Chapter Three

Results and Discussion

3.1 Introduction:

This chapter presents the results obtained from the experimental work and the discussion of each result related to the studied parameters that affect the degradation of Malachite green.

The results obtained in this study are presented here in two parts:

- The effect of the UV irradiation time.
- The effect of the amount of the semiconductor (CuO) added to the Malachite green.

In this research, the degradation of Malachite green was obtained using UV light source with different irradiation times and three different weights of CuO. The data are presented as absorption spectra where the intensity of the absorption peak of Malachite green was compared for all cases.

3.2 Absorption spectrum of Malachite green in 100 ml distilled water without irradiation:

The absorption spectrum of Malachite green (MG) was recorded without irradiation and without addition of semiconductor. Figure (3-1) shows the absorption intensity of (MG) versus wavelength. A strong absorption band can be seen at 616 nm.

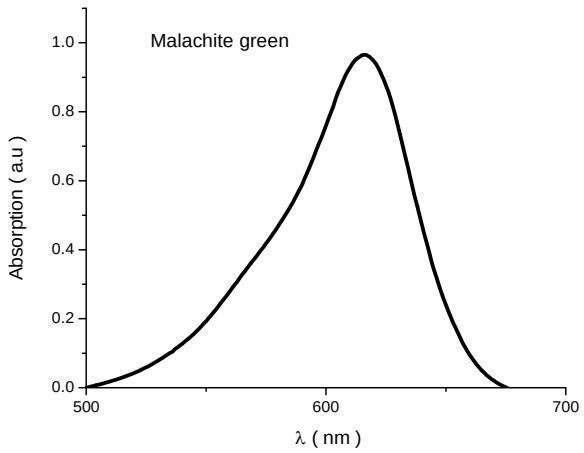

Figure (3.1): the absorption spectrum of malachite green in 100 ml distilled water without irradiation and without semiconductor

3.3 Absorption spectra of malachite green mixed with 300 mg of CuO and irradiated by UV light for different times:

Figure (3.2) shows the absorption spectra of Malachite green (MG) mixed with 300 mg of CuO at different exposure times. Table (3.1) lists the intensity of the peak at 616 nm for different irradiation times. From the figure and the table one can observed the decrease in the peak at 616 nm with increasing the exposure time. The decrease of this peak indicates the degradation of (MG).

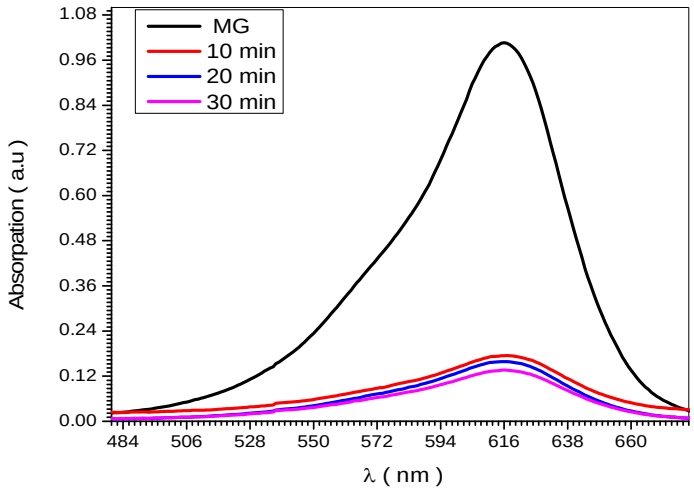

Figure (3.2): The absorption spectra of Malachite green mixed with 300 mg of CuO irradiated by UV light for different exposure times.

Table (3.1) The intensity of the peak at 616nm after addition of 300 mg CuO and irradiation with different exposure times.

Irradiation time (min)	Intensity of 616 (a.u)	Degradation percentage (%)
0	0.9708	0.00
10	0.1773	81.74
20	0.1569	83.84
30	0.1316	86.44

Figure (3.3) shows the relation between the exposure time and the degradation percentage of a mixture composed of 5 ml malachite green and 300 mg CuO irradiated by UV light for different times.

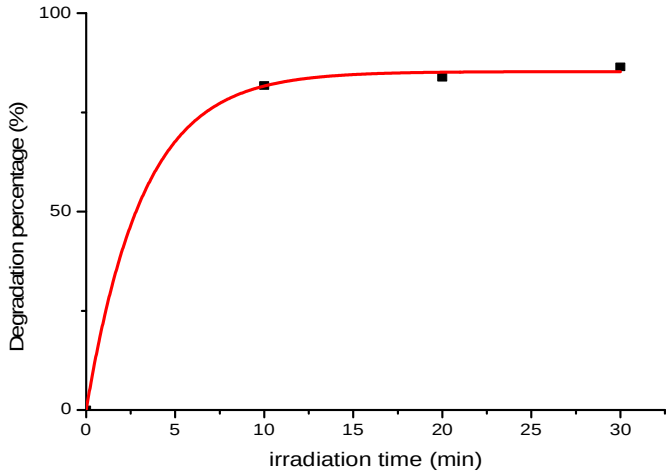

Figure (3.3) The relation between the exposure time and the degradation percentage of a mixture composed of 5 ml Malachite green and 300 mg CuO.

The mathematical relation is :

$$y = 85.27079 * (1 – \exp(-0.31557*x))$$

where :

Y:is the degradation percentage

X: is the irradiation time

3.4 The absorption spectra of Malachite green mixed with 500 mg of CuO irradiated by UV light for different times:

The absorption spectra of Malachite green mixed with 500 mg of CuO were recorded after irradiation by UV light for different exposure times (10, 20 and 30) minutes. Figure (3.4) and table (3.2) show the obtained results. The decrease in the intensity of the peak at 616 nm was very steep and the degradation of MG was 97.3%.

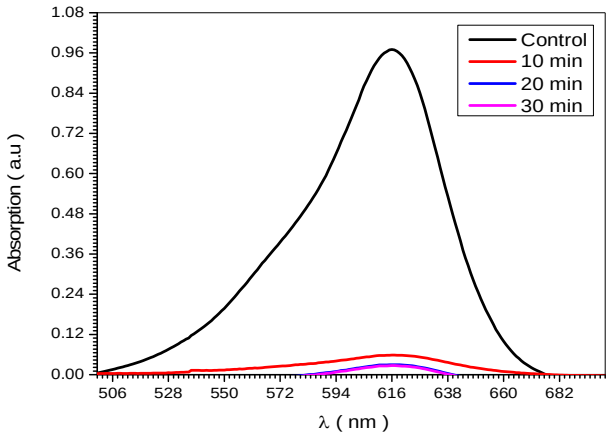

Figure (3.4): The absorption spectra of Malachite green mixed with 500 mg of CuO irradiated by UV light for different exposure times.

Table (3.2) The degradation percentage and intensity of the peak at 616 nm after addition of 500 mg CuO and irradiation with different exposure times.

Irradiation time (min)	Intensity of the 616 nm (a.u)	Degradation percentage (%)
0	0.9708	0.00
10	0.0584	93.98
20	0.0285	97.06
30	0.0262	97.30

Figure (3.5) shows the relation between the exposure time and the degradation percentage of a mixture composed of 5 ml malachite green and 500 mg CuO irradiated for different times.

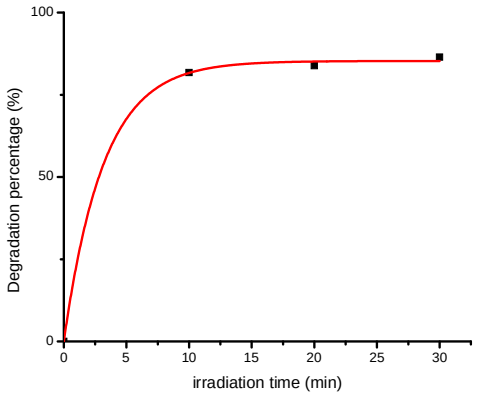

Figure (3.5) The relation between the exposure time and the degradation percentage of a mixture composed of 5 ml malachite green and 500 mg CuO.

The mathematical relation is :

$$y = 97.23877^* (1 – \exp (-0.33945^*x))$$

where:

Y: is the degradation percentage

X: is the irradiation time

3.5 The absorption spectra of Malachite green mixed with 1000 mg of CuO irradiated by UV light for different times:

Figure (3.6) shows the absorption spectra of the Malachite green mixed with 1000 mg of CuO after different exposure times.The effect of the irradiation time on the degradation of (MG) can be noticed through the decrease of the intensity of the peak at 616 nm with increasing time. Table (3-3) lists the obtained results.

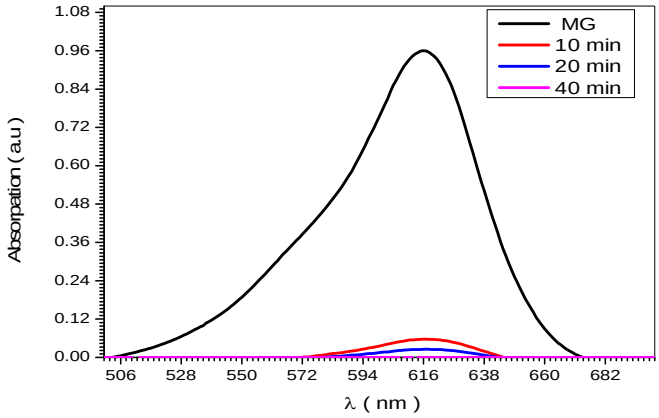

Figure (3.6): The absorption spectra of Malachite green mixed with 1000 mg of CuO irradiated by UV light for different exposure times

Table (3.3) The degradation percentage and the intensity of the peak at 616 nm after addition of 1000 mg CuO and irradiation with different exposure time.

Irradiation time (min)	Intensity of the 616 nm (a.u)	Degradation percentage (%)
0	0.9708	0.00
10	0.0523	94.61
20	0.0216	97.77
40	0.0000	100

Figure (3.7) shows the relation between the exposure time and the degradation percentage of a mixture composed of 5 ml malachite green and 1000 mg CuO irradiated for different time.

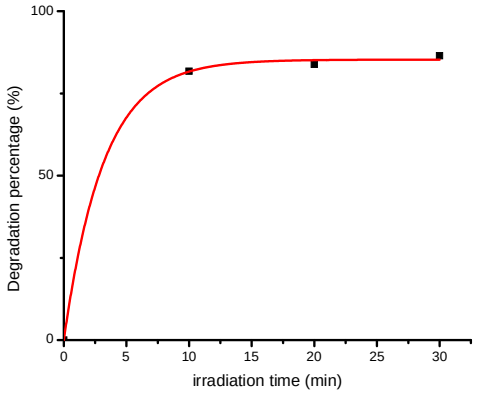

Figure (3.7) The relation between the exposure time and the degradation percentage of a mixture composed of 5 ml malachite green and 1000 mg CuO.

The mathematical relation is :

$$y = 99.03552 * (1 – \exp(-0.30866*x))$$

where:

Y: is the degradation percentage

X: is the irradiation time

From figures (3.3), (3.5) and (3.7), it can be noticed that the ratio of the degradation of the amount of Malachite green after irradiation was increasing exponentially with the increasing of exposure time.

Table (3.4) lists the degradation percentage of malachite green at different exposure times with different weights of CuO.

Irradiation time (min)	CuO Weight (mg)	MG Degradation percentage (%)
10	300	81.74
	500	93.98
	1000	94.77
20	300	83.84
	500	97.06
	1000	97.77
30	300	86.44
	500	97.30
40	1000	100

Figure (3.8) shows the degradation percentage of MG as a function of the amount of CuO.

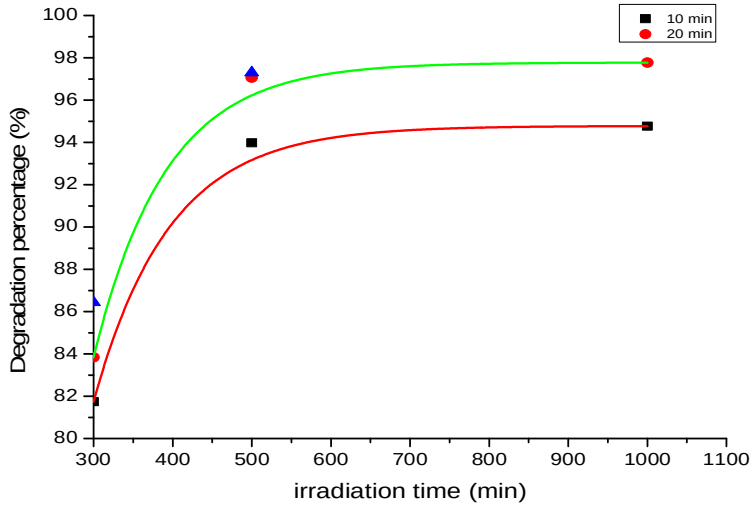

Figure (3.8) The relation between the weight (mg) and degradation percentage of a mixture composed of 5 ml malachite green and 500 mg CuO irradiated for different times.

The mathematical relation is :

$$y = 94.77869 + -13.03869*\exp(-(x-300)/95.71413)$$

where:

Y:is the degradation percentage

X:is the irradiation time

From table (3.8) and figure (3.8), it can be noticed that the ratio of the degradation of the amount of malachite green after irradiation was increased exponentially with increasing the weight of CuO.

3.6 The Discussion:

From the results of this study one noticed that photodegradation of Malachite green can occurred when semiconductor (CuO) catalyst is activated by the absorption of UV light that lead to the acceleration of chemical bond breaking of MG. This process depends on the generation of electrons in the conduction band and holes in the valence band by the UV photon energy which is greater than the band gap of CuO, which lead to the formation of hydroxyl radicals by oxidation of Malachite green (MG) solution with hole, and formation of superoxide radicals according to the reaction with electrons. Also it can be seen from the absorption spectra of Malachite green, that the of intensity of the absorption peak at 616nm was decreased with the increasing in the amount of CuO.

Figure (3.2) showed the decrease of the peak at 616nm after irradiation for 10 minutes, then significant decrease was happen with increasing the time to 20 minutes and 30 minutes. Increasing the weight of CuO to

500mg and increasing the exposure time from 10, 20 to 30 minutes led to more production of electron –hole pairs which react with (MG) in the solution and increasing its degradation. After addition of 1000 mg from CuO to solution, the intensity of the peak at 616 nm became zero after expoure time of 40 minunt, as shown in figure (3.4), this means a total removal of (MG).

From table (3.4) and figure (3.8), it can be noticed that the ratio of the degradation of Malachite green after irradiation was increased with the increasing of CuO amount.

Photodegradation of malachite green can be summarized by the following reaction mechanism:

$$MG \xrightarrow{hv} MG^{\circ} \qquad (3-1)$$

$$SC \xrightarrow{hv > Eg} SC\ (h^{+} + e^{-}) \qquad (3-2)$$

$$H_2O + h^{+} \rightarrow H^2O^{+} \rightarrow OH^{\circ} + H^{+} \qquad (3-3)$$

$$e^{-} + O_2 \rightarrow O_2 \qquad (3-4)$$

$$MG^{\circ} + H^{+} + 2e^{-} \rightarrow MGH^{-}(leuco) \qquad (3-5)$$

$$MGH^{-}(leuco) \rightarrow NH_4 + CO_2 \qquad (3-6)$$

Where:

$\boldsymbol{sc}$: The semiconductor catalyst.

$\boldsymbol{Eg}$: The energy gap of semiconductor.

$\boldsymbol{h^{+}}$: The hole in the valence band of semiconductor.

$\boldsymbol{e^{-}}$: The electron in the conduction band of semiconductor.

$\boldsymbol{MG^{\circ}}$: Malachite green

Malachite green absorbs the photons of the UV source and excited as shown in the equation (3-1). Copper oxide (CuO) also utilizes this energy to excite the electrons from the valence band to the conduction band and formation of electrons and holes as shown in equation (3-2). Equation (3-3) illustrates that H_2O reacts with the hole to produce OH° and H^{+} radicals. Electrons transfer from photocatalyst to oxygen in water as shown in equation (3-4). The MG° combines with electron and hole to give MGH^{-} as in equation (3-5). The leuco from of the dye ultimately degrades to final product containing NH_4 and CO_2 as shown in last equation.

Previously the ZnO has been used as a photocatalyst for the photo-degradation of malachite green. The efficiency of the catalyst was compared under three conditions of irradiations i.e. under dark, visible lamp source and solar radiation. The relative degradation efficiency of the catalyst was found to be highest under solar radiation than under the other sources. Therefore, knowing the best irradiation source is of paramount importance from the design and time conservation and economical points of view as these could affect the degree of degradation efficiency of catalysts (R. Aynalem & T. Tesfaye, 2014).

About 91% degradation of Malachite green was completed by adding different amounts of cerium –iron oxide from 0.01g to 0.05g after two hours. The rate of the reaction was also increasing with increasing the intensity of light up to 600W (K.L. Ameta, et.al, 2014).

3.7 Conclusions

Form the results obtained in this work, the followings can be concluded:

- The MG dye could be successfully degraded by CuO under UV irradiation.
- The degradation of Malachite green increases with increasing the exposure time.
- Increasing the semiconductor amount increase the degradation of Malachite green.
- Total removal of MG was obtained with 1000 mg of CuO and 40 minutes irradiation time.

3.8 Recommendations

The followings are recommended:

- Usage of other semiconductors such as ; TiO_2, ZnO, CdS.
- Degradation of other molecules like, Methylene blue.
- Utilization of UV laser with higher power to irradiate the sample.

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