

Photocatalytic Activity and Wettability Properties of ZnO/Sawdust/Epoxy Composites

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Abstract

In this work, zinc oxide nanoparticles (ZnONPs) and sawdust/epoxy composite (20:80) were mixed using a simple molding method with different ZnONPs concentrations of (0.1, 0.3, 0.5, 0.7, and 1.0 %). The samples of the nanocomposites were characterized by the Scanning Electron Microscopy (SEM) technique to demonstrate the homogeneity of the prepared ZnONPs/nanocomposites. The photocatalytic activity of the samples was examined using the methylene blue (MB) dye as a pollutant solution, through evaluation of the efficiency of the prepared compound in the treatment of organic pollutants under illumination by sunlight. The photocatalytic results showed that after 240 minutes of exposure to sunlight, the sample prepared using (0.5 vol.% of ZnONPs) appeared to rapid degradation of MB dye, with photolysis efficiency of 89% and 71% for dye concentrations 5 and 10 ppm, respectively. Wettability results confirmed that the water contact angles of samples (WCAs) were affected by the concentration of ZnONPs.

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1. Introduction

The term "composite material" refers to a type of material made up of two or more components with different chemical and physical characteristics. When two or more elements are integrated, a new material emerges with qualities that differ from the initial composition [1-3]. The components of the composite retain their individual, physical and chemical properties. However, they create a powerful set of specifications that cannot be produced individually [4]. Ceramic matrix composites, metal matrix composites, and polymer matrix composites are the three kinds of composite materials based on matrix ingredients. Nanoparticles (NPs) reinforced composites, for instance, are categorized based on the shape and size of the reinforcing material structure [5-7]. Zinc oxide nanoparticles (ZnONPs) are an n-type semiconductor material with a hexagonal Wurtzite crystal structure that has garnered a lot of interest due to their light sensitivity, stability, and broad bandgap [3, 8]. At ambient temperature, ZnO has a direct bandgap of 3.37 eV, and a deep violet electromagnetic radiation (UV) absorption [9]. ZnO is one of the most widely used photocatalysts due to its non-toxic nature, excellent oxidation capacity, and inexpensive cost [10-12]. In the realm of water and wastewater treatment, photocatalysis is one of the advanced oxidation processes used for the oxidative removal of micropollutants. In simple terms, the catalyst in the process absorbs light and speeds up the photoreaction. Heterogeneous photocatalysis may dissolve the majority of organic contaminants found in wastewater. Biodegradation of strongly decomposable compounds can be greatly accelerated in the pre-treatment phase of water and wastewater treatment using this technology [13-16]. When exposed to light, metal oxide semiconductors such as titanium dioxide (TiO₂), ZnO, tungsten trioxide (WO₃), and others have demonstrated high photocatalytic activity in the breakdown of

harmful organic pollutants into harmless molecules such as H₂O and CO₂ [17-19]. Self-cleaning surfaces are a remarkable technology for living a more environmentally friendly life [20, 21]. Similarly, waste generated by standard cleaning processes pollutes the source of fresh water. The two main forms of self-cleaning surfaces are hydrophobic and hydrophilic [22]. The surfaces with WCA ($\theta < 90^\circ$) are known as hydrophilic surfaces and at WCA approximately reaches ($\theta < 5^\circ$) are known as super hydrophilic surfaces [23]. Hydrophilic molecules are polar compounds with ionic groups that absorb water or polar solvents easily and dissolve in polar solvents such as water. As a polar protic solvent, it has the potential to form hydrogen bonds. Hydrophilic compounds are polar molecules that can readily form a hydrogen bond with water and dissolve [24, 25]. The action of self-cleaning for the hydrophobic surface appears when water droplets roll across the surface, eliminating dust and washing away impurities in the process [26]. This research aims to investigate the photocatalytic degradation of MB solution utilizing self-cleaning ZnO/sawdust/epoxy nanocomposites as photocatalytic surfaces. Comparative photocatalytic activity of ZnO/epoxy nanocomposites with different ZnONPs concentrations of (0.1, 0.3, 0.5, 0.7, 1 vol.%) for photodegradation of MB dye under sunlight irradiation has been reported. Also, the effects of ZnONPs load on the WCAs of samples have been studied.

1. Experimental Work

1.1. Materials

Table 1 show the materials that were used in this work.

Table 1: Chemicals that were used in this work.

Materials	Purity	Chemical Formula	Purpose of using	Source
Zinc oxide Nanoparticles 10-30 nm	99%	ZnO	Catalysis	USA
sawdust	99%	SD	reinforcement	Iraq
Epoxy	High. purity	-	Matrix	Egypt
Methylene Blue (MB)	99%	(C ₁₆ H ₁₈ N ₃ SC ₃ H ₂ O)	Study the Photocatalytic degradation	CDH - India

1.2. Preparation of Specimens and Thickness Measurement

Hardened (4,4-diphenylmethane DDM) and epoxy resin (Bisphenol A Di glycidyl Badge Ether) with the ratio of epoxy to hardening was 3 to 1 were obtained from the Swiss-Egyptian Chemical Industries Company. Sawdust was collected from the domestic industry as a by-product of the shavings process, and sawdust particles were sieved via a sieve with a particle diameter of 0.063 mm and a density of around 0.2 g/cm³. To remove moisture, the sawdust was dried at 60°C for 30 min. In a glass flask, ZnONPs in the ratios of (0.1, 0.3, 0.5, 0.7, and 1 vol.%) were introduced to the hardener solvent and stirred for 30 min using ultrasound equipment. Then, using a glass rod, a mixture of 80% epoxy resin and 20% sawdust was mixed with the initial

mixture to form a homogeneous solution. After that, the mixture is put into glass molds with dimensions of $(15 \times 10 \times 0.3) \text{ cm}^3$. Then the samples were cut using a Laser CNC Machine which gives accurate dimensions of the sample with little deterioration, as shown in Fig.1. In a separate glass mold, a homogeneous sawdust/epoxy composite was also prepared. At room temperature, the entire mixture in the molds is cured for 24 to 48 hours.

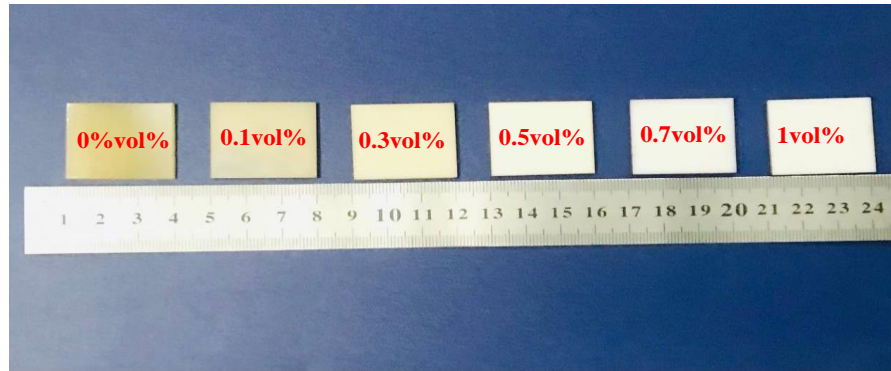


Figure 1: The prepared samples of ZnO/ sawdust /epoxy nanocomposite with different ZnO contents.

The surface morphology and elements information of ZnO/ sawdust/ and epoxy nanocomposites samples were obtained with scanning electron microscope (SEM) (Hitachi S-4800, Japan). The photocatalytic activity of the ZnO/epoxy nanocomposites samples was investigated by photodegradation of an MB dye aqueous solution under sunshine irradiation (between 10.00 AM and 2.00 PM); using samples $(3 \times 3 \times 0.3) \text{ cm}$. To equilibrate the adsorption and desorption of MB on the surface of the photocatalyst, these samples were immersed in MB aqueous solution (40 ml) at a concentration of (5 and 10 ppm) in a 10 cm diameter glass Petri dish and kept in the dark for 1 hour. The reaction solution was then taken up to 3 ml at regular intervals of every 60 minutes. The photodegradation of MB was measured using a spectrophotometer to measure the absorbance of solutions with water as a control, and the photodegradation efficacy was calculated using the intensity of the absorption at wavelength 664 nm. The tests were carried out in the Department of Chemistry, College of Science, University of Baghdad, using a Japanese UV-Vis Spectrophotometer Type 1800 Shimadzu. The photodegradation efficiency of MB dye was calculated by the equation [27]:

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

where (A_0) and (A_t) represent the absorbance values at the start of the experiment and at time t , respectively. The WCAs of ZnO / sawdust/ epoxy nanocomposites samples were determined using a Theta Optical Tensiometer (KSV Instruments, Ltd) with a digital camera connected to a computer. For each measurement, three microliters of distilled water were dripped onto the surface, and the average value of WCA was calculated at four separate locations on the sample.

3. Results and discussion

3.1. Surface Morphology (SEM) for ZnO/Sawdust/Epoxy Nanocomposites

This technique uses electromagnetic lenses to focus an electron beam on the surface of a sample kept in a vacuum. Because electrons have both particle and wave properties, they can be focused or condensed like ordinary light. The scanning electron microscopy (SEM) images of nanocomposite samples were used to show a homogeneous dispersion of NPs in the polymer matrix. Fig. 2 shows the morphological images of the ZnO/ sawdust /epoxy nanocomposite with 0.5 and 1 vol.% of ZnO contents. Images of Fig.1 (A1 and A2) show homogenous dispersion of ZnONPs in the matrix of the epoxy polymer. Images of Fig.2 (B1 and B2) show the non-homogeneous dispersion of ZnONPs in the matrix of the epoxy polymer due to increasing the agglomerates of ZnONPs in the epoxy [28].

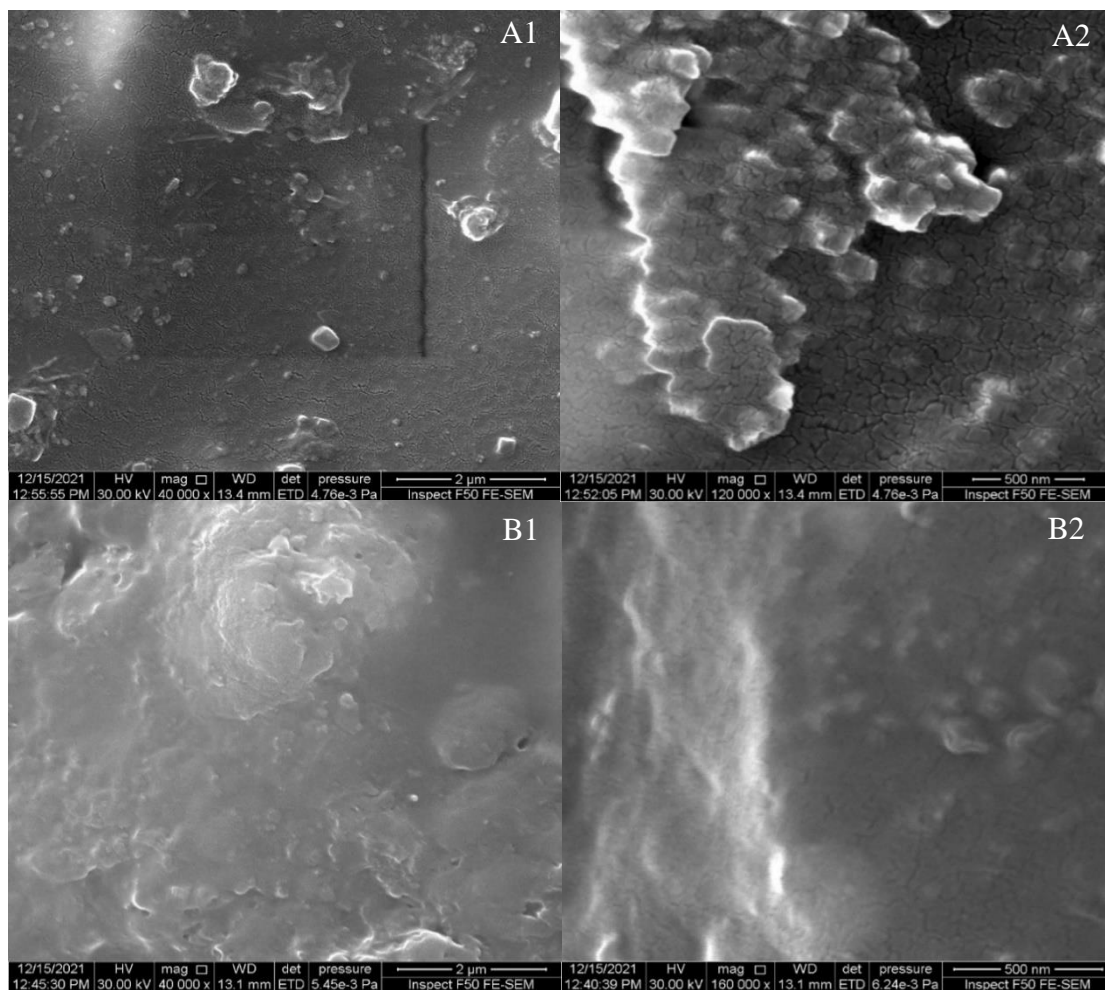
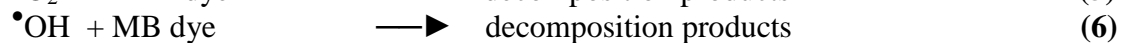
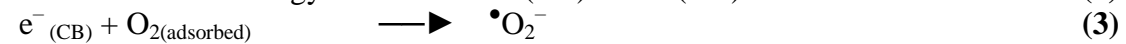


Figure 2: SEM morphological images of sawdust/epoxy nanocomposites with (A1 & A2) 1 vol.% of ZnONPs and (B1 & B2) 0.5 vol.% of ZnONPs.

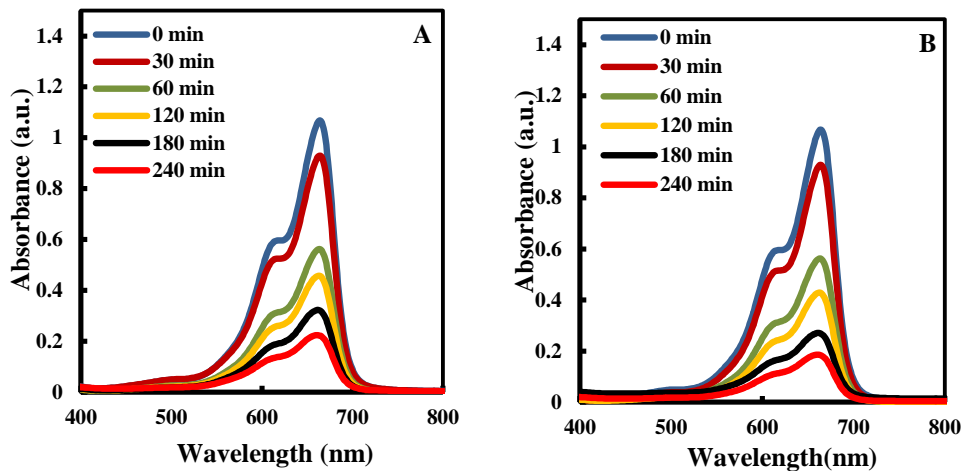
3.2. Photocatalytic Activity of ZnO/ Sawdust /Epoxy nanocomposite

The UV–Vis spectra of 5 and 10 ppm MB change as a function of irradiation duration during photodegradation of ZnO/ sawdust /epoxy nanocomposites at various concentrations (0.1, 0.3, 0.5, 0.7, and 1 vol.%) of ZnONPs are shown in Figs. 3 and 4. The results reveal that as the irradiation period increases from zero to 240 minutes, the intensity of the distinctive absorption peak (664 nm) steadily declines, meaning that the MB dye photodegrades by ZnO/epoxy nanocomposites. In general, the results

confirm that the samples show good photodegradation for the MB dye, and the best efficiency was achieved at a concentration of 0.5 vol.% of ZnONPs. Figs. 5 and 6 show the relation between ZnONPs ratios in the epoxy matrix and the photodegradation efficiency of MB dye at a concentration of 5 and 10 ppm. The results confirm that the sample (0.5 vol.% of ZnONPs) achieved the highest decomposition efficiency compared to the other samples. This behavior can be attributed to the good distribution of NPs in the epoxy polymer matrix, in addition to the low water contact angle of the sample, which supports the state hydrophilic effect on photodegradation. A possible mechanism can be proposed to explain the photodegradation process of MB dye by ZnONPs. When the sample containing ZnONPs is irradiated with sunlight, the electrons in the valence band absorb energy (excited electrons) and move to the conduction band, leaving a-holes in the valence band [29]. Then the free photoelectrons can react with oxygen molecules in solution to generate free radicals ($\bullet\text{O}_2^-$), while holes can react with water (H_2O) to generate ($\bullet\text{OH}$). When the adsorption process is achieved between the surface of the ZnONPs and the MB dye, the free radicals interact with the MB dye and decompose it into H_2O and CO_2 [30, 31]. The following are equations showing the previous reactions:



Furthermore, the outstanding performance of ZnONPs might be due to the influence of oxygen vacancies in the ZnO matrix, which operate as photogenerated electron traps and so promote photogenerated electron-hole pair separation [31].



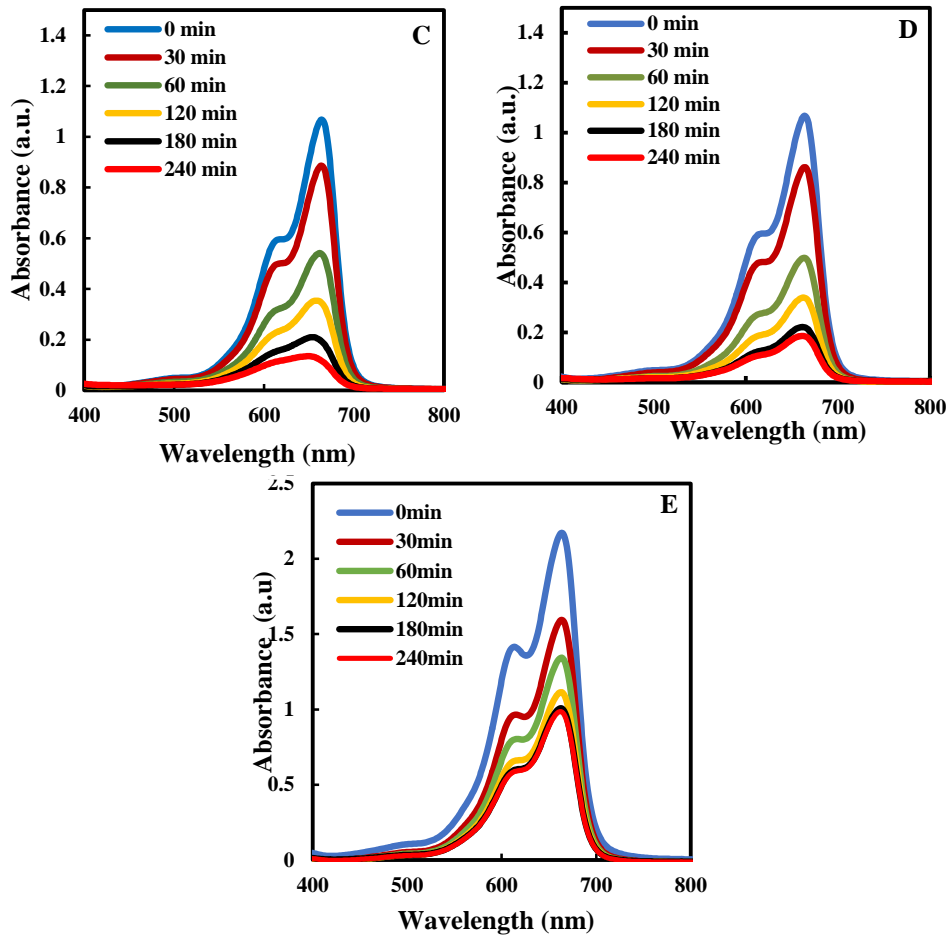
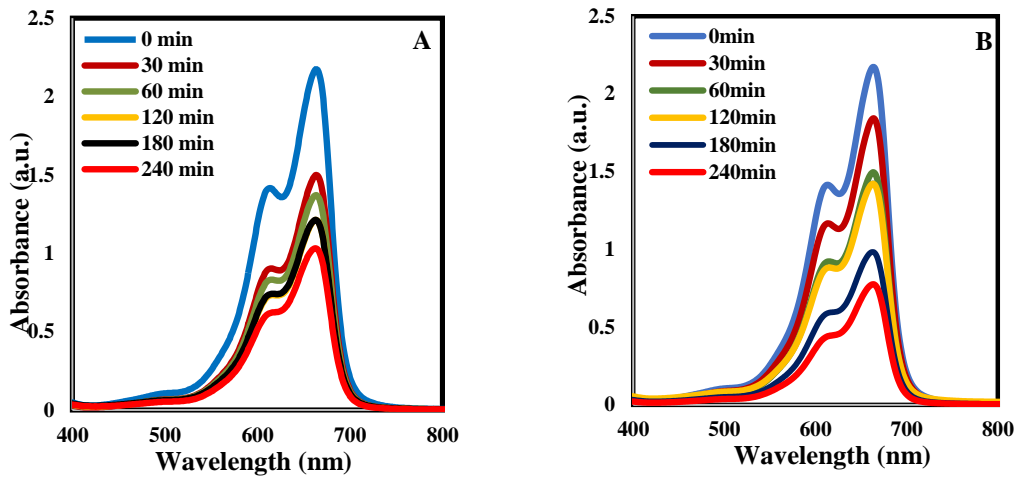


Figure 3: UV-Vis absorption spectra of photodegradation of MB dye (5ppm) by ZnO/sawdust/epoxy nanocomposite with different ratios of ZnONPs (A) 0.1 (B) 0.3 (C) 0.5 (D) 0.7, and (E) 1 vol.%, respectively.



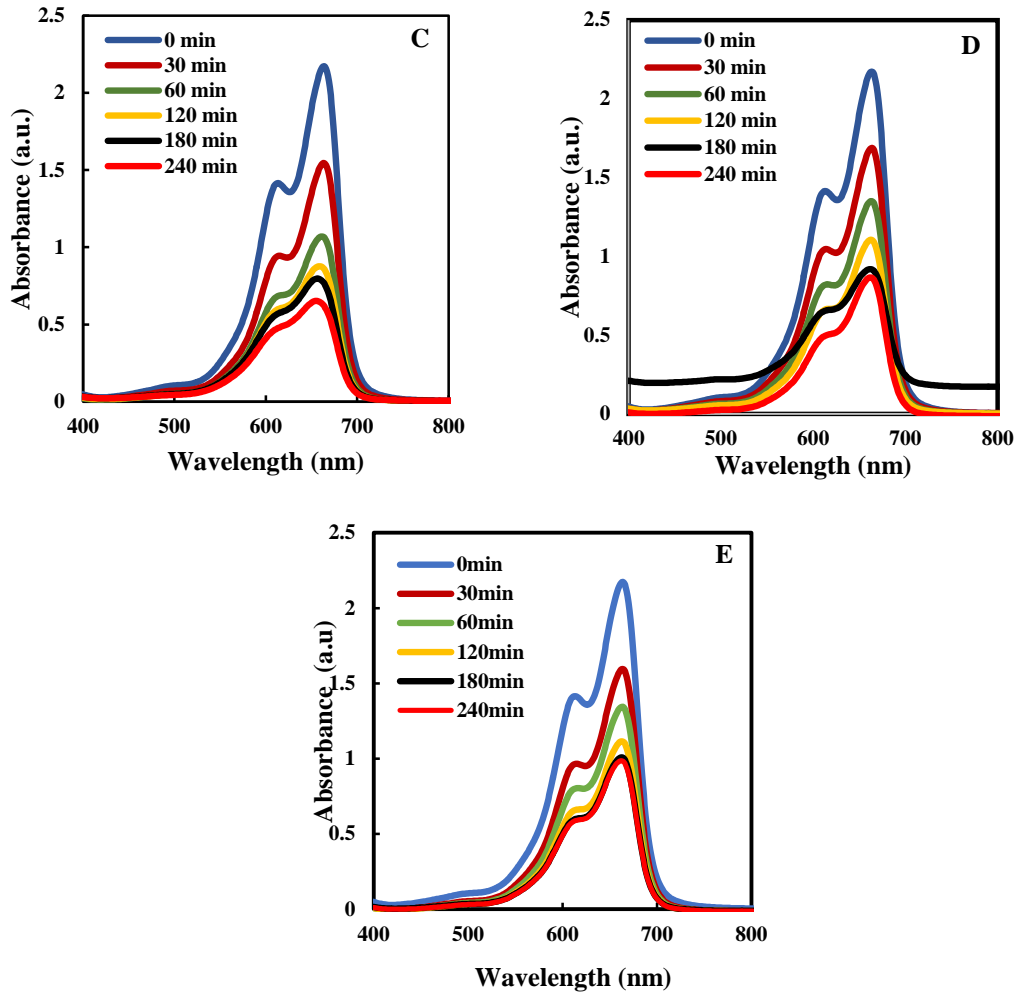


Figure 4: UV-Vis absorption spectra of photodegradation of MB dye (10 ppm) by ZnO/sawdust/epoxy nanocomposite with different ratios of ZnONPs (A) 0.1 (B) 0.3 (C) 0.5 (D) 0.7, and (E) 1 vol.%, respectively.

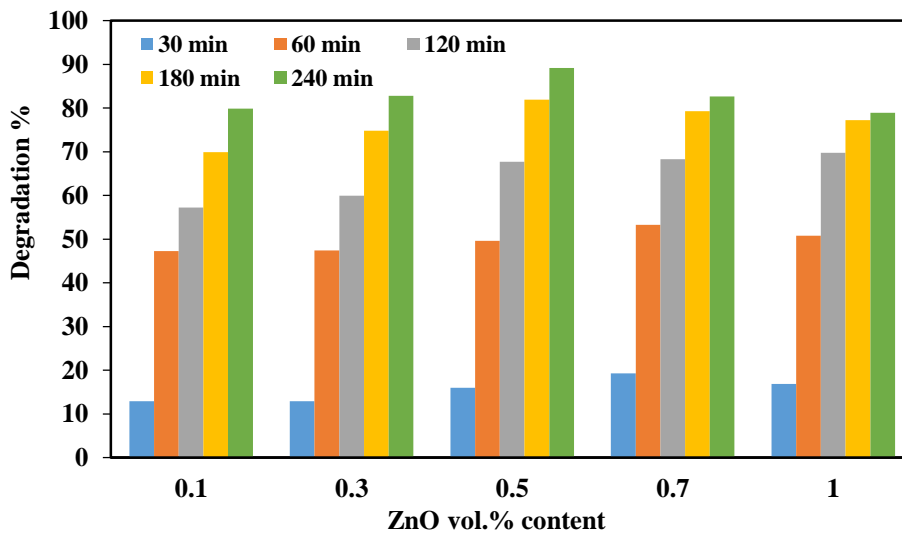


Figure 5: Photodegradation efficiency of MB dye (5ppm) by ZnO/sawdust/epoxy nanocomposite with different ratios of ZnONPs.

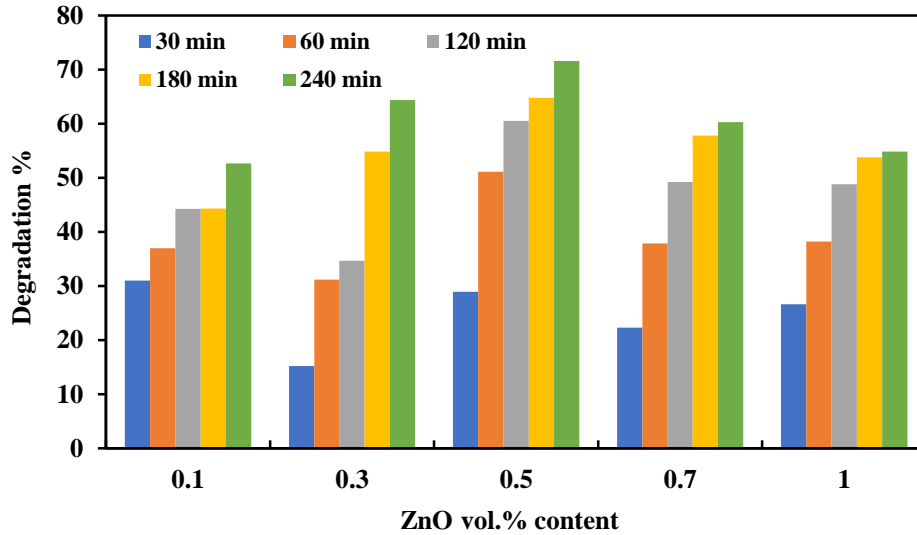


Figure 6: Photodegradation efficiency of MB dye (10ppm) by ZnONPs/epoxy nanocomposite with different volumes of ZnONPs.

3.3. Wettability Measurement

The wettability is the ability of a liquid to retain contact with a solid surface, and it is determined by the balance of cohesive and adhesive intermolecular interactions. Fig.7 showed the WCA of ZnO/sawdust/epoxy nanocomposites samples. From the figure, the results confirm that the values of WCAs ranged from 48.34° to 56.96° , as shown in Table 2. WCAs progressively rise with increasing ZnONPs concentration in the Epoxy matrix due to low surface free energy and increased surface roughness, which is a very desirable feature that makes this material a viable candidate for self-cleaning processes [32-34].

Table 2: WCA of ZnONPs/Epoxy composites.

ZnO Vol.%	WCA
0%	48.34°
0.1%	51.11°
0.3%	56.89°
0.5%	56.96°
0.7%	49.51°
1%	49.46°

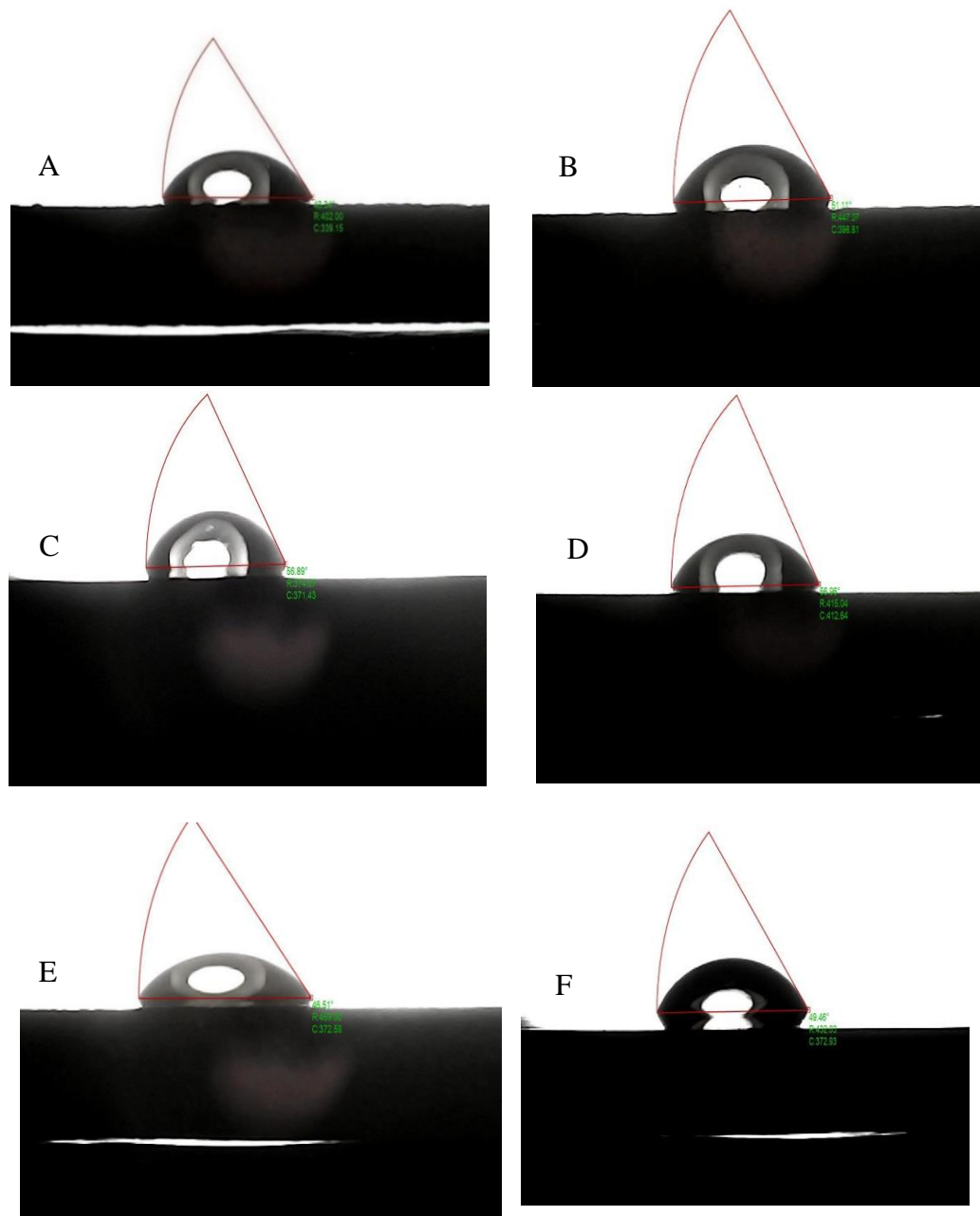


Figure 7: WCAs of ZnONPs/epoxy nanocomposite at the ZnO volume contents (A) 0%, (B) 0.1%, (C) 0.3%, (E) 0.5%, and (F) 0.7%.

4. Conclusions

Preparation of epoxy/sawdust-reinforced nanocomposites and different content of zinc oxide nanoparticles. SEM data show the presence of nanoclusters on the surface at 0.5 vol% ZnONPs and 1 vol% ZnONPs. Their presence can be attributed to the effect of ZnONPs. The wettability of prepared samples increased after adding ZnONPs into the epoxy matrix. The decomposition rate of methyl blue increases with decreasing dye concentration of the solution. By increasing the content of ZnO in the composite materials, the photocatalytic activity was increased. The samples were very

effective in removing methyl bromide dye (industrial pollutant) from aqueous solutions. The high sample efficiency (0.5 volume % of ZnONPs) can be attributed to the well-distributed ZnONPs on the surface of the epoxy matrix.

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Conflict interest

There is no conflict of interest in the current work.

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نشاط التحفيز الضوئي وخصائص الترطيب لمركبات ZnO / نشارة الخشب / الايبوكسي

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الخلاصة

في العقود القليلة الماضية، اكتسبت المركبات المقواة بالألياف الطبيعية اهتمامًا متزايدًا من الباحثين والمهندسين بسبب كثافتها المناسبة، وقوتها العالية، وتكلفتها المنخفضة، ووزنها الخفيف، وقابليتها لإعادة التدوير، وقابليتها للتحلل البيولوجي، واكتسبت فئة خاصة من المركبات الخضراء. في هذا العمل تم خلط الجسيمات النانوية من أكسيد الزنك (ZnONPs) ومركب نشارة الخشب / الايبوكسي (20:80) باستخدام طريقة تشكيل بسيطة مع تراكيز مختلفة من ZnONPs (0.1، 0.3، 0.5، 0.7، 1 حجم %). تم تمييز عينات المركبات النانوية بتقنية المسح المجهر الإلكتروني (SEM) لإثبات التوزيع المتجانس لجسيمات أكسيد الزنك النانوية لتشكيل مركب نانوي متجانس. تم فحص نشاط التحفيز الضوئي للعينات باستخدام صبغة الميثيلين الأزرق (MB) كنموذج ملوث، مع تقييم فعالية هذا المركب في المعالجة الفعالة للملوثات العضوية في وجود ضوء الشمس. أظهرت نتائج التحفيز الضوئي أنه بعد 240 دقيقة من التعرض لأشعة الشمس، كان للعينات (0.5 vol.%) تحلل ضوئي سريع لصبغ MB، بكفاءة تحلل ضوئي 89% لتركيز الصبغة 5 (جزء في المليون) و 71% لتركيز الصبغة 10 (جزء في المليون). تشير نتائج قابلية البلل إلى أن تركيز ZnONPs يؤثر على زوايا ملامسة الماء للعينات (WCAs).