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Original Research Article

Study the Effect of ZnO Concentrations on the Photocatalytic Activity of TiO_2/Cement Nanocomposites

Mays B. Al Taee*, Ban M. Al Shabander

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

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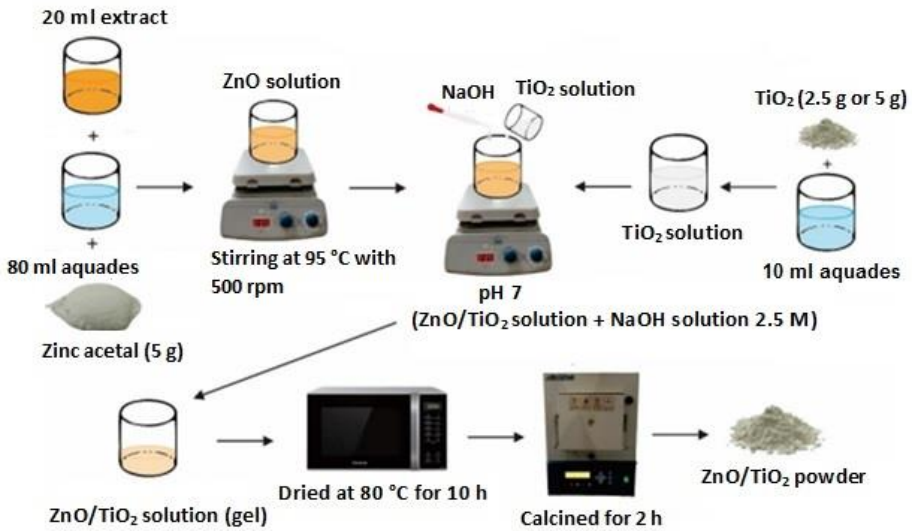
ABSTRACT

In this paper, ZnO/TiO_2/cement nanocomposites were fabricated by a simple casting method with different concentrations of ZnO (0, 0.4, 0.6, and 0.8 wt.%) and of TiO_2 (0.8, 0.4, 0.2, and 0 wt.%). The aim of this study was to understand the effect of dye concentration (5 and 10 ppm) on the photo-catalytic activity of TiO_2/ZnO/cement nanocomposite. The samples of the synthesized nanocomposites were characterized by the scanning electron microscopy (SEM) technique. The observed photocatalytic efficiency of the nanocomposites was investigated by decomposing the dye methylene blue in an aqueous solution under sunlight irradiation. (FE-SEM) image of the TiO_2/cement nanocomposite with 0.8 wt.% content was examined. It is clear that the TiO_2 nanoparticles were well attached to cement particles and they covered the cement surface the ZnO photocatalytic activity is apparently better than that of TiO_2 because ZnO exhibits greater electron mobility. According to the slope, the value of the k constant = 0.0721 min^{-1} for ZnO/TiO_2/cement nanocomposites (0.8 wt.%) at MB solution with 5ppm concentration. The contact angle of TiO_2/cement (0.8 wt.%) was 27.11 because the cement is hydrophilic surface. However, the contact angle increased when ZnO added to TiO_2/cement.

GRAPHICAL ABSTRACT



* Corresponding author: Mays B. Al Taee
✉ E-mail: Forat. mais.bassem1204a@sc.uobaghdad.edu.iq

Introduction

As an active method for the destruction of organic contaminants, photocatalysis by sun radiation has been proposed. It is one of the most practical instruments available for solving the widespread issue of the environmental contamination. Simply photocatalytic processes are reactions that are triggered by absorption of light of a solid material [1]. TiO_2 has been considered very close to an ideal semiconductor for photocatalysis because of its high photo-stability, low cost, and safety toward both humans and the environment [2]. Titanium dioxide (TiO_2) one-dimensional (1D) nanostructured materials (nanorods, nanowires, nanotubes, and nano fibers) have attracted considerable attention because of their applications in various fields such as in dye-sensitized, solar cells, photo catalysis, photo-electrochemical applications, gas sensors, and water splitting [3]. To seek a superior photocatalyst is one of the most significant problems in photocatalysis technology [4]. However, TiO_2 and ZnO band gaps need near the UV light for photo-activation. Therefore, numerous techniques have been investigated to successfully use these oxides for visible light photocatalysis [5, 6]. These metal oxides have been nanostructured by using a variety of techniques. These techniques include green, physical, and chemical ones. The metal salt is mixed with a solvent in a chemical process that also includes casting, gelation, aging, drying, and densification. Reagents used in chemical synthesis can be dangerous to both people and the environment. Wet chemical synthesis is its prime example [7]. Thus, metal oxide photocatalysts such as ZnO and TiO_2 are attractive materials for the degradation of such organic pollutants in the presence of the UV light and/or solar radiation [8]. One of the most effective mechanisms for degrading contaminants in water is semiconductor photo-catalysis mineral oxides such as. ZnO, TiO_2, ZrO_2, and ZnS [9].

The aim of this work is to study the effect ZnO concentration on the photo-catalytic activity of TiO_2/cement nanocomposites as self-cleaning surfaces. The observed photocatalytic efficiency of the composites would be investigated by decomposing the dye methyl blue aqueous solution under sunlight irradiation. The introduced of ZnO nanoparticles functioned as co-catalysts on the TiO_2surface can affect the photocatalytic activity of composites would be also studied along with their reaction kinetics.

Materials and Methods

The material used in the preparation of nanocomposite is cement. The type of used cement is Portland cement Iraqi ordinary Portland cement commercially known as (TASLUJA). It was stored in a dry place to minimize the humidity effect on cement properties. Titanium oxide (TiO_2) powder nanoparticle was manufactured by (Changsha Santech) Company with particle size of (30±5) nm and 99.8% purity. Silane coupling agents (USA) were used to modify zinc oxide (ZnO) nanoparticles, which have a particle size range of around 10 to 30 nm.

Preparation of ZnO /TiO_2/cement nanocomposites

To prepare cement samples, the cement to water ratio was 2:1. The TiO_2 nanoparticles powders are incorporated with cement directly, which is called as the internal doping method. In this experiment, for the internal doping method, the cement mix was equivalently substituted by the TiO_2/ZnO nanoparticles with different contents of ZnO and TiO_2, as listed in Table 1. TiO_2 and ZnO were mixed well with an electric mixer, and then poured into glass molds and left to dry for 24-48 hours. All tested TiO_2/ZnO/cement block samples are 6 cm in diameter, 0.5 cm in thickness, and 23 g in weight. The TiO_2/ZnO/cement nanocomposites samples prepared by the method mentioned above are displayed in Figure 1.

Table 1: ZnO/TiO_2/cement nanocomposites samples

Sample	ZnO	TiO_2	wt.%	Cement
A	0	0.8	0.8	99.2
B	0.4	0.4	0.8	99.2
C	0.6	0.2	0.8	99.2
D	0.8	0	0.8	99.2

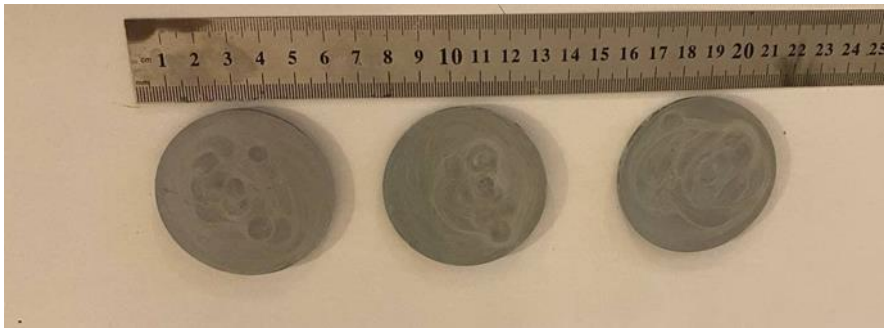


Figure 1: The prepared samples of ZnO/TiO_2/cement nanocomposite

Characterization techniques

Field Emission-Scanning Electron Microscope (FE-SEM) was utilized to view the morphology of samples of TiO_2/ZnO/cement nanocomposites at a higher magnification, a higher resolution, and deeper focus (Inspect F50 FE-SEM). The UV-Visible spectrophotometer SHIMADZU: UV-1800 was used to measure the UV-vis adsorption spectra by using a quartz cell by using contact angle system, from (Dataphysics Company/Germany) model (OCA/15 Plus).

Photocatalytic activity

By degrading the aqueous solution, the photocatalytic activity of the ZnO/TiO_2/cement nanocomposite samples was evaluated. Methyl Blue (MB) illuminated by the sun irradiation (between 10.00 a.m. and 14.00 p.m.). Methyl blue dye 5 ppm, 10 ppm was prepared. To achieve MB adsorption-desorption equilibrium on the surface of the photocatalytic, the samples were placed in a 50 mL dye solution, exposed to sunlight in a glass.petri dish with a 10 cm diameter, and maintained in the dark for one hour. At regular intervals of 60 minutes, three milliliters of the reaction mixture were collected. A spectrophotometer was used to measure the absorbance of the solutions with DI water as a reference to track the MB degradation, and the efficacy of the degradation was calculated from the intensity of the absorbance at 663 nm. It has been seen that the hue of dye solution was changed by time till it became translucent. Percentage degradation of MB was calculated by the following equation:

$$\text{Degradation } \% = \frac{A^{\circ} - A}{A^{\circ}} \times 100\% \qquad (1)$$

Where, A° and A_t represent the absorbance levels at the beginning and at time t, respectively. The control kinetic for photo-degradation is the pseudo-first order kinetics. MB solution has the following formula:

$$Ln\,\frac{A_{\circ}}{A} = -\,kt \qquad (2)$$

Where, the unit of the photo-degradation rate constant is k in (min^{-1}) [10].

Contact angle

Hydrophilic behavior was evaluated by measuring the contact angle of a water droplet on the films by using contact angle system, from (Dataphysics Company/Germany) model (OCA/15 Plus). A water droplet is injected on the surface of the film by using micro-injector (2μL) syringe pointed vertically down onto the sample surface. A high resolution (CCD) camera which was built in the system captured the image of the

water droplet, and then it was analyzed by using image analysis software.

Results and Discussion

Scanning electron microscopy (SEM)

Figure 2 represents the (FE-SEM) image of TiO_2/cement nanocomposite with 0.8 wt. % content. It is clear that the TiO_2 nanoparticles were well-attached to cement particles and they covered the cement surface. It is important to make sure that the TiO_2 nanoparticles are immobilized and distributed homogeneously on the cement surface to make sure the high surface area of TiO_2 nanoparticles on cement surface can be achieved for the MB photo-degradation.

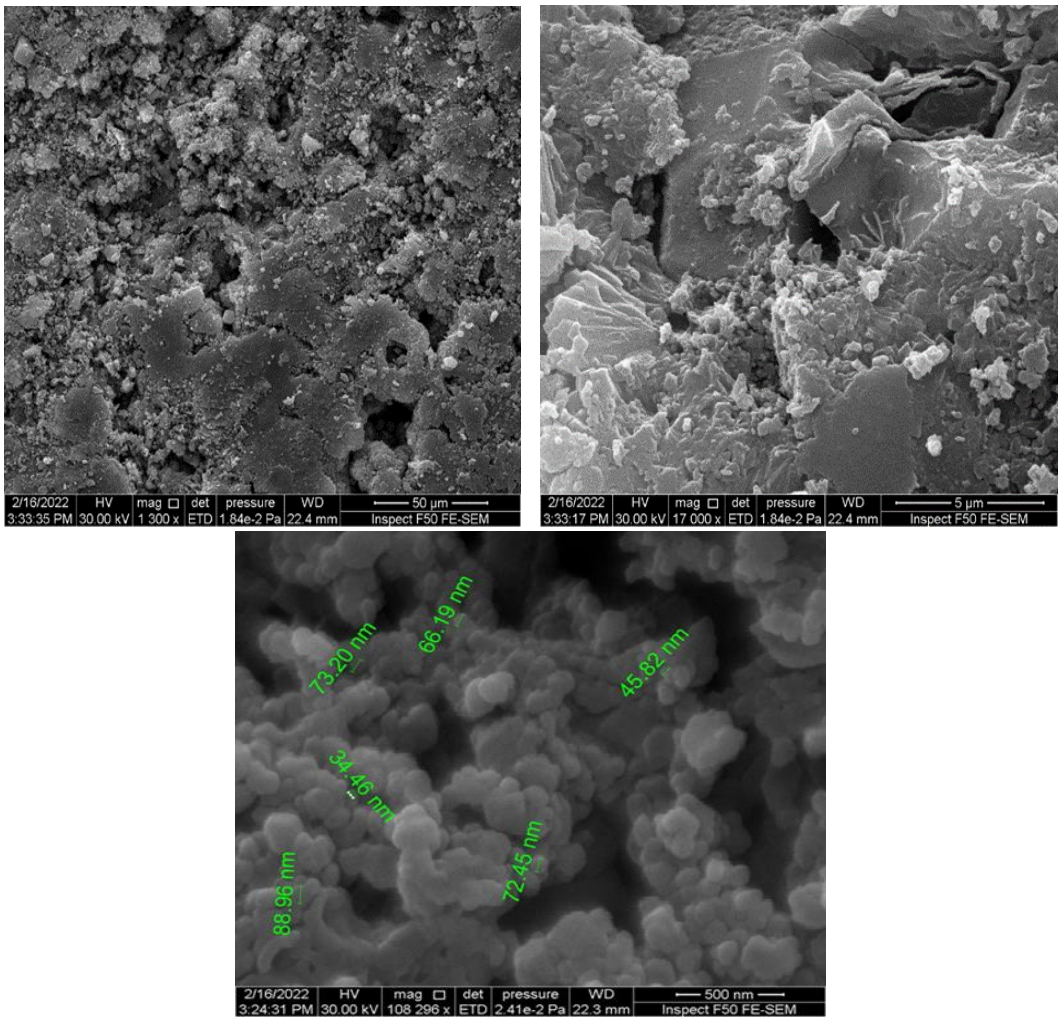


Figure 2: FE-SEM images of a cement nanocomposite containing 0.8 wt% of TiO_2 nanoparticles

UV–Visible spectroscopy

In this study, the self-cleaning capabilities of ZnO/TiO_2/cement nanocomposites samples were investigated under sunlight by using MB dye as a model of organic pollution. Under sunlight irradiation, photocatalytic degradation of the MB dye solution with 5 ppm and 10 ppm concentrations was examined in nanocomposite with various amounts of ZnO nanoparticles (0.4, 0.6, and 0.8 wt.%). Due to photocatalytic oxidation under solar light irradiation, the MB absorption reduces over time. The TiO_2 addition in Portland cement resulted in better reactivity by the large presence of hydration products and the appearance of unreacted titanium oxide which is responsible for the photo-catalysis process. The cement pastes containing ZnO had clearly indicated the retarding the ZnO effect in the hydration of Portland cement. The UV-Vis spectrum of MB dye solution shows absorption peak at 663 nm, which is the characteristic peak of MB. In general, the absorbance peak for MB at

10 ppm was higher than 5 ppm. At a high concentration of dye, the dye molecules may absorb a significant amount of light rather than the catalyst and this may also reduce the catalytic efficiency [11, 12]. Figure 3 illustrates the absorbance spectra of 5 ppm MB was degraded by ZnO/TiO_2/cement nanocomposite under sunlight irradiation.

The degradation percentage of MB solution (5 ppm) in the presence of ZnO/TiO_2/cement nanocomposites after 30, 60, and 90 min under sunlight irradiation are depicted in Figure 4. It can be seen that the degradation of dye increases with increasing the ZnO contents, this is because the increase in the amount of catalyst initially can be contributed to increased number of active sites on the photocatalyst surface. With increasing the ZnO content in TiO_2/cement nanocomposite, the degradation of MB (10 ppm) was found to increase at higher ZnO contents (0.8 wt. %) after 90 min under sunlight irradiation.

This improves the effectiveness of interfacial charge transfer to the adsorbed substrates, induces an efficient charge separation, and lengthens the lifetime of charge carriers. The final result is an increase in the photo-catalytic activity of ZnO/TiO_2/cement nanocomposites. As indicated in Figure 5, the calculated plot of Ln Å/A vs. t results in straight lines for all tests with various initial ZnO concentrations. The slopes can be used to get the apparent first-order rate constant values of k, as reported in Table 2.

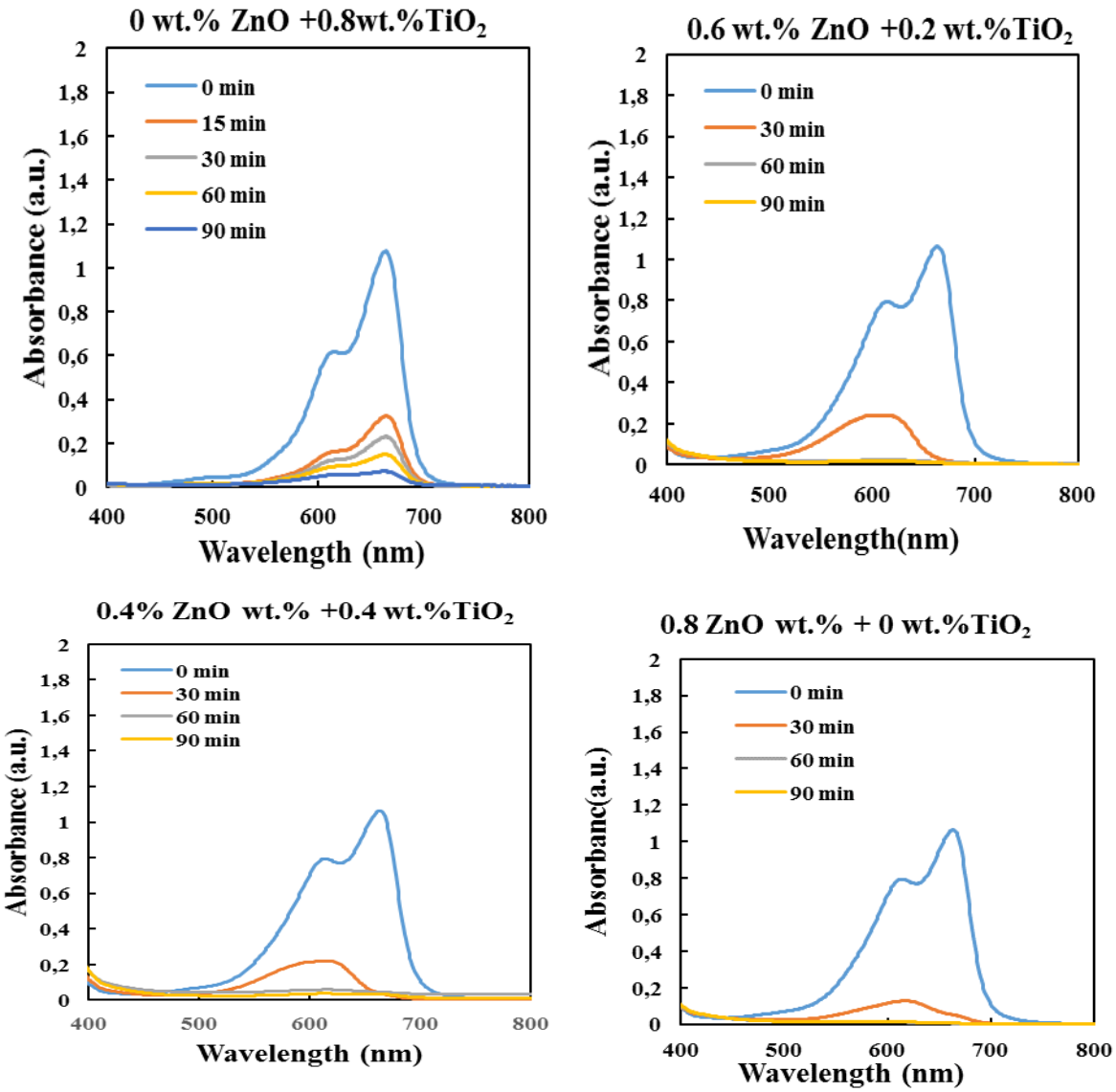


Figure 3: UV-vis absorption spectra of ZnO/TiO_2/cement nanocomposite with various compositions during the catalysis of MB (5 ppm)

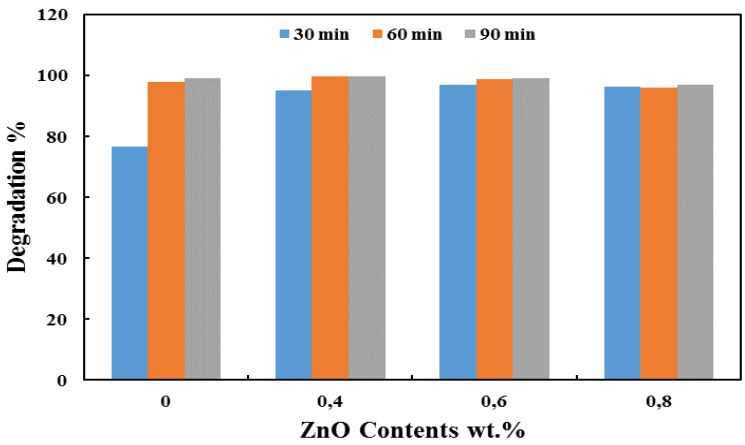


Figure 4: The percentage of MB (5 ppm) that was degraded by the ZnO/TiO_2/cement nanocomposite when exposed to sunlight

Figure 6 reveals the absorbance spectra of MB (10 ppm) decomposed in the presence of ZnO/TiO_2/cement nanocomposite photo-catalyst. The spectra have a peak at a wavelength of 663 nm and span 400 nm to 700 nm. It is evident that during the photodegradation process, MB's typical absorption peak intensity declines without experiencing any distinguishing spectral alterations, besides the color of the solution changed from blue to colorless in the photo-catalytic reaction under sun light irradiation (Figure 7). The kinetics of MB photodegradation was examined to quantify the photocatalytic activity. Nanostructured photo-catalysts offered large surface to volume ratios allowing a higher adsorption of the target molecules. On the other hand, a dye sensitized mechanism may also be possible as indicated in experiment carried out for dye degradation over pure ZnO nanoparticles under a visible light source. Furthermore, MB dye is visible light absorbing and get excited in visible light. The excited dye can transfer the electron to the conduction band of ZnO nanoparticles [13].

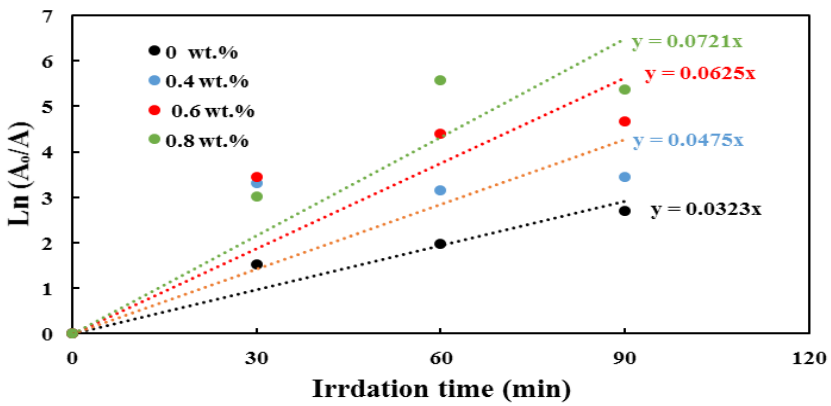
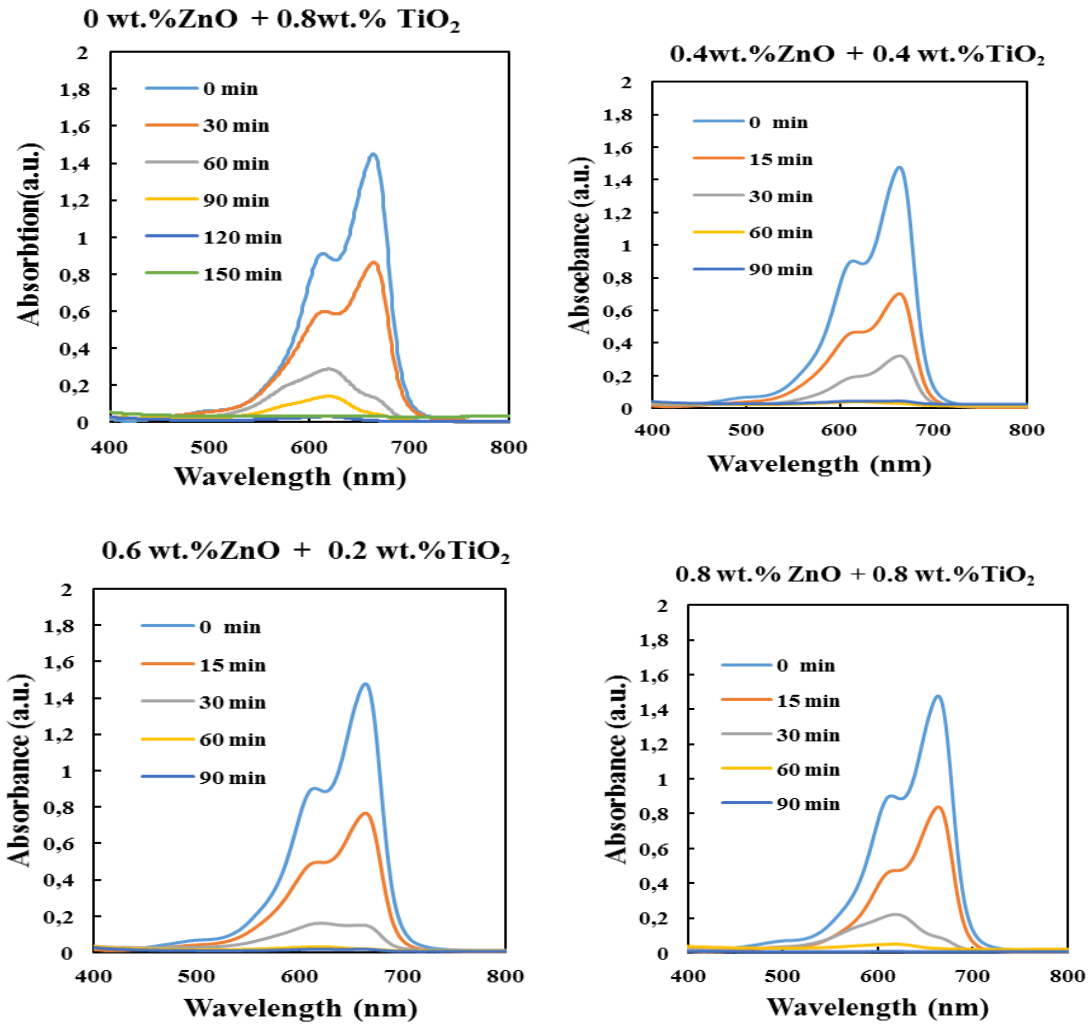


Figure 5: Relationship between Ln (A_o/A) and reaction time t by ZnO/TiO_2/cement nanocomposite vs. irradiation time for MB (5 ppm) under sunlight irradiation

Table 2: Degradation rate constants for different ZnO /TiO_2/Cement nanocomposite (5ppm)

ZnO wt.%	Rate constant (k) min^{-1}
0	0.0323
0.4	0.0475
0.6	0.0625
0.8	0.0721



Figures 6: UV-vis absorption spectra of ZnO/TiO_2/cement nanocomposite with various compositions during the catalysis of MB (10 ppm)

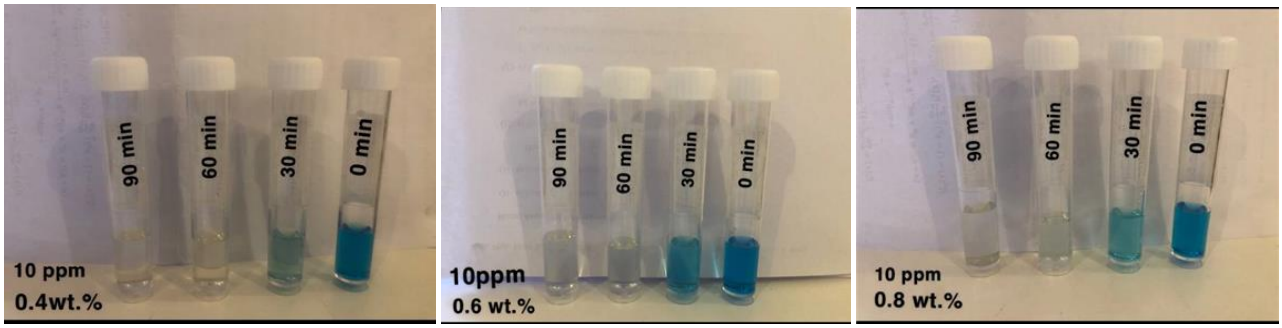


Figure 7: De-coloration of MB (10 ppm) at a different photo degradation by ZnO/TiO_2/cement nanocomposite

Figure 8 show the decrease in the degradation at a higher dye concentration under sunlight irradiation may be due to: (a) decreased photons accessing the adsorbent active sites due to the screening action of excess catalyst and (b) decreased specific surface area of adsorbent due to aggregation of photo-catalyst particles [14]. Remarkably, the ZnO addition to TiO_2, nanocomposite exhibited increased absorption in both the UV and visible regions, which is ascribed to the transfer of electrons from the valence band (VB) to the conduction band (CB). The successful formation of TiO_2-ZnO hetero-junctions reduces the recombination rate of the photo-induced

electron–hole pair and enhances the photo-catalytic activity of theTiO_2-ZnO nanocomposite [15].

The rate constants (k) can be obtained from the slope of linear plots between ln(A◦/A) and time are presented in Table 3 and Figure 9, from the slope apparent the value of k constant at the best sample 0.8 wt.% and k=0.0641 min^{-1}.

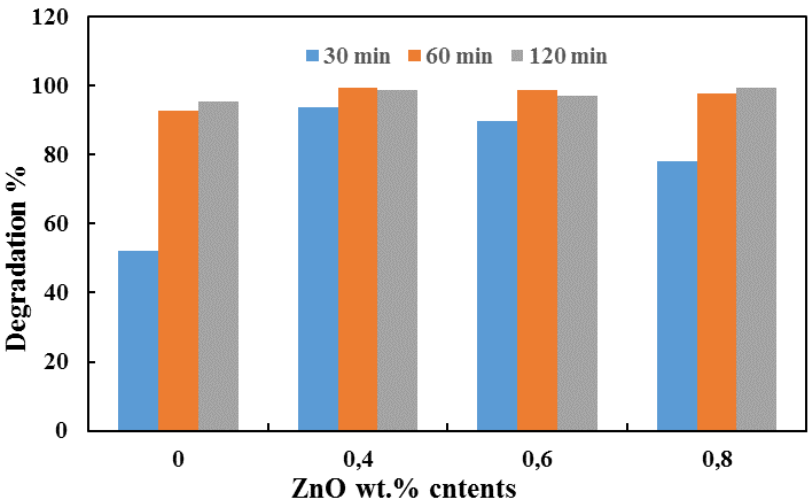
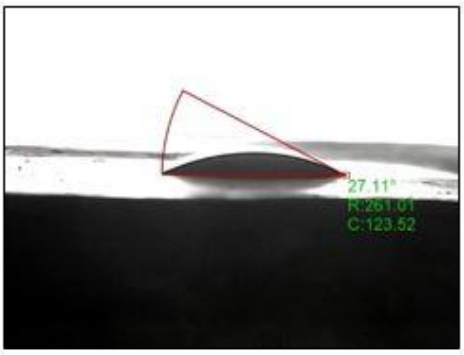


Figure 8: The percentage of MB (10 ppm) that was degraded by the ZnO/TiO_2/cement nanocomposite when exposed to sunlight

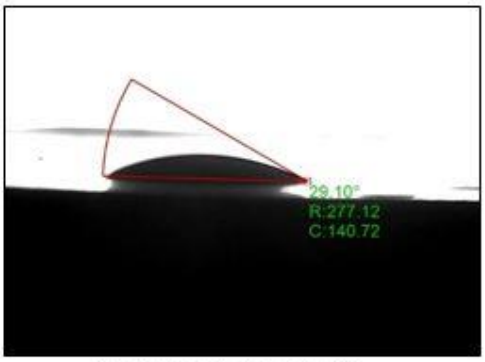
Table 3: Degradation rate constants for different ZnO+TiO_2/cement nanocomposites (10 ppm)

ZnO wt.%	Rate constant (k) min^{-1}
0	0.0375
0.4	0.0468
0.6	0.0574
0.8	0.0641

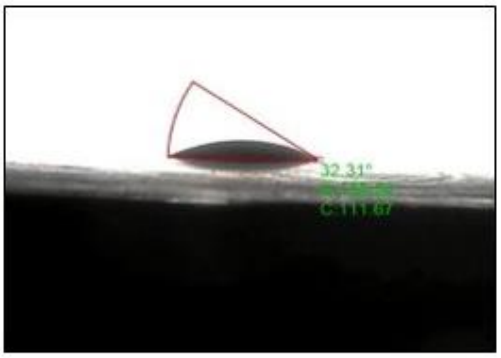
0 wt.% ZnO +0.8 wt.%TiO_2



0.4 wt.% ZnO +0.4 wt.%TiO_2



0.6 wt.% ZnO +0.2 wt.%TiO_2



0.8 wt.% ZnO +0 wt.%TiO_2

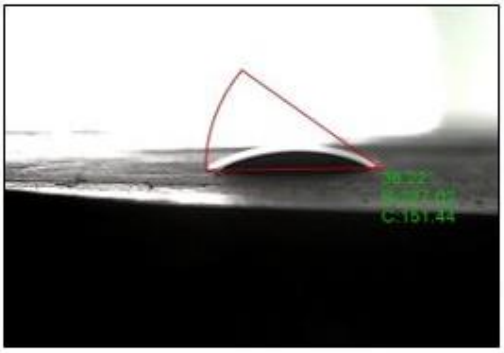


Figure 9: Relationship between Ln (A_o/A) and reaction time t by TiO_2/ZnO/cement nanocomposite vs. irradiation time under sunlight irradiation

Contact angle measurement

Figure 10 depicts the contact angle of water droplets on ZnO (wt%) /TiO_2/cement composite pellets. Before the contact angle experiment, distilled water was used to completely saturate all ZnO/TiO_2/cement nanocomposite pellets. The hydrophobicity or hydrophobicity of the water is shown by its contact angle. The hydrophilic nature of cement is shown by the water contact angle for the TiO_2/cement particle in this instance, which is (27.11°). When the ZnO percentage is increased by 0.4%, 0.6%, and 0.8 % in ZnO/TiO_2/cement nanocomposite, the water contact angle rises to 29.1°, 32.31°, and 38.22°, respectively. This finding reveals that the ZnO addition to cement will cause the hydrophilicity of the cement surface to change to hydrophobicity. As a result, the ZnO/TiO_2/cement nanocomposite material becomes more hydrophobic when ZnO is added to cement. According to the reports, cement begins to degrade when water is in touch with it for an extended period of time. Conversely, cement with a higher hydrophobicity increases the longevity of the material [16].

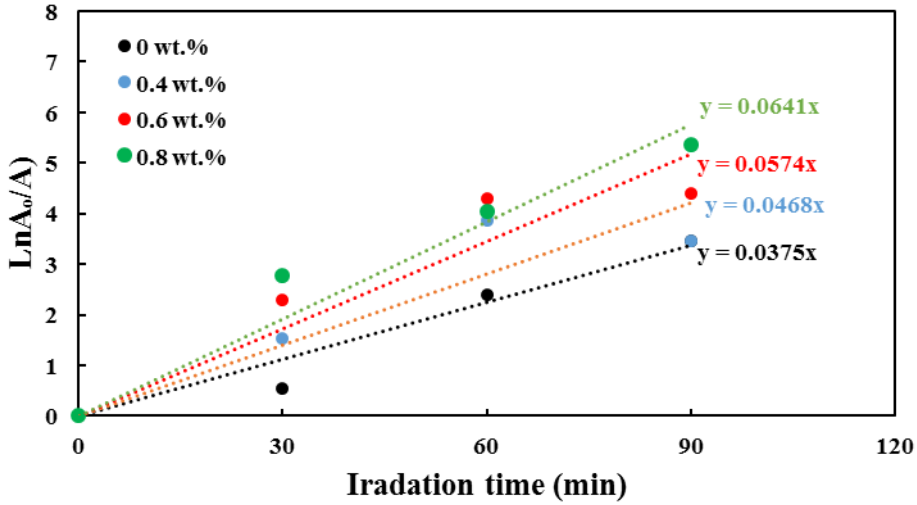


Figure 10: Contact angle for ZnO/TiO_2/cement nanocomposites

Conclusion

The addition of ZnO/TiO_2 nanoparticles to cement allows it to absorb organic molecules that are presented on the cement matrix, giving cement the potential to eliminate pollutants by exposing them to visible. The ZnO/TiO_2/cement nanocomposite was successfully created as a photocatalytic for a self-cleaning surface, and the results show that the MB breakdown rate increases as the dye content in the solution decreases. It is found that the MB decomposition rate increases with the decrease in the dye concentration of the solution. The photo-catalytic activity enhances by increasing ZnO in composite material. Under visible light, samples with a concentration of 0.8 percent produced the greatest results, followed by ZnO samples. Furthermore, specimens containing ZnO nanoparticles in TiO_2/cement nanocomposites exhibited the highest photocatalytic activity than TiO_2/cement nanocomposites. We found that cement surface is hydrophilic. When ZnO and TiO_2 were added to cement, better photocatalytic properties were obtained. The results of the optimized TiO_2/ZnO/cement nanocomposite show the excellent photo-catalytic activity.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

There are no conflicts of interest in this study.

ORCID:

Mays B. Al Taee
https://www.orcid.org/0000-0002-0318-234

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