Effect of Degradation of Methylene Blue Dye (MB) by Using Erbium Oxide (Er_2O_3) NPs.

Lect. Dr. Hind Ahmed Jasim*, Assist. Lect. Farah Farman Abbass, Lect. Dr. Sarah A. Hamood*, Lect. Dr. Hind Mohammed Hassan*, Prof. Dr. Mohammed Sellab Hamza***

*Al-Esraa University College, Dept. of Biomedical Engineering, Baghdad / Iraq
**Alqalam University College, Dept. of Biomedical Engineering, Karkuk / Iraq

E-Mail: hind.ahmed@esraa.edu.iq,
farah.farman@alqalam.edu.iq,sarahashour@esraa.edu.iq,
hind.mohammed@esraa.edu.iq,mohammed.salab@esraa.edu.iq

تأثير التحفيز الضوئي لصبغة المثيلين الزرقاء باستخدام اوكسيد الاربيوم النانوي

م. د. هند احمد جاسم* – م. م. فرح فرمان عباس**-
م. د. سارة عاشور حمود*- م. د. هند محمد حسن*-
أ. د. محمد صلاب حمزة*
*كلية الاسراء الجامعة, قسم هندسة الطب الحياتي. بغداد \ العراق
**كلية القلم الجامعة, قسم هندسة الطب الحياتي, كركوك \ العراق

Abstract

Using varied concentrations of Er_2O_3 nanoparticles, photo catalytic degradation of methylene blue was investigated. The experiment was conducted with and without sunshine, as well as in the absence of a UV source. The existence of a UV source was also a factor in the research. UV–Visible spectroscopy is used to characterize the catalysts. By monitoring dye absorbance at regular time intervals and changing the dye concentration, the rate of dye degradation was tracked by spectrophotometry. The best degradation of the methylene blue dye was observed during a 5 hour irradiation time and in the presence of a UV source, according to the findings. Also discussed the characterization of Er_2O_3 nanoparticles.

Keywords: Er_2O_3 nanoparticles NPs; methylene blue; degradation; spectroscopy

المستخلص

تمت دراسة تراكيز مختلفة من جزيئات Er_2O_3 النانوية، وتم دراسة التحلل التحفيزي الضوئي لأزرق الميثيلين. أجريت التجربة مع أشعة الشمس وبدونها ، وكذلك في حالة عدم وجود مصدر للأشعة فوق البنفسجية. كان وجود مصدر للأشعة فوق البنفسجية عاملاً أيضًا في البحث. يستخدم التحليل الطيفي المرئي للأشعة فوق البنفسجية لتوصيف العوامل الحفازة. من خلال مراقبة امتصاص الصبغة على فترات زمنية منتظمة وتغيير تركيز الصبغة ، تم تتبع معدل تحلل الصبغة بطريقة القياس الطيفي. لوحظ أفضل تدهور لصبغة الميثيلين الزرقاء خلال فترة إشعاع 5 ساعات وفي وجود مصدر للأشعة فوق البنفسجية ، وفقًا للنتائج. ناقش أيضًا توصيف الجسيمات النانوية Er_2O_3

الكلمات المفتاحية: اوكسيد الاربيوم، تحفيز ضوئي، الصبغة الزرقاء، التحلل الضوئي

Introduction

Environmental contamination on a large scale, as well as a lack of sufficient, clean energy sources, has piqued interest in the development of environmentally friendly chemical technology, processes, and materials (Jassim, *et al.,* 2016- Hamza, *et al.*, 2016). A photo catalyst is described as a material that is activated by photon absorption and helps to speed up a reaction without wasting energy (Hassena, 2016). One of the processes that can be classified as advanced oxidation activities is photo catalysis. Under acceptable conditions, these activities can totally convert organic contaminants into harmless inorganic elements like CO_2 and H_2O (Shahrezaei, *et al.*,2012) The extra UV/Er_2O_3 activities could be due to the well-known fact that when Er_2O_3 is illuminated with UV/light, electrons are raised from the valance to the conduction bands of the semiconducting oxide, allowing electron hole pairs to form (Hamza, 2015 - Hamza, *et al.,* 2016) The valence band hole (h+ vb) potential has been shown to be positive, indicating that hydroxyl radicals can be produced at the surface. Furthermore, the electron/ conduction/band (ecb) was sufficiently negative to reduce the amount of oxygen molecule in the solution, potentially resulting in the formation of another hydroxyl radical series (Jassim , *et al.*2017- Abbas, *et al.,* 2020). The eclectic degradation of contaminants was second hopeful, area in photo-catalytic water treatment. Selective degradation might be beneficial, for mixtures of extremely, toxic contamination in minimal, concentrations and lower harmful chemicals in higher concentrations (Lazar, *et al.,*2012- Hamza, *et al.,* 2014) .Phenolic compounds have been shown to have high stability and environmental toxicity, as well as carcinogenic qualities, and may harm human health (Luenloi, *et al.*,2011- Choquette, *et al.*,2014). Compounds

with phenolic groups had been notify to have a high stability and high environmental toxicity with carcinogenic properties and may damage human health (Luenloi, *et al.,* 2011- Choquette, *et al.*,2014). Methylene MB dye is a crystalline powder that comes in a variety of colors. It's soluble in water, chloroform, and alcohol, but only slightly. It's a photoactive dye that belongs to the phenothiazine family. MB dye is a colorful substance that biologists employ as a dye to help them observe life beneath the microscope lens. It is an aniline-based dye for the textile industry. The use of erbium oxide nanoparticles as a catalyst for this esterification has several advantages, the most important of which is the reduction in reaction time. Minor advantages of using erbium oxide NPs include a straightforward synthesis method, high yield, and recyclability.The size and structure of Er_2O_3 NPs were investigated using X- ray powder diffraction (XRD) and scanning electron microscopy (SEM).

Materials and Methods

First / Materials

1. Materials

Fluka Company provided all of the materials for this project, which were used without additional purification.

2. Sample preparation

As a catalyst, Er_2O_3 nanoparticles were made (0.1 gram diluted in 100 ml methanol). A delicate balance was used to weigh erbium oxide Er_2O_3 and methylene. Methylene blue is a common catalytic test dye (0.05 g diluted with 500 ml methanol).

3. Set-up of Photo-catalytic

UV-source as a lamp (6 watt) of cylindrical form 22cm body length and 16cm arc length was employed as a photo source in the photocatalytic set-up. This lamp was placed in a sample container (a mixture of Erbium oxide and methylene blue) and then on a magnetic stirrer (to mix and scatter solutions prepared at high speeds for a long time) (Lazar, *et al.*, 2012) .

Second / Methods

1- Irradiation time effect

The temperature of the Er_2O_3 nanoparticles and methylene blue mixture was set to 25°C on a magnetic stirrer. Inside the sample container, the UV lamp was turned on. Irradiation times of 1, 2, 3, 4, and 5 hours were used. After each hour, the photo deterioration is measured. The absorbance of all of the samples was measured using a UV spectrometer.

2- Dye concentration effect

Methylene blue concentrations ranging from (0.1, 0.2, 0.5, 1, 1.5, 2) wt percent and 0.1wt percent from Er_2O_3 nanoparticles were utilized. For each concentration of methylene blue, samples were taken from the mixture without photo catalysts and after 15 minutes. The optical absorbance of the samples was measured using a UV-visible spectrophotometer.

3- Scanning Electron Microscopy (SEM)

SEM was used to investigate the morphology of Erbium oxide nanoparticles. The JEOL JSM-6390LV was used to record it. A secondary electron detector has been added to the SEM.

4- X-ray diffraction (XRD)

In Malaysia's UKM University Laboratories, the crystallinity of Er_2O_3 powder was investigated using the X-ray diffraction (XRD) technique. The crystallite size of Er_2O_3 nanoparticles was measured in order to examine their structural features.

Results and Discussion

Absences of daylight

The following are the findings with and without sunlight: Without being exposed to sunlight, Figure 1 depicts the relationship between optical absorbance and photocatalytic time. Because of the degradation process that occurred to sample, the values of absorbance increased as the photo degradation time was increased up to 4 hours. This behavior is consistent with (Lazar, *et al.*, 2012). Figure 2 depicts the absorption spectra of Er_2O_3 in the absence of sunlight, demonstrating that the lowest absorption occurs in the wavelength range (323-490nm) for various irradiative times.

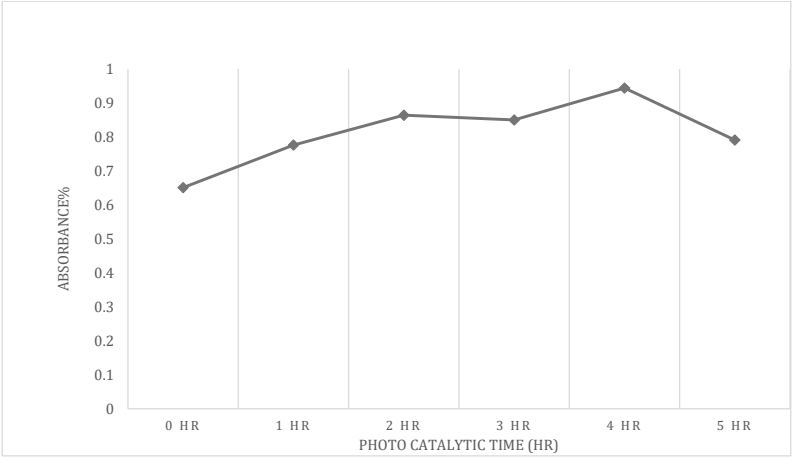

Figure (1): Photocatalytic time (hour) versus absorbance without daylight

The absorption spectra of Er2O3 nanoparticles in the absence of sunlight is shown in Figure 2. It can be demonstrated that for various irradiative times, the minimum absorption occurs in the wavelength range (323-490nm). Because more light is passed through the sample, the highest intensities in a transmission spectrum are at wavelengths where the absorption is weakest. The highest intensities in an absorption spectrum are found at wavelengths where the absorption is strongest. Some of the light energy is absorbed when the electron is promoted to a higher energy orbital when sample molecules are exposed to light with an energy that matches a likely electronic transition within the molecule. Some of the light energy is absorbed when the electron is promoted to a higher energy orbital when sample molecules are exposed to light with an energy that matches a likely electronic transition within the molecule. The wavelengths at which absorption occurs, as well as the degree of absorption at each wavelength, are recorded using an optical spectrometer. As with the isoprene spectrum, the resulting spectrum is shown as a graph of absorbance vs wavelength. Because isoprene is colorless, it does not absorb light in the visible spectrum, hence this section of the spectrum is not represented on the graph. Absorbance is commonly measured in units of 0 (no absorption) to 2 (99% absorption) and is clearly specified in relation to spectrometer operation.

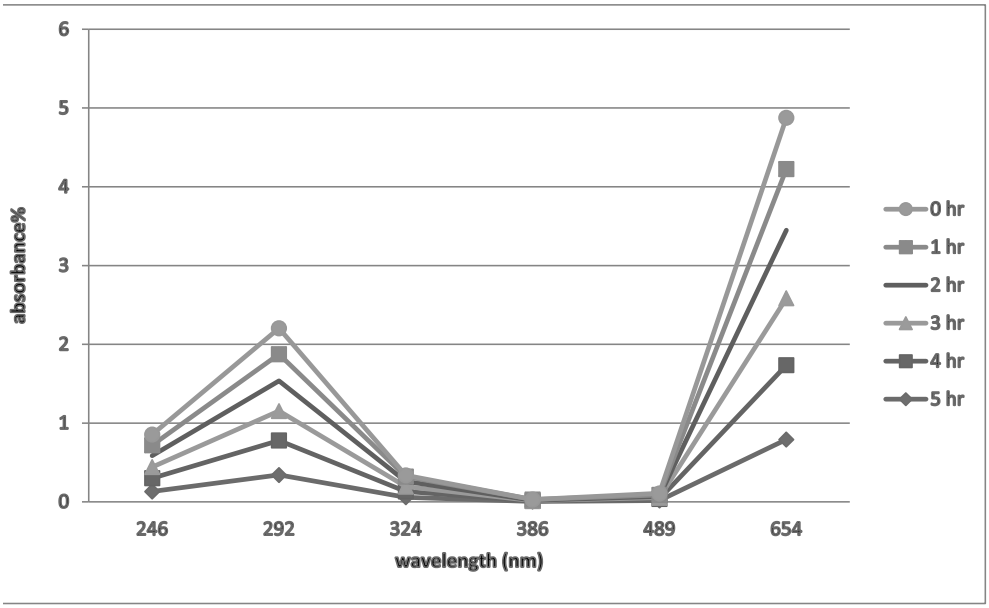

Fig. (2): UV–visible spectrum of Er2O3 NPs without daylight.

Presence of daylight

Figure 3 demonstrates the photocatalytic degradation of different phenols in the presence of Er2O3 nanoparticles when exposed to sunshine. The inclusion of Er2O3 nanoparticles was explored as a key factor in the degrading process improvement. Within 2 hours of irradiation time and considering the optimum catalyst loading, higher degradation efficiency was discovered. After 120 minutes of irradiation time with Er2O3 nanoparticles, another peak can be seen after a 5 hour irradiation duration. When the role of sunlight is taken into account, the improvement in phenolic compound degradation can be concluded (Fig. 3).

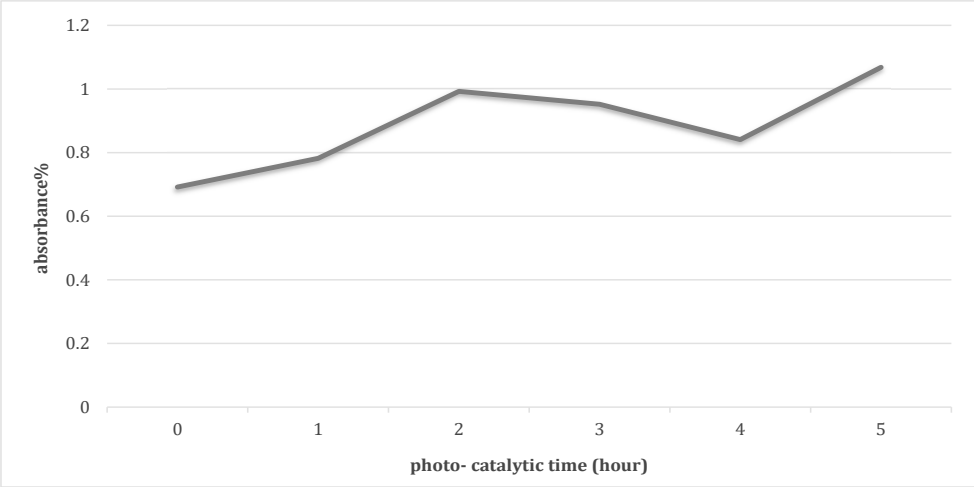

Fig. (3): A Function of irradiation time with daylight shows the degradation of MB.

As demonstrated in Figure 4, the rate of reaction increases and reaches its maximum after four hours. It might be explained by increasing the UV source's operation period, which increased the number of photons per unit area incident on the sample, resulting in a high rate of deterioration in the mixture of Erbium oxide and methylene blue, which increased the absorption value (Dakhil, *et al.,* 2019) .

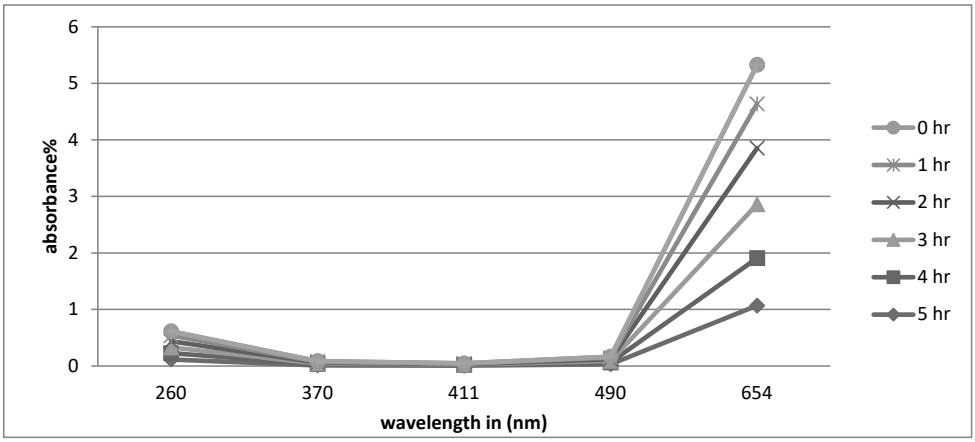

Fig. (4): UV-visible spectrum of Er2O3 NPs with daylight.

Impact of methylene blue MB Concentration

The methylene blue effect was studied in two situations with / without UV irradiation as follows:

Impact of methylene blue MB concentration without irradiation

As the MB dye concentration rises, the absorbance rises as well, as illustrated in Fig (5). When the concentration was adjusted from (0.5 to 1) wt percent, the highest change in absorbance was observed. Using an ultraviolet visible spectrometer, the effectiveness of MB dye degradation was assessed. Pinnacles were found between (600 and 700) nanometers, indicating the presence of the Methylene blue degradation. As indicated by Beer-Lambert Law, Methylene blue fixation is straightforwardly corresponding to its absorbance (Ramli, *et al.*, 2014)

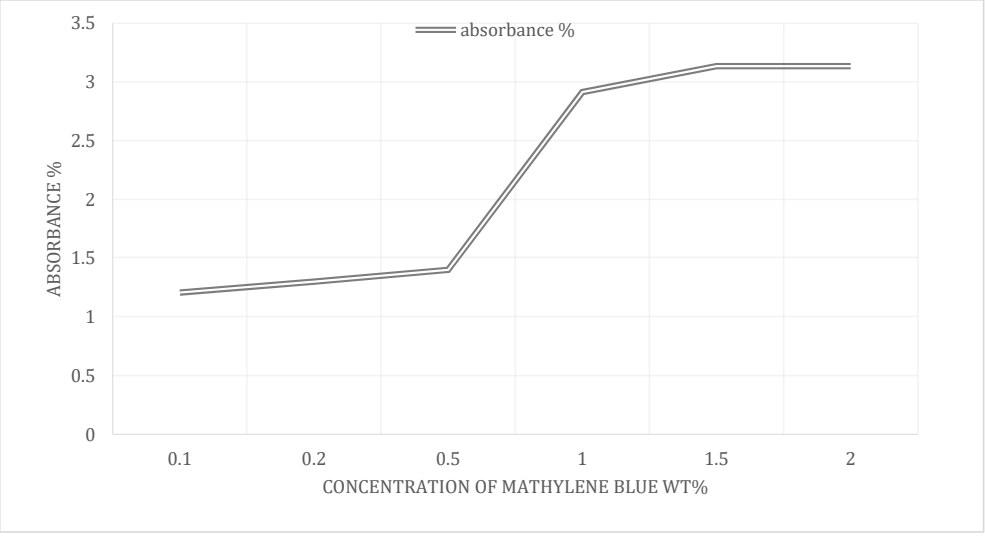

Figure (5): The absorbance vs. with MB dye concentration at wavelength of 654nm without irradiation

Impact of MB dye concentration with irradiation

The absorption spectra range of MB dye at various concentrations with irradiation is depicted in Figure (6). When the quantity of methylene blue is raised, the value of absorbance expands after 15 minutes of irradiation, as shown in the figure. When the concentration was adjusted from (0.5-1) wt percent, the most dramatic expansion in absorbance was seen. This can be explained by the fact that when dye concentrations rise, the reaction average rises as more molecules are added. The absorbance value remains constant at (3.135 percent) as the dye concentration is increased, causing reaction retardation due to an increase in the frequency of collisions between MB dye molecules, while collisions between dye and OH radicals decrease. As a result, the proportion of people who reacted decreased (Karunakaran, *et al.*, 2014- Karunakaran, *et al.,* 2004).

The major rate of debasement is seen at the lit side, where the power of light is much greater than on other sides. As a result of the restriction in light infiltration, the debasement method for MB dye with higher focus diminishes at sufficiently significant distances from the light source or the response zone.

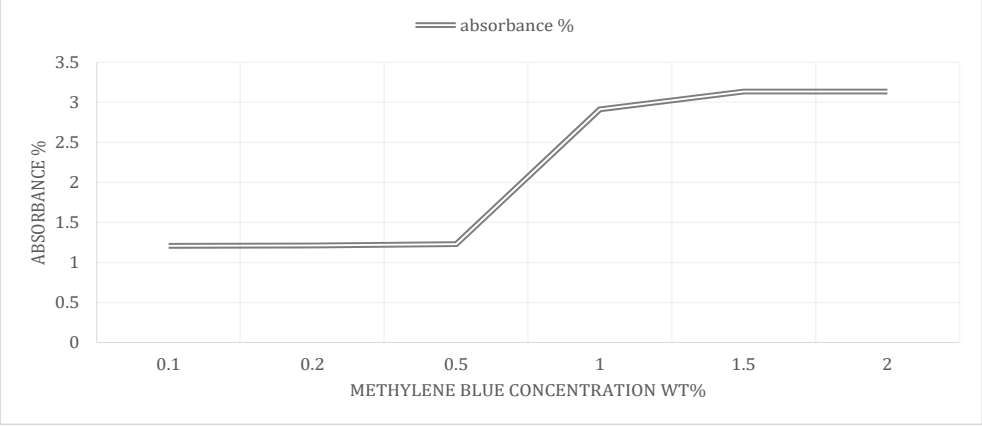

Fig. (6): The absorbance as a function of MB dye concentration at wavelength 654nm and irradiation time of 15 minute.

The primary of MB dye concentration build the response between the oxidizing species and MB dye molecules additionally expands, prompting an upgrade in the decolonization rate. Actually, the corruption productivity of the MB dye declines when the MB dye concentration increments as appeared in Fig. (7). The presumed motivation for this behavior was the formation of hydroxyl at high MB dye concentrations and the MB dye's UV-screening effect. Because the convergences of OH and O_2 are declining, a lot of UV may be consumed by the MB dye atoms rather than the Er_2O_3 nanoparticles at high dye concentrations, reducing the productivity of the synergist reaction (Baeissa, 2016). Figures 8 and 9 shows the absorption spectrum of erbium oxide before and after irradiation after 15 minutes at different concentration.

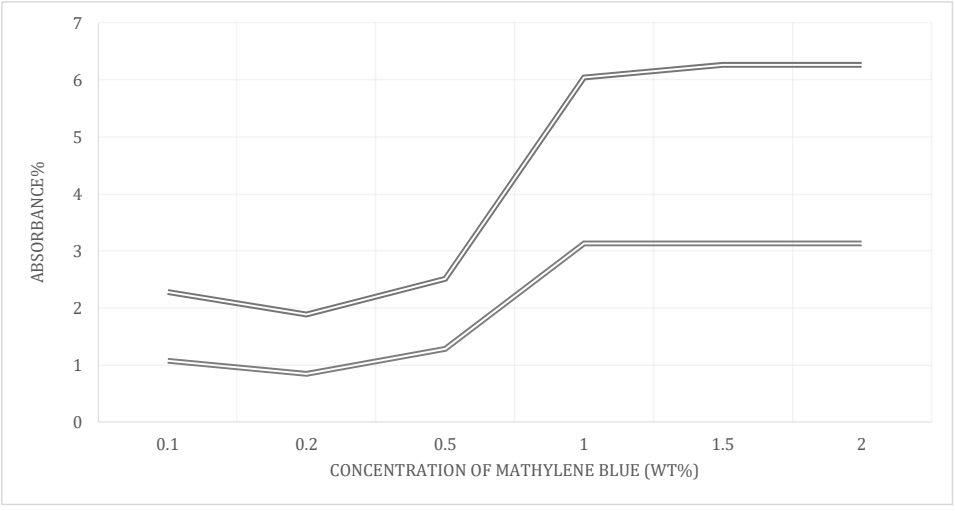

Figure (7): The methylene blue dye concentration vs the absorbance, without irradiation (blue line) and with irradiation (red line).

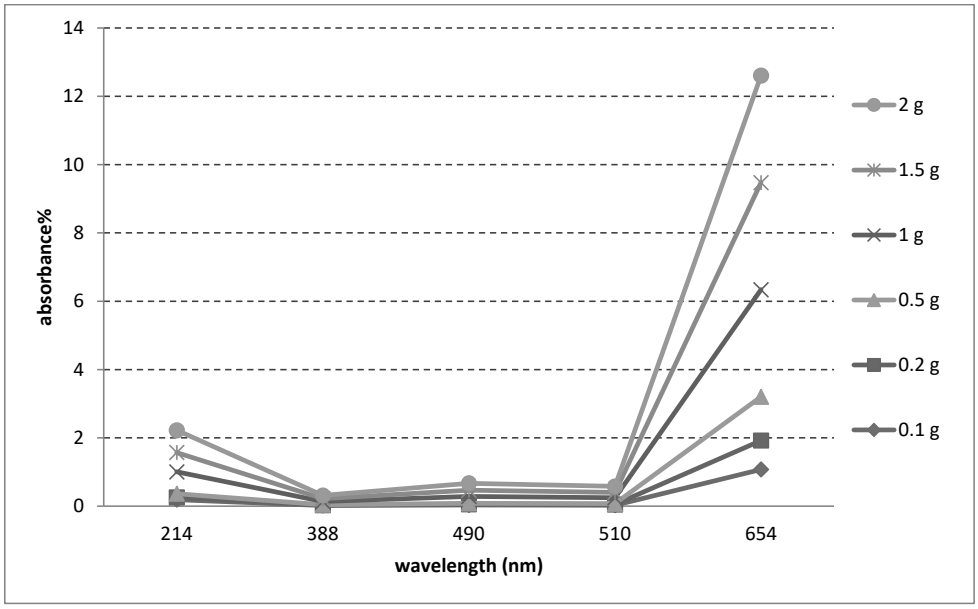

Figure (8): UV–VIS spectrum of Er2O3 nanoparticles before irradiation.

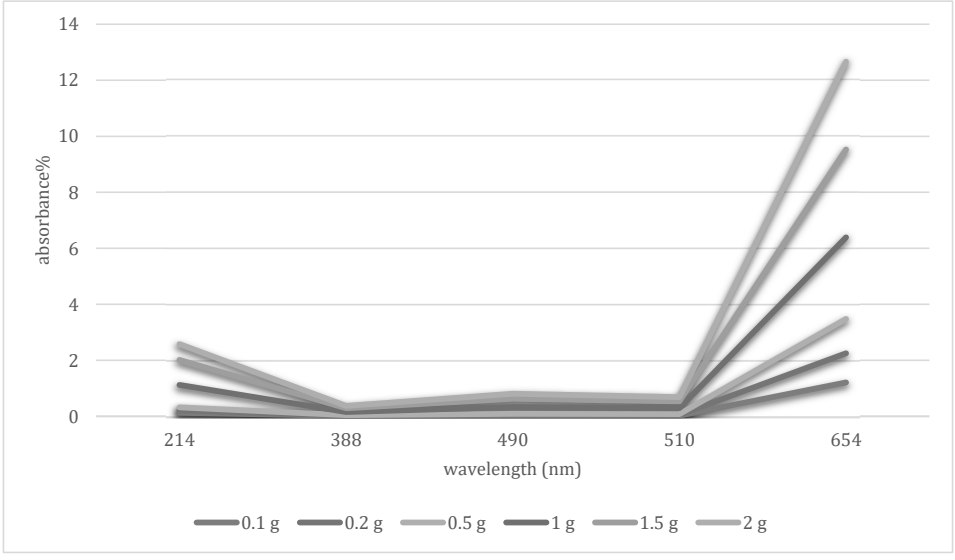

Figure (9): UV–VIS spectra of Er2O3 nanoparticles at irradiation time of 15 minute.

The results of Morphology

Figures (10A, 10B, 10C, 10D) show SEM micrographs of the synthesized samples, which reveal the morphology and dispersion of erbium oxide Er_2O_3 NPs. The average size of the Nanoparticles was found to be (16nm) and they looked to be uniform.

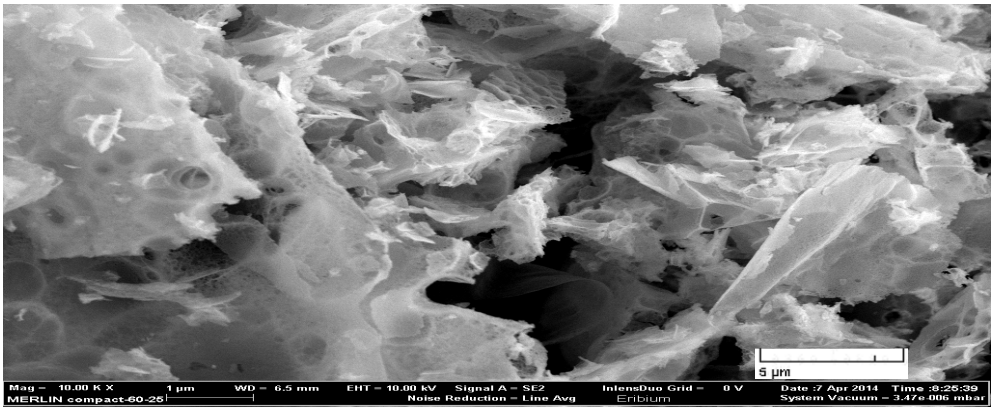

Figure (10A): Erbium oxide particles distribution shows in SEM image.1000KX.

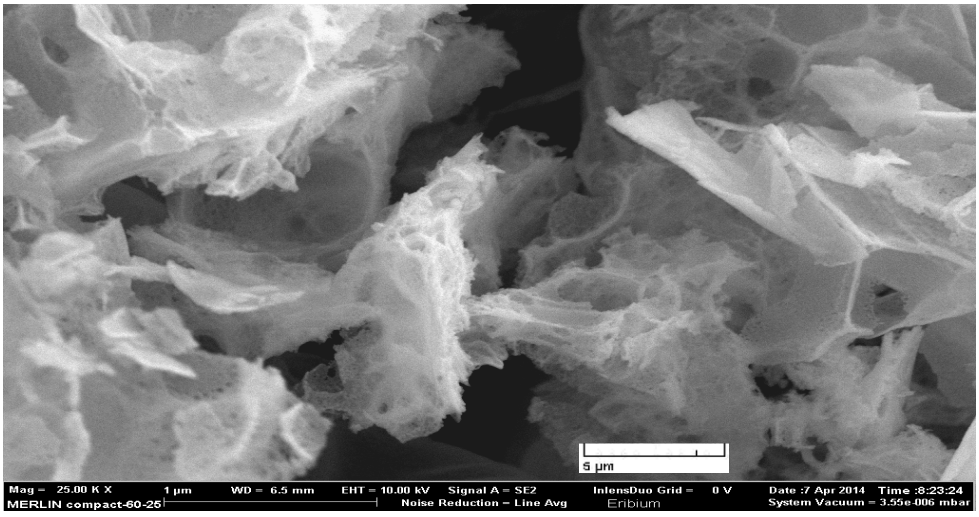

Figure (10B): Erbium oxide particles Shows an even distribution in SEM (2500KX).

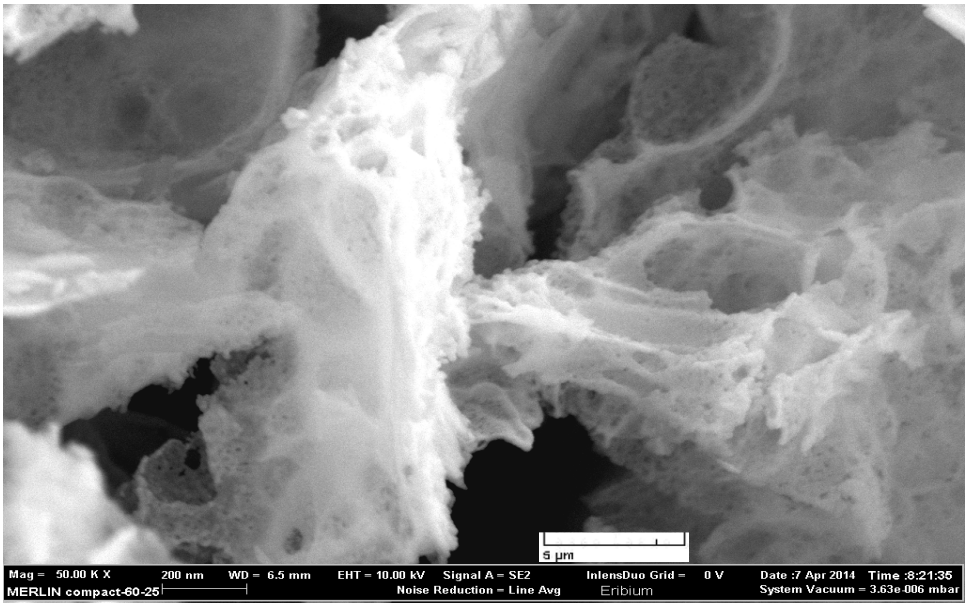

Figure (10C): The erbium oxide Nano-sized in SEM image (5000KX).

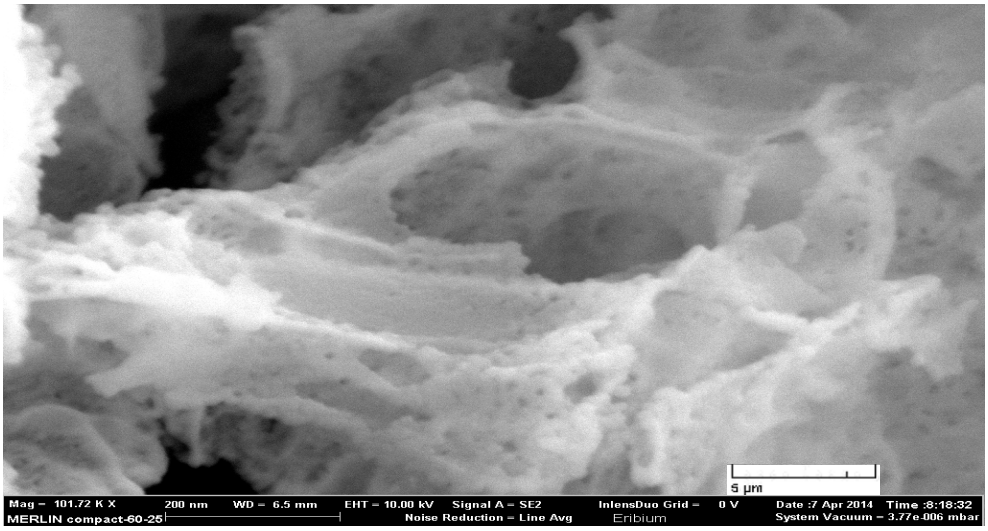

Figure (10D): The erbium oxide Nano-sized in SEM image (101.72KX).

The results of XRD

The synthesis of Erbium oxide nanoparticles was explained using X-Ray Diffraction. Each reflection was well indexed to the cubic phase of erbium oxide Er_2O_3 NPs, as shown in Fig. (11), X-Ray Diffraction boundary of erbium oxide Er_2O_3 NPs with a space group of I 21 3 (199) and cell boundaries of a=10.540. The lack of contaminants and high crystallinity can be deduced from the XRD pattern's exact number and sharpness of peaks. It also demonstrates that the product is one step. The results of SEM and X-ray diffraction, respectively, have been analyzed. Erbium

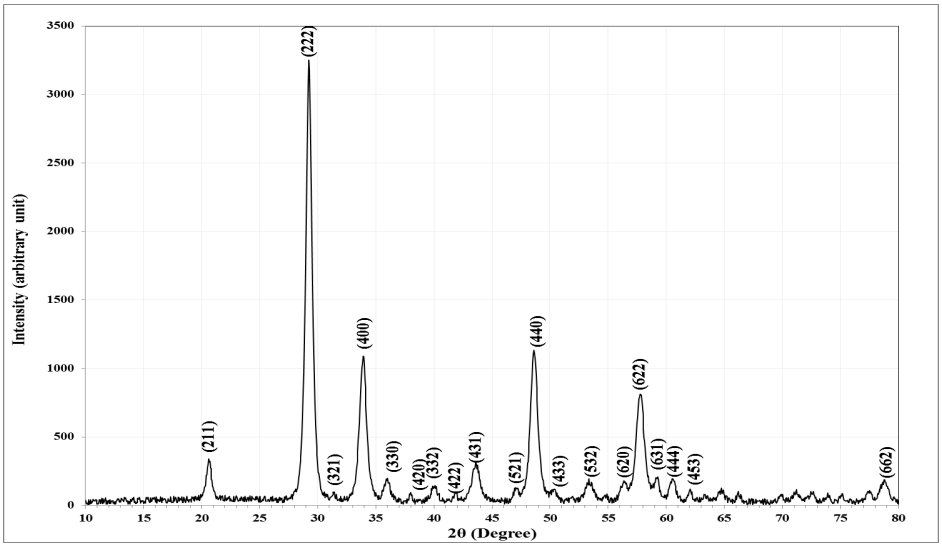

Figure (11): X-Ray Diffraction of Er2O3 NPs.

Table 1: X-Ray Diffraction parameter of Er2O3 NPs.

2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	Phase	Card No.	δ
20.6330	0.4972	4.3013	16.2	(211)	4.3029	Cub. Er_2O_3	96-101-0593	0.0004
29.2389	0.6119	3.0519	13.4	(222)	3.0426	Cub. Er_2O_3	96-101-0593	0.0031
31.4191	0.3060	2.8449	27.0	(321)	2.8169	Cub. Er_2O_3	96-101-0593	0.0100
33.9052	0.6884	2.6418	12.1	(400)	2.6350	Cub. Er_2O_3	96-101-0593	0.0026
35.9706	0.6120	2.4947	13.7	(330)	2.4843	Cub. Er_2O_3	96-101-0593	0.0042
37.9978	0.2677	2.3661	31.4	(420)	2.3568	Cub. Er_2O_3	96-101-0593	0.0040
40.0249	0.6119	2.2509	13.8	(332)	2.2471	Cub. Er_2O_3	96-101-0593	0.0017
43.6203	0.8032	2.0733	10.7	(431)	2.0671	Cub. Er_2O_3	96-101-0593	0.0030
47.0626	0.4208	1.9294	20.6	(521)	1.9243	Cub. Er_2O_3	96-101-0593	0.0026
48.6308	0.7267	1.8708	12.0	(440)	1.8632	Cub. Er_2O_3	96-101-0593	0.0041
50.3137	0.5737	1.8121	15.3	(433)	1.8076	Cub. Er_2O_3	96-101-0593	0.0025
53.3736	0.7650	1.7152	11.6	(532)	1.7098	Cub. Er_2O_3	96-101-0593	0.0031
56.3187	0.6120	1.6322	14.7	(620)	1.6665	Cub. Er_2O_3	96-101-0593	0.0206
57.7722	0.8032	1.5946	11.3	(622)	1.5890	Cub. Er_2O_3	96-101-0593	0.0035
59.1874	0.4972	1.5598	18.4	(631)	1.5540	Cub. Er_2O_3	96-101-0593	0.0037
60.5643	0.6120	1.5276	15.0	(444)	1.5213	Cub. Er_2O_3	96-101-0593	0.0041
62.0560	0.4590	1.4944	20.2	(543)	1.4906	Cub. Er_2O_3	96-101-0593	0.0026
78.7705	0.8032	1.2140	12.8	(662)	1.2090	Cub. Er_2O_3	96-101-0593	0.0041

Conclusion

Oxide of erbium under daylight, Er2O3 nanoparticles improve the adequacy of phenolic compound debasement for (methylene blue dye) or, in other words, the removal of mixture polluted by methylene blue MB dye. The improved photo synergist reactivity of Er2O3 NPs is due to photo-catalytic action under light irradiation and UV. The Er2O3 nanoparticles have reached a stage where they are ready to swallow a large amount of photo-catalytic in the visible light area, resulting in appropriate photochemical degradation responses. The results of the XRD and SEM have been analyzed. The production of erbium oxide Er2O3 NPs was studied using X-Ray Diffraction. Each reflection was well indexed to Er2O3 NPs cubic. Spectroscopy was used to characterize erbium oxide. Erbium oxide Er2O3 NPs have a normal crystallite size of 16 nanometers.

References

- A. Pandey, S. Kalal, C. Ameta, R. Ameta, S. Kumar and P. B. Punjabi,(2015) Journal of Saudi Chemical Society, 19, 528.
- C. Karunakaran, S. Senthilvelan, S. Karuthapandian and K. Balaraman,(2004). Catal Commun,
- ES Baeissa,(2016). Photocatalytic Degradation of Methylene Blue Dye Under Visible Light Irradiation Using In/ZnO Nano-composite, Frontiers in Nano-science and Nanotechnology, Volume 2(5),1-5.
- F. Shahrezaei, A. Akhbari, A. Rostami,(2012). International Journal of Energy and Environment, 3,267.
- Hind A Jassim, Abdulhadi Khadhim, Ahmed A Al-Amiery,(2016). Photo Catalytic Degradation of Methylene Blue by Using CuO Nanoparticles, Int. J. Computer. Appl. Sci.
- H.A. Jassim, A. Khadhim, A. Al-Amiery,(2017). Photovoltaic Degradation of Methylene Blue Dye Using CuO Nanoparticles Prepared by SOL–GEL Method, International Journal of Computation and Applied Sciences IJOCAAS, Volume2, Issue 2.
- H. A. Abbas, Rabab A Nasr, Aya Khalaf , (2020).Photo-catalytic Degradation of Methylene Blue Dye by Fluorite Type Fe 2 Zr 2- x W x O 7 System Under Visible Light Irradiation, Ecotoxicology. Environ. Saf.,196,110518.
- Haile Hassena,(2016). Photocatalytic Degradation of Methylene Blue by Using Al2O3/Fe2O3 Nano Composite Under Visible Light, Mod. Chem. Appl., Vol. 4 Issue 1.
- Mohammed S. Hamza, Suaad Salim Shaker. khitam Salim Shaker.(2016). Study of Morphological Properties of ZnO Nano Powder. J. of Engineering, Volume 22, Number 4.
- Mohammed S. Hamza, Fadhil A.Chyad, Zainab I. Dhary,(2015). Studding the Dielectric Properties, Microstructure and Morphology of Doped Nanoferrite Composition, 4(2).
- Mohammed S. Hamza, Fadhil A.Chyad, Zainab I. Dhary.(2016). Physical and Mechanical Properties of Synthesized Doped Nanoferrite, Al-Khawarizmi Engineering Journal. Vol.12,No.2,10-17.
- Mohammed S. Hamza,(2014). Production of Micro and Nano Zirconia Particle by Pulsed Laser ablation, Journal of Engineering and Technology, University of Technology, Vol.32,part (A),No.10.
- M. Lazar, S. Varghese and S. Nair,92012) Catalysts, 2,572.
- M. Choquette-Labbé, W. A. Shewa, J. A. Lalman and S. R. Shanmugam,(2014). Water 6,1785.
- Rifat Mohammed Dakhil, Tayser Sumer Gaaz, Ahmed Al-Amiery, Mohd S. Takriff , and Abdul Amir H. Kadhum,(2019). Synthesis and Characterization of Erbium Trioxide Nanoparticles as Photocatalyzers for Degradation of Methyl Orange Dye , Drink. Water Eng. Sci., 12, 15–21.

- T. Luenloi, B. Chalermsinsuwan, T. Sreethawong and N. Hinchiranan,(2011). Desalination, 274, 192.
- Zatil Amali Che Ramli, Nilofar Asim, Wan N. R. W.Isahak, Zeynab Emdadi, Norasikin Ahmad-Ludin, M. Ambar Yarmo, and K.Sopian,,(2014). Photocatalytic Degradation of Methylene Blue under UV Light Irradiation on Prepared Carbonaceous TiO2 , The Scientific World Journal, Article ID 415136.