Fe_2O_3@SiO_2 Nanoparticles: Synthesis and characterization for Photodegradation Applications

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Abstract
Iron oxide (Fe_2O_3), silicon oxide (SiO_2), and Fe_2O_3@SiO_2 nanomaterials were synthesized by pulsed laser ablation technique in liquids (PLAL) for photodegradation of methyl orange dye. Field Emission scanning electron microscopy (FESEM) has been used to investigate the surface morphology of the nanoparticles. From the images of (FESEM), it can be noticed that the particles have sizes within nanometer range and they have sphere- like shaped. The optical characteristics were examined using UV-Vis spectrophotometer. UV-visible results of the prepared materials showed that the highest absorbance has been obtained for the highest concentrations which were prepared using the highest number of pulses. The absorbance edges of Fe_2O_3, SiO_2 and Fe_2O_3 @SiO_2 nanoparticles lie at (275 nm) , (250 nm), and (260 nm) respectively. Adsorption Activity of the synthesized Fe_2O_3, SiO_2, Fe_2O_3@SiO_2 nanomaterials confirms that Fe_2O_3 photocatalyst is more efficient which has the efficiency of (94.49%), while the efficiency of SiO_2 reaches to (73. 14%) and the efficiency of Fe_2O_3@SiO_2 is (90. 72%).
Keywords: silicon oxide, iron oxide, photodegradation, FE-SEM

1. Introduction

A core-shell nanoparticle is a kind of nanostructure that consists of two kinds of material one at the core and the other is the shell. These structures are monodispersed and adjustable comparing with the traditionally supported catalyst. The core-shaell nanomaterials can have the advantage of minimized agglomeration. In addition, the particle size and structure can be controlled by manipulating the surface [1]. Core-shell nanoparticles can provide modern methods to synthesis nanomaterials for photodegrading pollutants and other sensing devices, since they have changeable surface and optical properties [2-3].
Metal oxide nanoparticles have explained their enormous interest in solar cell optoelectronics, sensing, catalysis, as well as other applications due to their exceptional characteristics, in comparison with the bulk [4]. Iron oxide is a common catalyst in the chemical industry, as well as in gas sensors, pigments, and photoelectrochemical cells. The nanostructures of γ -Fe_2O_3 in particular frequently exhibit unusual phase-, size-, and shape-dependent physical and chemical properties that are both technologically important and scientifically interesting [5]. Despite this, γ -Fe_2O_3 is a ferromagnetic substance which is iron oxide in low-temperature phase, and when heated to high temperatures, it rapidly transforms into the more stable phase, hematite (α -Fe_2O_3). Because hematite's antiferromagnetic character might adversely damage the desired ferromagnetic behavior of the final nanocomposites [6], a SiO_2 shell would help these magnetic nanoparticles in terms of functionalization and biocompatibility [7-8]. SiO_2 is a fascinating substance with well-ordered nanopores and a lot of surface area Because of its large pore diameter and vast surface area; it is frequently employed as a good supportive agent. Other benefits, such as facile surface modification, the ability to recover from the reaction mixture, and the ability to reuse the catalyst, are also crucial considerations from an economic and environmental standpoint [9].
Methyl orange (MO) is usually used as a coloring agent in many areas. Its degradation methods must be investigated due to the toxic effects and the slow decomposition upon disintegration when discharged into water bodies, posing several health risks, [10]. The usage of adsorption to remove colors has a variety of advantages, including fast action and adaptability. The sorbents have large, well-defined, and well-accepted surface areas. In this work, Fe_2O_3, SiO_2 and Fe_2O_3 @SiO_2 nanoparticles have been synthesized by pulsed laser ablation in liquids as photodegradation catalysts of methyl orange dye and the degradation efficiency of Fe_2O_3, SiO_2 and Fe_2O_3 @SiO_2 nanoparticles were studied.

2. Experimental

(Fe_2O_3, SiO_2, Fe_2O_3@SiO_2) nanomaterials with purity (99.99%) were prepared by pulsed laser ablation in liquids at room temperature with a wavelength of 1064 nm, pulse energy (260 m J) of (6 Hz). The pellets of all prepared materials were about of 5 gm. The

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number of laser pulses have been used for preparing (Fe_2O_3, SiO_2) were (300, 400, 500) pulses. The concentration of core shell Fe_2O_3@SiO_2 was prepared using number of pulses of 500 for (Fe_2O_3), and for SiO_2 the number of pulses were (300, 400, 500). Figure (2-1) demonstrates the laser ablation of the targets immersed in distilled water. The absorption spectra of the nanoparticles were measured using UV-VIS spectroscopy. Field Emission - Scanning Electron Microscope (FE-SEM) is used to examine the morphology of the prepared material. Various concentrations of methyl orange were used to study the photodegradation of the synthesized materials ranging from ($1*10^{-3}$, $1*10^{-4}$, $5*10^{-4}$, $1*10^{-5}$, $2.5*10^{-5}$, $5*10^{-5}$, $7.5*10^{-5}$). The adsorption of the nanoparticles was evaluated by removing the colour of methyl orange. 2ml of (Fe_2O_3,SiO_2, Fe_2O_3@SiO_2) was added to 1ml of methyl orange (MO) solution.

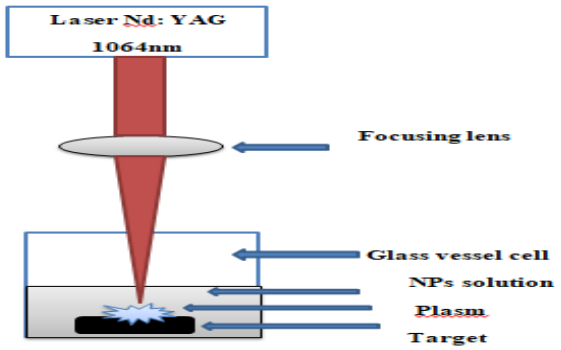

Fig. 2-1: Experimental setup for nanoparticles synthesis by PLAL process

3. Results and Discussion

3-1 FE-SEM measurements

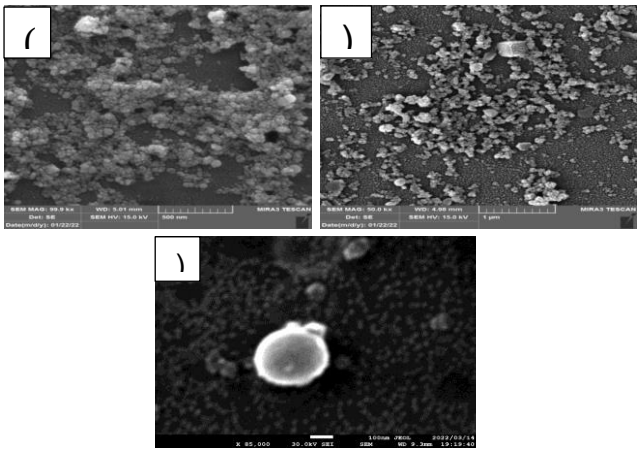

Figure 3-1: FE- SEM images For samples: (a) Fe_2O_3,(b) SiO_2, (c)Fe_2O_3 @SiO_2

Figure (3-1) shows the FE-SEM of Fe_2O_3, SiO_2 and Fe_2O_3 @SiO_2 nanoparticles. In the fig (3-1- a), the FE-SEM of Fe_2O_3 with high concentration 500p, the size of nanoparticles is about 80 nm. As the pluses number increases, the particles shapes become more like spherical shape [11], In addition, the size of the SiO_2 is about 100 nm as shown in (3-1- b), due to the target of Fe_2O_3 inside the liquid is more fragile than SiO_2, so this behaviour leads to extirpate the nanoparticles from the top of the target surface is easier than SiO_2. The FE-SEM image of Fe_2O_3@SiO_2, (500P@300P), indicates that the size of core is about 80 nm and the thickness of the shell is about 20 nm, and these sizes for each core and shell depend on the number of the laser pulses on the targets. The shell thickness in this style has a good optical property due to the ability of the photon to reach to the core of nanoparticles when the light interaction with surface of nanoparticles, as shown in the fig (3-1-c).

3-2 Optical properties

The optical properties of Fe_2O_3 ,SiO_2 and Fe_2O_3 @SiO_2 have been studied with range of (300 -900 nm) using spectrophotometer at room temperature. The absorbance spectrums of Fe_2O_3 ,SiO_2 ,and Fe_2O_3 @SiO_2 have been showed in Figures (3-2),(3-3),and(3-4) with three different concentration for each samples according to number of laser pulses. As shown in the figures, the absorbance spectrum increases as increasing the concentration of nanoparticles within the liquid along the bath of the incident light [12]. The absorbance edges of Fe_2O_3 ,SiO_2 and Fe_2O_3 @SiO_2 nanoparticles lie at (275 nm) , (250 nm), and(260 nm), respectively. As increasing the concentration of nanoparticles in the solution, the absorbance edges have blue shift.

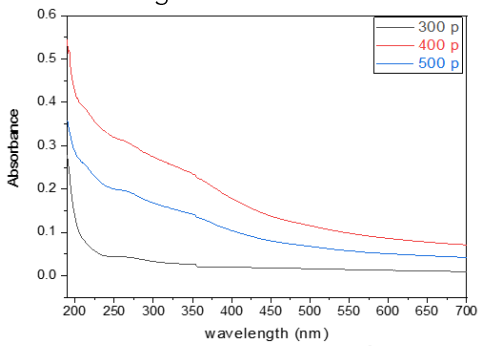

Figure 3-2: absorption spectra for Fe_2O_3

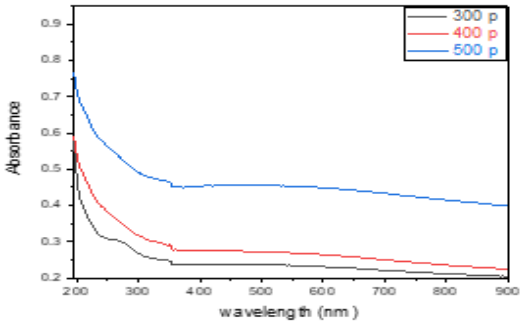

Figure 3-3: absorption spectra for SiO_2 .

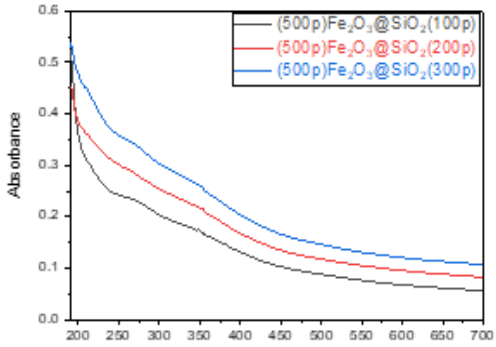

Figure 3-4: absorption spectra for Fe_2O_3 @ SiO_2 .

3-3 Adsorption Activity of the synthesized Fe_2O_3, SiO_2 and Fe_2O_3 @SiO_2 nanomaterials

Several works have been done to characterize the photocatalytic activity of the synthesized of Fe_2O_3 ,SiO_2 and Fe_2O_3 @SiO_2 nanomaterials, which involved removing some dyes from its aqueous solution by adsorption them onto the surface of the synthesized nanomaterials. The relation (1-3) has been used to estimate the photocatalytic degradation efficiency [13].

(1-3) ---------- PDE % = $\frac{A_o - A_t}{A_o} \times 100$

Where: A_o and A_t is the reactant concentration at t = 0 and t = t

3-4 The effect of light intensity on photodegradation of Methyl orange dye using Fe_2O_3 nanomaterial:

Different experiments were accomplished for studying the influence of irradiance on photocatalytic degradation of MO dye via changing the light intensity range (300P, 400P, and 500P). The results in Table 3-1 and Figures (3-5, 3-6) show that the photocatalytic degradation of dye increases gradually with light intensity. Higher intensity means larger odds of photon activation on the catalyst surface, hence stronger photocatalytic action. However, additional intensity increase does not affect activation number. This limits the rate of reaction rate even at high optical irradiance levels [14,15].

Table (3-1): chang of A_t/A_0 through irradiation-time on light intensity of laser for Fe_2O_3.

500P	400P	300P	light intensity of laser
A_t/A_0			Time (min)
1	1	1	0
0.92	0.83	0.78	15
0.72	0.63	0.56	30
0.49	0.40	0.34	60
0.27	0.21	0.17	90
0.18	0.12	0.06	120

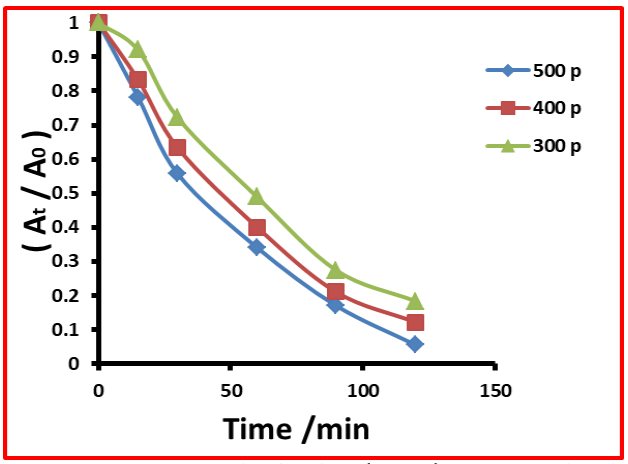

Fig.3-5: Variation in (A_t / A_0) with irradiation time (min) at different light intensity of leaser using nanomaterial Fe_2O_3.

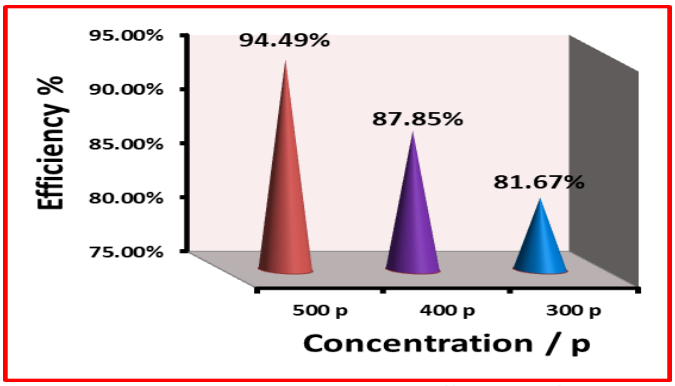

Fig.3-6: Photocatalytic degradation efficiency of dye using Fe_2O_3 nanomaterial

3-5 Effect of intensity on the photodegradation of Methyl orange dye using SiO_2 nanomaterial:

Different experiments were accomplished for studding the influence of intensity on photodegradation of Methyl orange (MO) dye by changing the concentration of the nanomaterial (300P, 400P, 500P). The results are shown in Table 3-2 and Figure 3-7. As noted from the figure (3-8), the photodegradation process of dye increases gradually with increasing light intensity. At high optical power densities, the photodegradation rate is not affected by the level of irradiance. This happens because the ratio of electron–hole formation to electron–hole recombination is very high while, at high optical intensities, it is almost unity. [16, 17].

Table (3-2): change of A_t/A_0 through irradiation-time on different-light intensity of laser.

500P	400P	300P	light intensity of laser
A_t/A_0			Time (min)
1	1	1	0
0.79	0.71	0.52	15
0.62	0.54	0.43	30
0.53	0.45	0.35	60
0.42	0.37	0.27	90
0.37	0.31	0.07	120

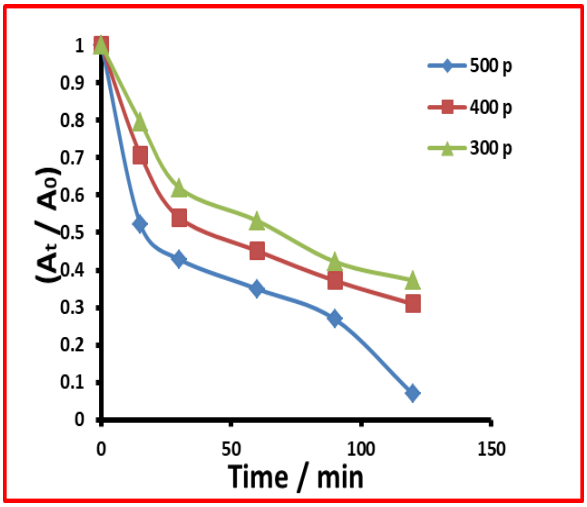

Fig.3-7: Variation in (A_t / A_0) with irradiation time (min) at different light intensity of leaser using nanomaterial SiO_2.

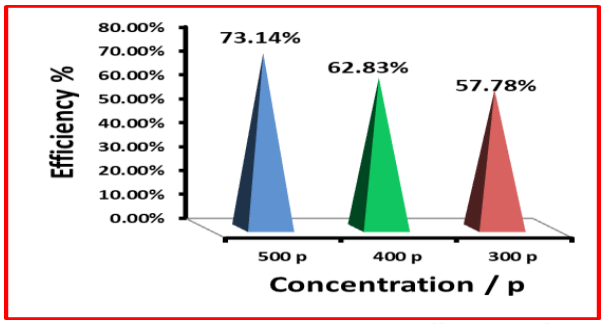

Fig.3-8: Photocatalytic degradation efficiency of dye using light intensity of laser with SiO_2 nanomaterial.

3-6 Effect of light intensity of laser on photodegradation of Methyl orange dye using Fe_2O_3 @SiO_2 nanocomposite.

The influence of intensity on photocatalytic degradation of Methyl orange (MO) dye by changing the light intensity of laser rang (300P, 400P, 500P) are shown in Table 3-3 and Figure 3-9. As shown in the figure (3-10) the photocatalytic degradation process of dye increases gradually with increasing light intensity. The photo degradation rate became independent of light irradiance as it increases. The separation of photoexcited electrons and holes competes with their recombination at low light intensities, preventing the production of reactive radicals, according to the theory. As light intensity rises, electron-hole formation becomes the main activity, resulting in a faster rate of photodegradation. Despite the fact that the light intensity continues to increase, the total active sites for photodegradation stay constant, and the reaction rate reaches a maximum value [18, 19].

Table (3-3): change of A_t/A_0 through irradiation-time on different- light intensity of laser using Fe_2O_3@SiO_2.

300p	200p	100p	light intensity of laser
A_t/A_0			Time (min)
1	1	1	0
0.89	0.84	0.72	15
0.76	0.67	0.51	30
0.61	0.55	0.37	60
0.44	0.37	0.26	90
0.22	0.14	0.09	120

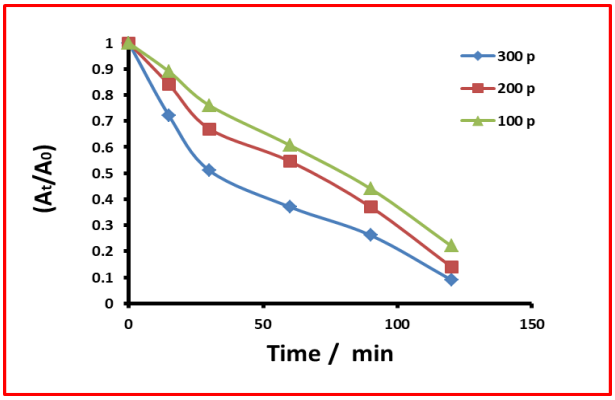

Fig.3-9: Variation in (At / A_0) with irradiation time (min) at different light intensity of laser using nanocomposite (Fe_2O_3@SiO_2).

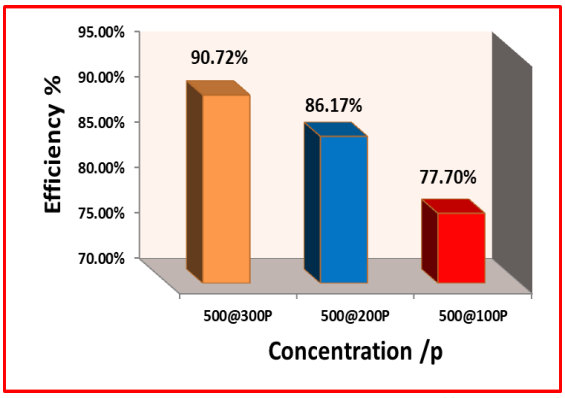

Fig.3-10: Photocatalytic degradation efficiency of Fe_2O_3@SiO_2 nanocomposite.

4. Conclusions

Nanoparticles of Fe_2O_3, SiO_2, and Fe_2O_3@SiO_2 have been successfully synthesized by laser ablation in liquids and used as catalysts. The methyl orange dye was successfully degraded in the presence of catalysts. The results obtained show that the dye degradation increases as the concentration of the nanoparticles increasing. The results indicate that Fe_2O_3 has the best degradation efficiency of dye (MO) which is about 94.49% at 500 P, while the degradation efficiency of SiO_2 of 73.14% at 500 P. The highest value of degradation efficiency has been obtained by Fe_2O_3@SiO_2 nanoparticles, which is about 90.72%.

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