

Variation of pH and Composite Dosage on the Photocatalytic Activity for ZnO/epoxy Nanocomposites

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Abstract

In this research, Zinc oxide (ZnO)/epoxy nanocomposite was synthesized by simple casting method with 2wt. % ZnO concentration. The aim of this work was to study the effect of pH and composite dosage on the photocatalytic activity of ZnO/ epoxy nanocomposite. Scanning electron microscopy (SEM) technique images proof the homogeneous distribution of ZnO nanoparticles in epoxy. A synthesized nanocomposite samples were characterized by Fourier Transform Infrared spectrometer (FTIR) measurements. Two spectra for epoxy and 2wt.% ZnO/epoxy nanocomposites were similar and there are no new bonds formed from the incorporation of ZnO nanoparticles. Using HCl and NaOH were added to Methylene blue (MB) dye (5ppm) to get pH values 3 and 8. The degradation of the dye was 90.816% were pH =8 after 180 min. under sun-light. The degradation was 6.131% were pH=3 after 240 min. under sun-light irradiation. It is found that the base solution help in accelerating the photocatalytic process, pH with high value provides greater concentration of hydroxyl ions which interact with h^+ to form hydroxyl radicals OH^\cdot that give an enhancement degradation rate of dyes. The dose of ZnO was increased from 3g to 6g with Methylene blue MB (5ppm) the degradation was 94.3755% after 240 min. under sun-light irradiation. This means that increasing the dose of ZnO, the photocatalytic activity will be increased.

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1. Introduction

In the last decades, photocatalysis by solar radiation raised as an active mechanism for the degradation of organic pollutants. It is one of the most useful tools obtainable for the arrangement of the global problem of environmental pollution. Merely, photocatalytic processes are reactions activated by the absorption of light by a solid material [1]. Photocatalysis is one of the important and promising advanced oxidation processes that includes photo-catalyst excitation by solar light or ultraviolet irradiation. The energy value of light irradiation must be equal to or higher than its band gap energy (E_g) to result in excitation of e^- from the valence band to the Conduction band leading to the formation of $e^- - h^+$ pairs [2]. The metal oxide semiconductors such as TiO_2 , ZnO, WO_3 , etc. have shown to possess good photocatalytic activity toward the degradation of toxic organic pollutants into nontoxic molecules such as CO_2 and H_2O under illumination of light [3].

ZnO is a semiconductor which has direct band gap width 3.37 eV, large excitation binding energy 60 meV and deep violet/borderline ultraviolet (UV) absorption at room temperature [4].The self-cleaning properties for ZnO result from the oxidation of organic contaminants by photocatalysis process. ZnO is one of the most photocatalyst

which has been vastly used because of its strong oxidizing power, non-toxic nature, and low cost [5].

The main purpose this work is to study the photocatalytic activity of ZnO/epoxy nanocomposite by degradation methylene blue MB solution at a concentration of 5ppm. Various tests were done by varying the pH between 3 and 8 using 0.1 N HCl and 0.1 N NaOH. Also, the dosage between 3 g/40 mL and 6 g/40 mL of ZnO/epoxy nanocomposites have been utilized.

2. Experimental work

The materials used in preparation of ZnO/epoxy nanocomposites were epoxy resin (Bisphenol A diglycidyl ether BADGE). Hardener (4,4diamino diphenyl methane DDM) manufactured by Egyptian Swiss chemical industries company supplied by IBC Construction Baghdad, Iraq. The epoxy ratio to hardening was 3 to 1. Zinc Oxide nanoparticles (ZnO) with particle size of about 10-30 nm were modified with Silane Coupling Agents (USA). Methylene blue (MB) CDH –India. NaOH and HCL solutions were prepared with (0.1N).

In order to prepare ZnO/epoxy nanocomposites samples. A measured amount of ZnO was added to the hardener was placed in a glass beaker and thoroughly mixed. Three percent of moisture-free epoxy resin was then added and the mixture was thoroughly agitated with a glass rod to get a homogeneous solution. The mixture was then poured into glass molds, $(12 \times 9 \times 0.3) \text{ cm}^3$ dimension, coated with releasing agent. The homogeneous resin mixture without ZnO was also considered in a separate glass mold coated with releasing agent. The glass molds were kept at room temperature for 24 h. The prepared composite specimens were with 2 wt. % ZnO and without ZnO. All the photoreaction experiments were performed under natural sunlight from 10.00 am to 14 pm. Samples were cut to size $(3 \times 3 \times 0.3) \text{ cm}^3$ with a laser beam.

UV-Vis. adsorption spectra were measured with UV–Visible spectrophotometer (SHIMADZU: UV-1800) using a quartz cell. Field Emission-Scanning Electron Microscope (FE-SEM) (Hitachi model S-4160 –Japan-Daypetronic Company) was used to observe the morphology of ZnO/epoxy nanocomposites samples at higher magnification, higher resolution and depth of focus. Fourier transform infrared spectrometer (FTIR) measurements (IR Prestige-21 Shimadzu,) were done in $400\text{--}4,000 \text{ cm}^{-1}$ by KBr pellet method to characterize materials. It provides direct information about bonding characteristic of molecules.

Photocatalytic activities of the ZnO/epoxy nanocomposites samples were evaluated by degradation the aqueous solution of Methyl Blue (MB) under sun light (between 10.00 am and 14.00 pm). ZnO/epoxy nanocomposite sample with dimensions $(3 \times 3 \times 0.3) \text{ cm}^3$ was immersed in MB aqueous solution (40 mL) of 5 ppm concentration in a glass petri dish of 10 cm diameter and was kept under dark for one hour to attain adsorption-desorption equilibrium of MB on the surface of the photocatalyst. Three milliliter of reaction mixture was collected at a regular interval of 60 min. The degradation of MB was monitored by measuring the absorbance of the solutions with DI water as a reference and the degradation efficacy was determined from the absorbance intensity at 663 nm wavelength with a spectrophotometer. Percentage degradation of MB was calculated by [6]:

$$\text{Degradation}\% = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where A_0 and A_t are the absorbance values at the initial stage and at time t respectively. Pseudo first order kinetics is the control kinetic for photo degradation of MB solution, which can be expressed as [7]:

$$\ln \frac{A_0}{A} = kt \quad (2)$$

where photo degradation rate constant is k in (min^{-1}) .

3. Results and discussion

Scanning electron microscope images of ZnO/epoxy nanocomposites with 2wt.% content of ZnO is illustrated in Fig.1. The images show uniform dispersion of ZnO nanoparticles in epoxy. It indicates that silane has the ability of improving compatibility between the nanoparticles and the epoxy matrix. SEM image gave proof to the homogeneous distribution of ZnO nanoparticles in epoxy.

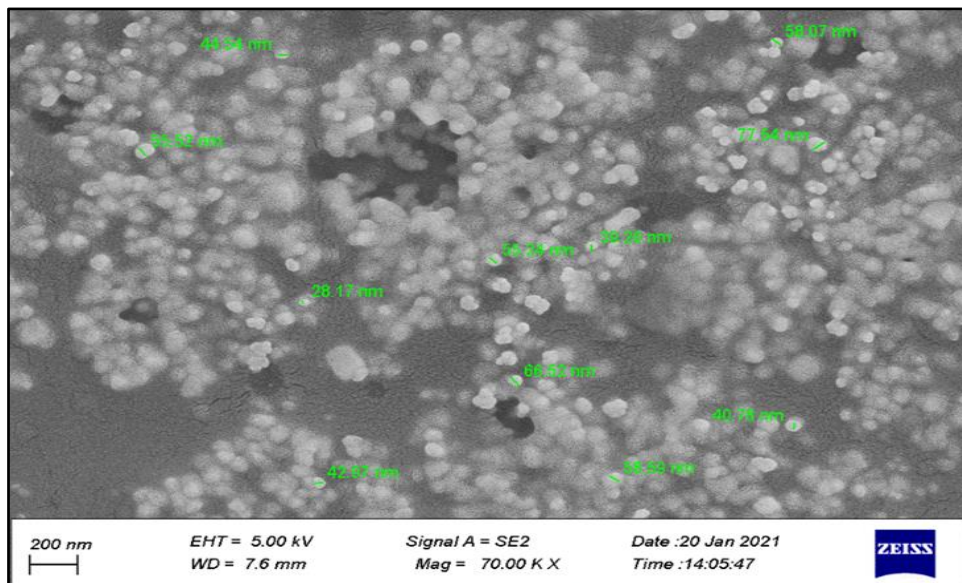
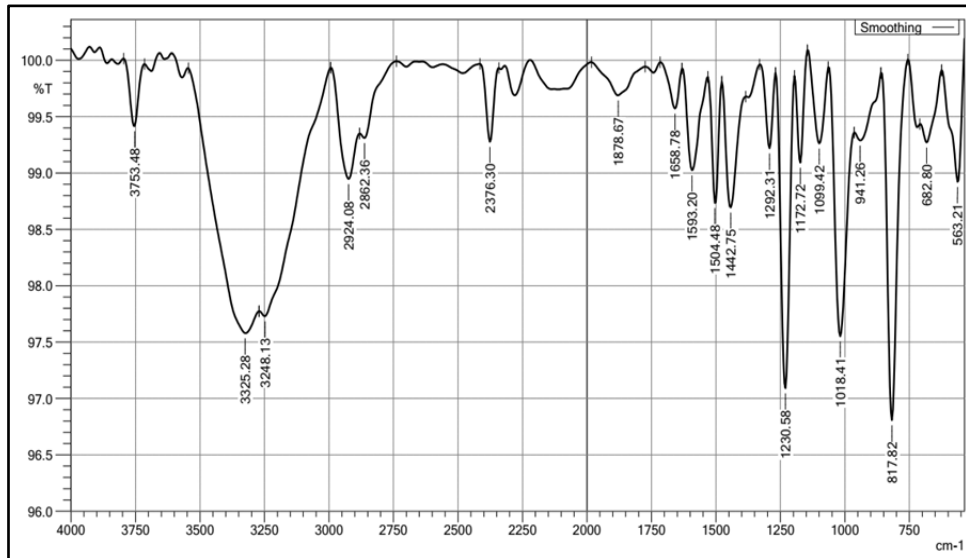
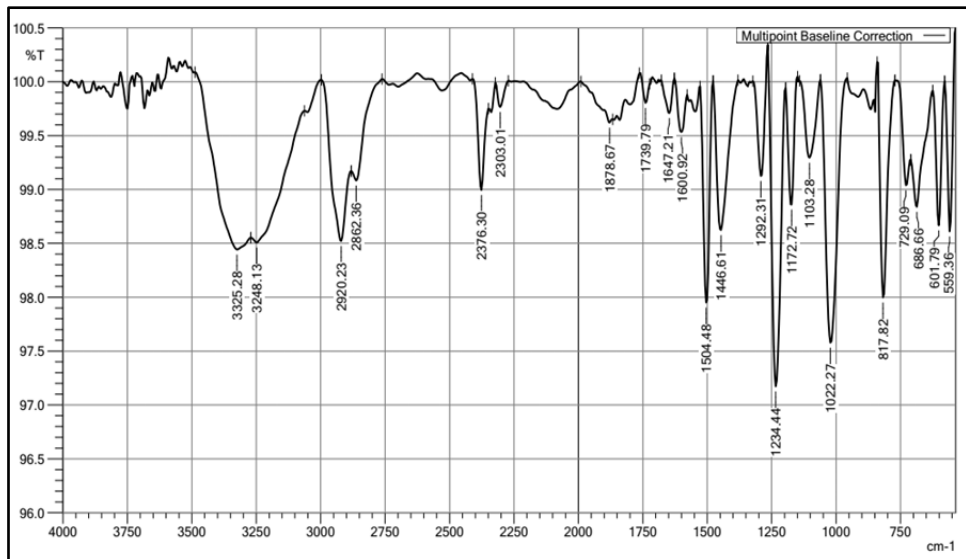


Figure 1: SEM images of ZnO/epoxy nanocomposite with 2 wt. % content of ZnO.

Fig.2 (a and b) show the FTIR spectra of the epoxy and ZnO/epoxy nanocomposites with a weight of 2 wt. % ZnO content respectively. It is evident from the two spectra that both are very similar and that there are no new bonds resulting from the fusion of ZnO nanoparticles. The only difference is the intensity of the elongated peak of the OH-peak ($\sim 3750 \text{ cm}^{-1}$) for FTIR/ZnO/epoxy nanoparticles. The appearance of the OH peak in the nanocomposite spectrum is due to the hydrogen bond between the OH groups on the surface of the nanoparticles and the water molecules from the atmosphere of this sample. Hydroxyl groups blocked by hydrogen (OH) bond on the surface of nanoparticles and epoxy are the only possible reaction mechanism. The hydrogen bonding does not result in the formation of any new peaks in the FTIR spectra. To examine the effect of pH on the degradation of pollutants, the pH of the effluent was varied from 3 to 8 using (0.1 N) HCl and (0.1N) NaOH. Drops of HCL and NaOH were added after dilution to the solution containing MB to study the effect of acidity and basicity on photocatalysis. The photocatalysis of the MB solution at a concentration of 5 ppm was studied using the $(3 \times 3 \times 0.3) \text{ cm}^3$ ZnO/epoxy nanocomposite (2wt.%) samples under sunlight irradiation. The aqueous MB solution was hydrolyzed based on its absorption over time as shown in Fig.3. It was noted that the photolysis of the NaOH-containing solution was very fast. This means that basic solutions help to speed up the photocatalysis process. As for the solution containing HCl, it was noted that photolysis did not occur effectively. This means that acidic solutions do not help photocatalysis, as shown in Fig.4.



(a)



(b)

Figure 2: FTIR images of: a. epoxy b. ZnO/epoxy nanocomposite with 2wt.%content of ZnO.

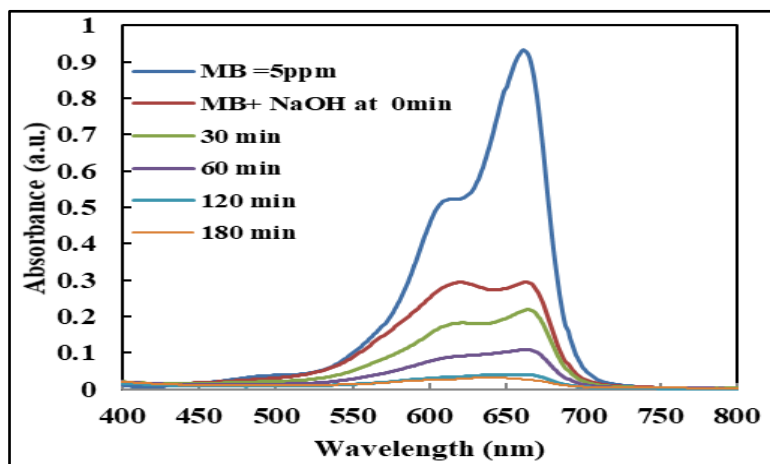


Figure 3: UV-Vis. absorption spectra of MB (5ppm) with pH =8 catalysis by ZnO/epoxy nanocomposite (2 wt. %).

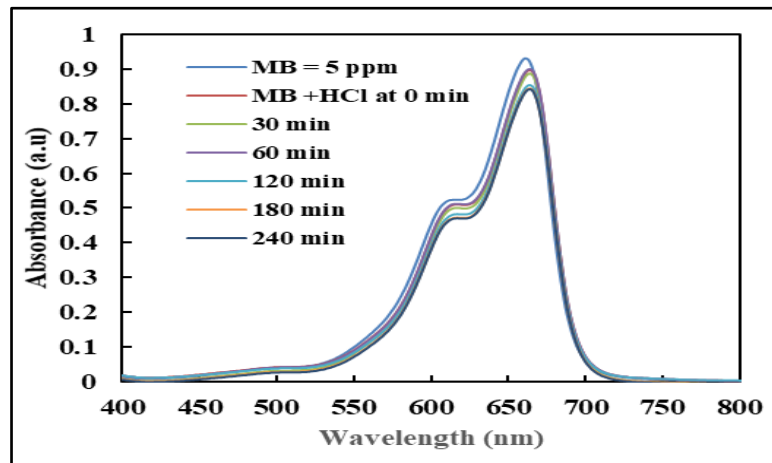


Figure 4: UV-Vis. absorption spectra of MB (5ppm) with pH =3 catalysis by ZnO/epoxy nanocomposite (2 wt. %).

The degradation percentage of MB which was calculated by Eq.(1) using ZnO/epoxy nanocomposite after 180 min and at pH=8 under sun light irradiation was up to 90%, as shown in Fig.5(a). While, the degradation percentage of MB using ZnO/epoxy nanocomposite after 240 min and at pH=3 under sun light irradiation was less than 6%, as shown in Fig.5(b). Actually, the decomposition of dyes occurred on the surface of the photocatalyst material. The adsorption of a dye is an important point in a degradation process. Although the dye with high adsorption degrades faster, but the effect sites that absorbing light radiation with raise the adsorption.

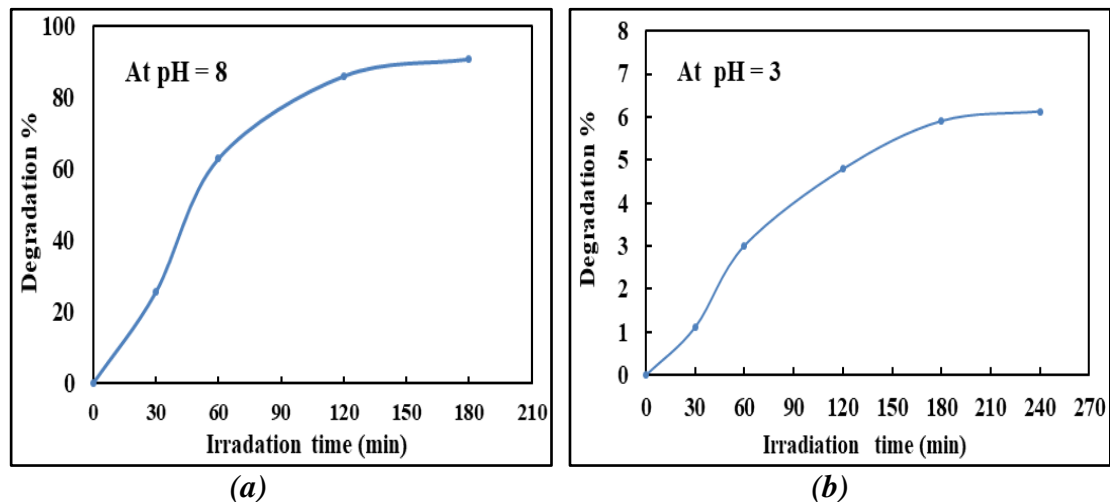


Figure 5: Degradation percentage of MB(5ppm) by ZnO/epoxy nanocomposite (2wt.%) with (a) pH=8, (b) PH=3 verses irradiation time under solar light irradiation.

In addition, high value pH could provide greater concentration of hydroxyl ions which interact with h^+ to form hydroxyl radicals OH^\cdot that give an enhancement degradation rate of dyes [8, 9]. The degradation rate is determined by the adsorption onto photocatalyst surface and the concentration of the hydroxyl radicals. The efficiency in degradation of organics is generally improved with increasing the loading of photocatalyst in the matrix. It is expected that the higher dosage of photocatalyst in the polymer matrix would increase the availability of reaction sites on the composite surface. The photodegradation was studied by varying the amount of dosage from 3g to 6 g per 40 ml all the other parameters were kept constant. At a composite dosage of

6 g/40 mL, the maximum reduction in MB solution UV-Vis. absorption spectrum under sun light irradiation occurred when compared it with 3g/40mL as shown in Fig.6 & 7.

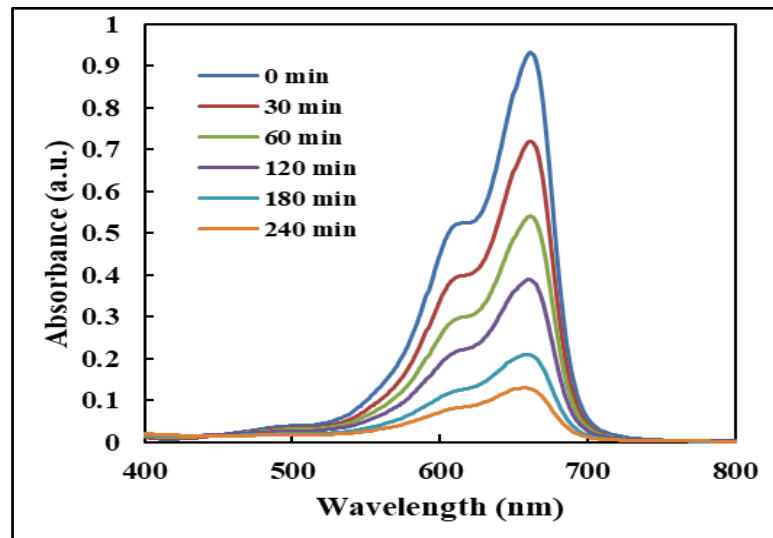


Figure 6: UV-Vis. absorption spectra of MB (5ppm) catalysis by 3g/40 ml for ZnO/epoxy nanocomposite (2wt.%).

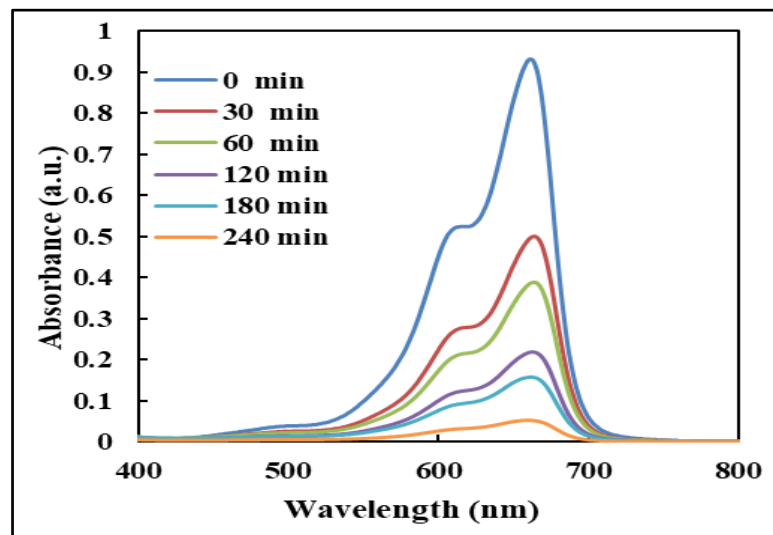


Figure 7: UV-Vis. absorption spectra of MB(5ppm) catalysis by 4g/40 ml for ZnO/epoxy nanocomposite (2wt.%).

In this study, the percentage degradation of MB for ZnO/epoxy nanocomposite with dosage 6 g/40 mL was found to be more than 92% within 240 min, while it was 86 %for the dosage 3g/40 mL under sun light irradiation as shown in Fig.8. With increasing the dosage of photocatalyst, the number of active sites will increase and leads to the enhancement of positive holes which will cause the production of a large number of hydroxyl radicals, that oxidized the pollutants. A similar trend was reported by Inagaki et al. [10] and Lago et al. [11].

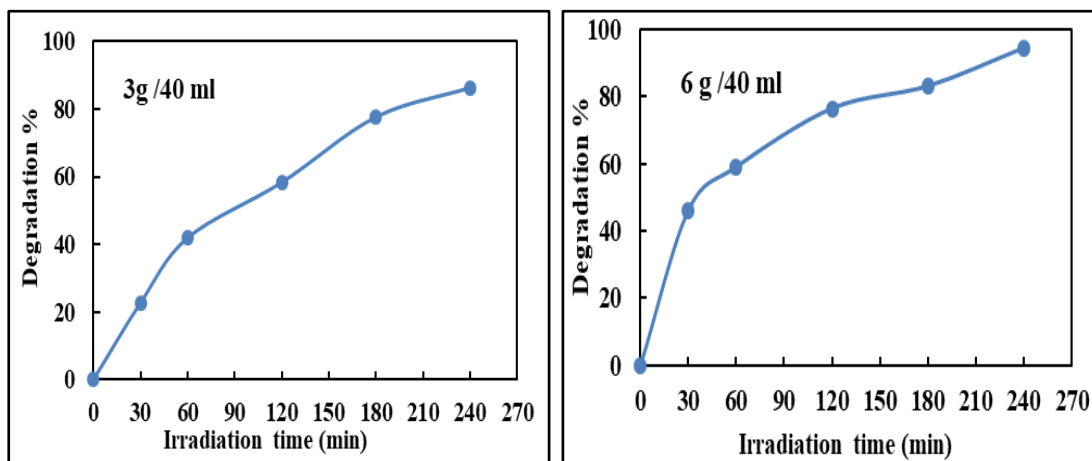


Figure 8: Degradation percentage of MB(5ppm) by ZnO/epoxy nanocomposite (2wt.%) versus irradiation time under solar light irradiation.

4. Conclusions

The preparation of ZnO/epoxy nanocomposite as photocatalyst for self-cleaning surfaces has been successfully prepared. Based on the results, it can be found that the rate of degradation of MB by nanocomposite with NaOH (pH=8) was higher than that with HCl (pH =3). It is clear that the composite dosage affects the degradation of MB solution. The degradation rate of MB increased from 86% to 92% as the composite dosage was increased from 3g to 8 g per 40 mL, keeping all the other parameters constant. ZnO polymer composite was found to be effective for the self-cleaning without harming human health and environment.

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Conflict of interest

Authors declare that they have no conflict of interest.

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تأثير تغيير pH وجرعة المتراكب على فاعلية التحفيز الضوئي للمترابكات النانوية اوكسيد الخارصين \ ايبوكسي

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الخلاصة

في هذا البحث ، تم تحضير المركبات النانوية اوكسيد الخارصين / ايبوكسي بطريقة الصب البسيطة بوزن 2% من اوكسيد الخارصين. الهدف من هذا العمل هو دراسة تأثير الأس الهيدروجيني والجرعة المركبة على فعالية التحفيز الضوئي لمركب اوكسيد الخارصين/ ايبوكسي النانوي. استخدمت تقنية المسح المجهر الإلكتروني (SEM) لتوضيح التوزيع المتجانس للجسيمات النانوية اوكسيد الخارصين في عينات ايبوكسي لتكوين مترابك نانوي متجانس التركيب . اما بالنسبة لفحص مطياف فورييه للأشعة تحت الحمراء وجد ان الطيفان متشابهان ولاتوجد روابط جديده ناتجه عن جمع الجسيمات النانوية. تمت إضافة NaOH و HCl إلى صبغة MB (5 جزء في المليون) ، وكان تحلل الصبغة 90.816% عند إضافة NaOH بعد 180 دقيقة تحت ضوء الشمس. كان التحلل 6.131% عند إضافة حمض الهيدروكلوريك بعد 240 دقيقة تحت إشعاع ضوء الشمس. وجد أن الحل الأساسي يساعد في تسريع عملية التحفيز الضوئي. تمت زيادة جرعة اوكسيد الخارصين من 3 جرام إلى 6 جرام مع MB (5 جزء في المليون) وكان التحلل 94.3755% بعد 240 دقيقة تحت إشعاع الشمس ، وهذا يعني أن زيادة جرعة ZnO ستزيد المحفز الضوئي.