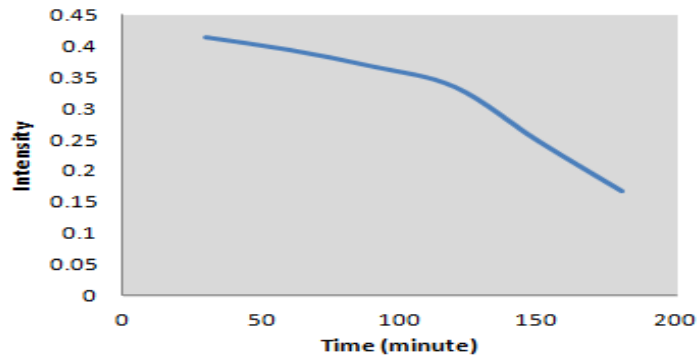


Figure 15- The peak intensity of sunlight

Table 3-The number of absorbance and intensity peak of sunlight source

Time (min)	Absorbance	Intensity
0	0.3	1
30	0.124	0.41
60	0.118	0.39
90	0.11	0.36
120	0.1	0.33
150	0.074	0.24
180	0.05	0.16

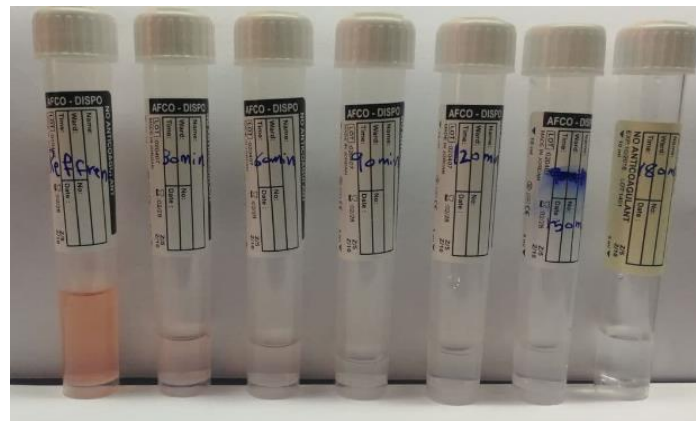


Figure 16-The shape of the dye during the purification stage of sunlight source

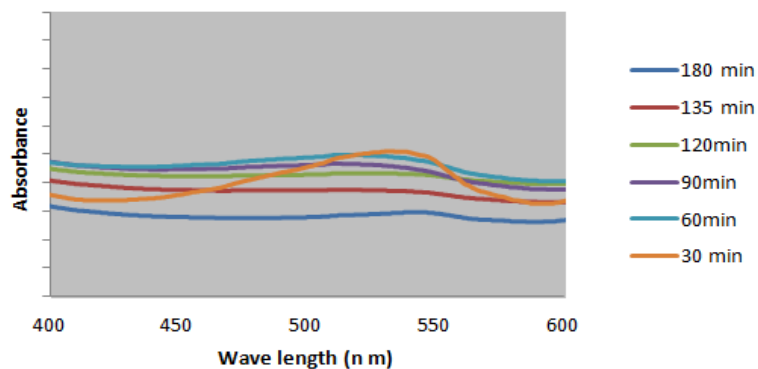


Figure 17-The peak absorbance of UV lamp source

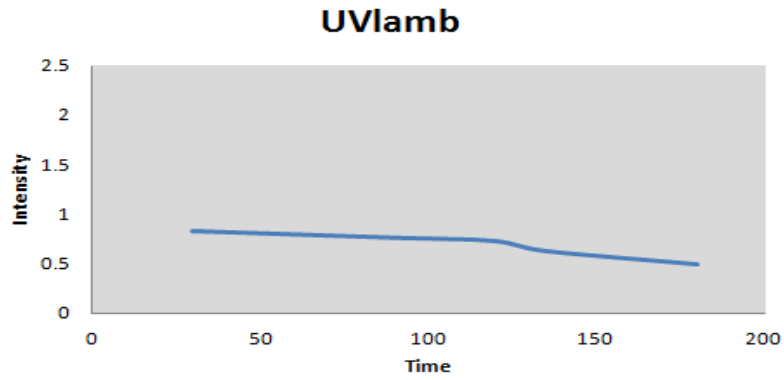


Figure 18-The peak intensity of UV lamp source

Table 4- The number of absorbance and intensity peak of UVlamp source

Time (min)	Absorbance	Intensity
0	0.3	1
30	0.25	0.83
60	0.24	0.8
90	0.23	0.76
120	0.22	0.73
135	0.19	0.63
180	0.15	0.5

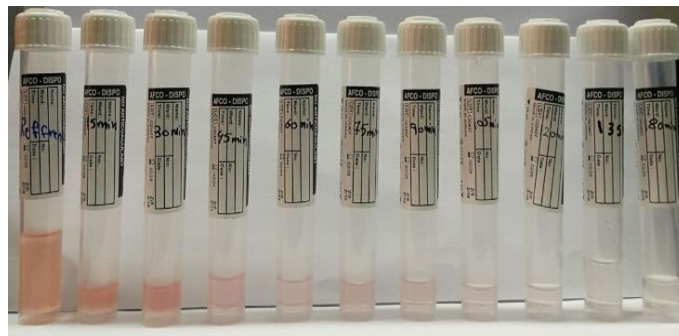


Figure 19-The shape of the dye during the purification stage of UVlamp source

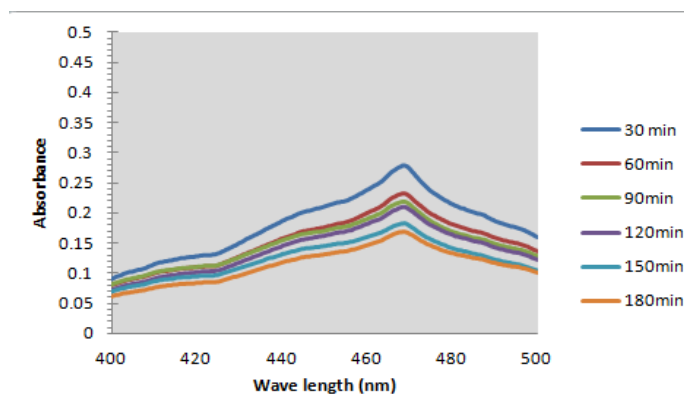


Figure 20- The peak absorbance of blue laser

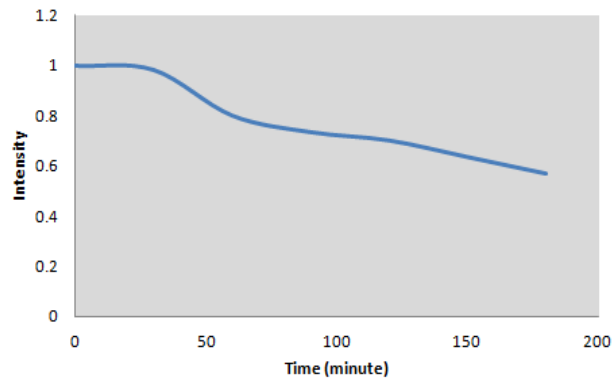


Figure 21-The peak intensity of green laser source of blue laser source

Table 5-The number of absorbance and intensity peak of blue laser source

Time (min)	Absorbance	Intensity
0	0.3	1
30	0.295	0.98
60	0.24	0.8
90	0.22	0.73
120	0.21	0.7
150	0.19	0.63
180	0.17	0.56

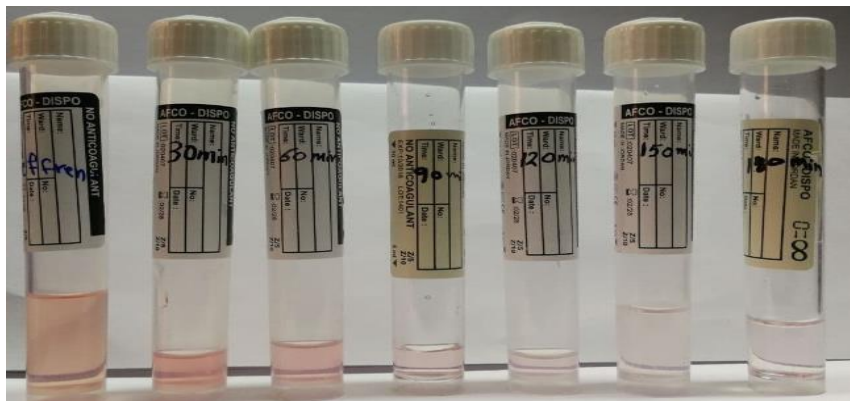


Figure 22- The shape of the dye during the purification stage of blue laser source

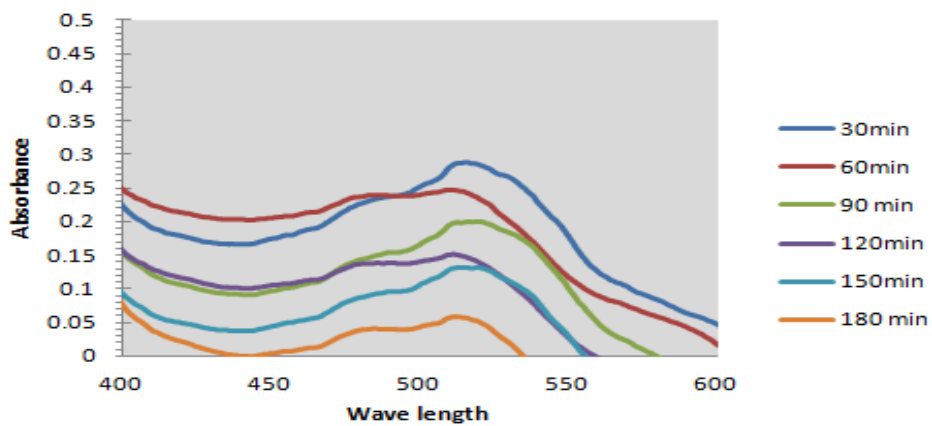


Figure 23- The peak absorbance of green Laser Source

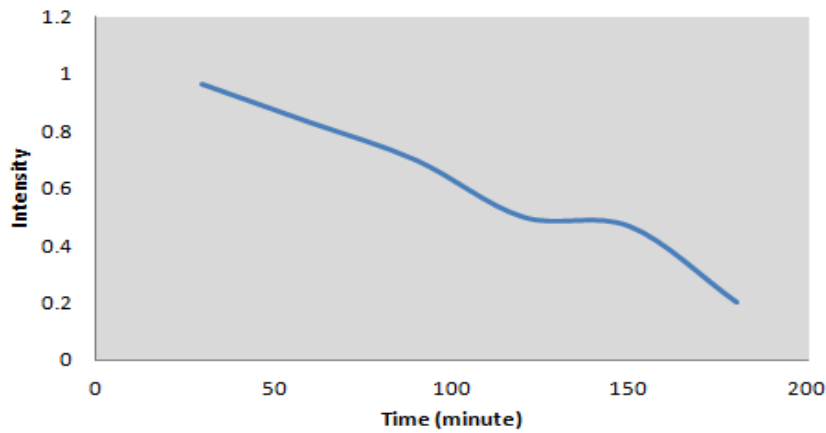


Figure 24- he peak intensity of green laser source

Table 6-The number of absorbance and intensity peak of green laser source

Time (min)	Absorbance	Intensity
0	0.3	1
30	0.29	0.96
60	0.25	0.83
90	0.21	0.7
120	0.15	0.5
150	0.14	0.46
180	0.06	0.2

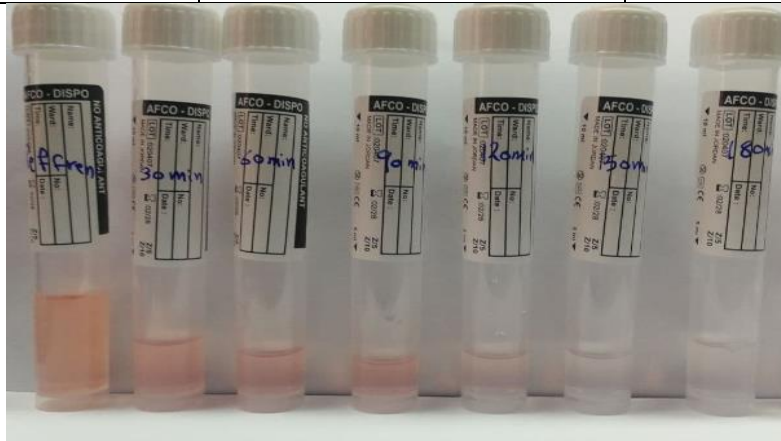


Figure 25- The shape of the dye during the purification stage of green Laser Source

Conclusions:

In this study, a purification disk was prepared from a mixture of (Au+TiO₂) nanoparticles with a PVA host. The pollutant dye solution was exposed to different types of light (sunlight, blue laser, green laser, UV, and combined UV light and green laser) at different exposure times. Results were tabulated and shown with corresponding graphs. It was concluded that the best result was obtained when using a combined UV light and green laser with an exposure period of about 70minutes, and the disk purified the polluted dye solution in 70 minutes which has led to a reduction in the purification period from 180 to 70minutes.

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