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Photocatalytic Degradation of Methyl blue by TiO_2 Nanoparticles Incorporated in Cement

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Abstract

In this study, titanium dioxide (TiO_2) nanoparticles incorporated with cement were synthesized by a simple casting method as a function of the concentration of TiO_2 (0.2, 0.4, 0.8, 1, and 2 wt%). The prepared samples were characterized using the techniques of Field Emission Scanning Electron Microscope (FESEM) and UV-Visible spectrophotometer, which were used to measure the adsorption spectra. The observed photocatalytic efficiency of TiO_2 nanoparticles (NP) incorporated with cement was investigated by decomposing the dye methyl blue (MB) solution under sunlight irradiation. According to the slope, the value of the k constant at the best sample is 0.8 wt%, k = 0.8265 min^{-1}. FESEM images of the TiO_2/cement with 0.8 wt% content show the TiO_2 NPs were well-attached to cement particles, and they covered the cement surface. The increase in photocatalytic (PC) activity was due to an increase in TiO_2 concentration in the cement, which best occurs at 0.8 wt% of TiO_2 in cement. The degradation at the MB (5 ppm) was 98.864 % after 120 min of sunlight irradiation. The method involves easily and simply preparing TiO_2/cement that is used in self-cleaning and studying the effect of different festive factors, including the concentration of the dye. The preparation of TiO_2/cement was successful as a photocatalyst for a self-cleaning surface.

Article Info.

Keywords:
Photocatalytic, TiO_2 Nanoparticles, Cement, MB dye, self-cleaning.

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1. Introduction

Portland cement is a chemical mixture of calcium, silica, aluminium, iron, and minor amounts of other substances that are carefully managed [1]. Cement is causing a lot of concern because it is one of the leading sources of air pollution [2]. Photocatalysis can be defined as follows: a change in the rate of chemical reactions or their generation under the action of light in the presence of substances called photocatalysts that absorb light quanta and is involved in the chemical transformations of the reactants [3]. In addition, titanium dioxide (TiO_2) exposed to UV exhibits photo catalytically induced super hydrophilicity, which converts the surface's hydrophobic character to hydrophilic and produces a homogeneous water layer that prevents inorganic or organic components from adhering to its surface and keeps it clean [4, 5]. Semiconductor photocatalysis is one of the most effective methods for reducing pollutants in water [6]. TiO_2 is an important material for many physical applications, including solar cells and heterogeneous catalysis [7]. TiO_2 photocatalyst has a wide bandgap (i.e., 3.2 eV for anatase and 3.0 eV for rutile) and hence absorbs only the UV light, which accounts for only 4% of the total sunlight, to generate charge carriers for promoting the surface redox reactions [8]. Photocatalytic modern technology has been recognized as one of the most efficient solutions for managing air pollutants due to its superior photocatalytic (PC) activity, low cost, and 100% degradation [9]. Photocatalytic oxidation, which involves photocatalyst activation by solar light or UV irradiation, is one of the most significant and potentially improved oxidation processes [10]. A photocatalytic is a

semiconductor with the capacity to operate as a sensitizer for light-reduced redox processes because of its electrical structure, which contains a filled valence band and an empty conduction band. For instance, a semiconductor will promote an electron from the valence band when a photon with hv energy matches or surpasses the band-gap energy (VB) to the conduction band (CB); a hole (h+) is left in its wake. Excited-state conduction band electrons and valence band holes can interact with one another to produce heat and create metastable surface states, or they can react with electron acceptors to establish surface states [11].

The purpose of the work is to investigate how the ratio of TiO_2 affects the photocatalytic activity of self-cleaning surfaces made of TiO_2 and cement. By breaking down the dye's methyl blue (MB) aqueous solution when exposed to sunlight, the observed photocatalytic efficiency of the composites will be examined. The physical combination was used to add various elements into the TiO_2, including photocatalyst load, and dye concentration, which served as catalysts on the surface of TiO_2 can have on composites' photocatalytic activity will be examined along with their reaction kinetics.

2. Experimental Work

2.1. Materials

Three commercial materials have been used, including TiO_2 nanoparticles (NPs), cement, and MB dye. TiO_2 with an average particle size of 30 nm and a purity of 99.8% was purchased from Changsha Santech Company. The cement used in this work is Iraqi common Portland cement, also known commercially as (TASLUJA). It was kept in a dry environment to reduce the effect of humidity on the cement's characteristics. MB was used as an organic pollutant, which is purchased from CDH in India, in the experiment to evaluate the TiO_2/cement nanocomposite's photocatalytic degradation effectiveness by measuring its absorbance.

2.2. Preparation of TiO_2/Cement

In order to prepare cement samples, the TiO_2 NPs powders are incorporated with cement directly, a process known as internal doping. In this experiment, the internal doping approach was used, the cement mix was equivalently substituted by the TiO_2 NPs with different ratios of (0.2, 0.4, 0.8,1 and 2 wt%) and the ratio of cement adds to water is 2:1 to prepare the TiO_2/ cement block samples, mixing well, and then poured into glass molds with a diameter of 6 cm and left to dry for 24-48 hours. All TiO_2/ cement block samples tested have a 6 cm diameter, a thickness of 0.5 cm, and a weight of 23 g. Fig.1 illustrate the TiO_2/cement samples shapes.

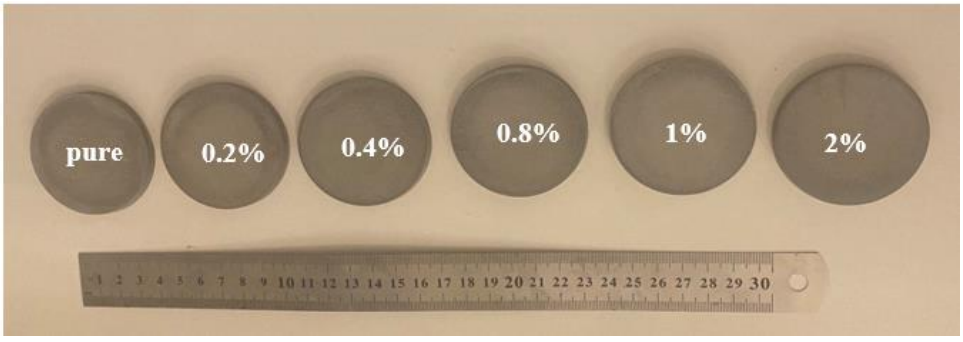


Figure 1: The shapes of samples of TiO_2 /cement.

2.3. Photocatalytic Activity

By examining the degradation of MB dye solution in the presence of sunlight, the photocatalytic activities of TiO_2/cement samples were assessed. They were exposed to sunlight for 4 hours. In order to reach MB equilibrium of adsorption-desorption on the photocatalytic surface, it was made with methyl blue dye (5 and 10 ppm). The samples were added to 50 ml of the dye solution, exposed to sunlight in a 10 cm diameter glass petri dish and kept in the dark for one hour. By evaluating the solutions' absorption in comparison to deionized water and the efficacy of the degradation, the degradation of MB, was calculated using a spectrophotometer and the absorbance intensity at 663 nm wavelength. The dye solution color changed with time, a transparent color means that it was self-cleaning. The following equation was used to calculate the percentage of MB deterioration [12]:

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

where $A_\circ$ and A are the absorbance values at the start of the experiment and time t respectively. The kinetic regulation of photodegradation of MB solution is kinetics of a pseudo-first order, which may be represented as:

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

where k in (min^{-1}) unite is the photodegradation rate constant [12, 13].

2.4. Characterization Techniques

Scanning Electron Microscopy with Field Emission (FESEM) (Inspect F50 FESEM) was used to investigate the structure of TiO_2/cement samples at higher magnification, resolution, and depth of focus [14]. The adsorption spectra were measured using a UV-Visible spectrophotometer (UV-1800 SHIMADZU).

3. Results and Discussion

Fig. 2 displays FESEM images of 0.8 wt% TiO_2/cement. The image shows cement with TiO_2 NPs. TiO_2 micrographs show spherical particles in clusters or singletons. Agglomeration creates TiO_2 crystals in the spheres. To achieve a high cement surface area of TiO_2 nanoparticles, they must be immobilized and dispersed uniformly.

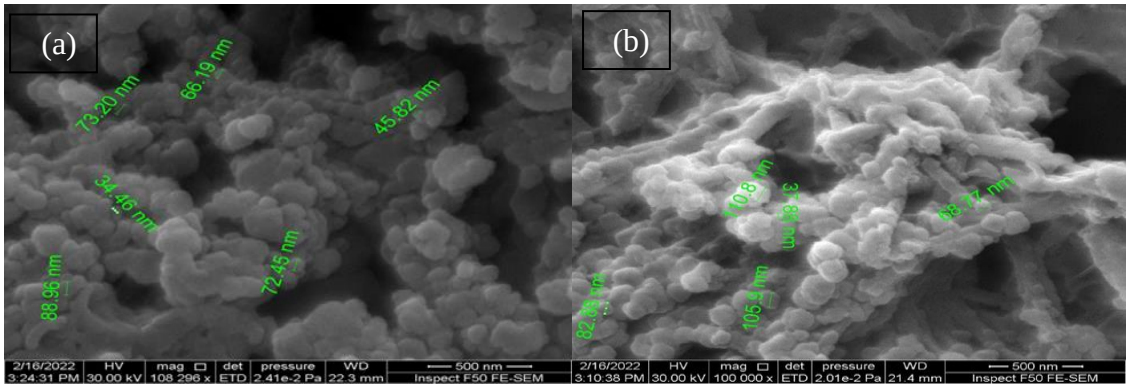


Figure 2: (a) shows FESEM images of a cement/TiO_2 with a TiO_2 component of 0.8wt%, (b) of pure cement content.

Using MB dye in sunlight, TiO_2/cement (0.2, 0.4, 0.8, 1, and 2 wt%) PC activities were investigated. The typical absorption peak of MB dye solution is 663 nm in the

UV-Vis spectrum. Photocatalytic degradation of the MB dye solution at 5 and 10 ppm concentrations was investigated. The absorbance of MB gradually decreases with the passage of time because of photocatalytic oxidation when exposed to sunlight, as demonstrated in Fig.3. This is taken as an indication of each material's photocatalytic activity.

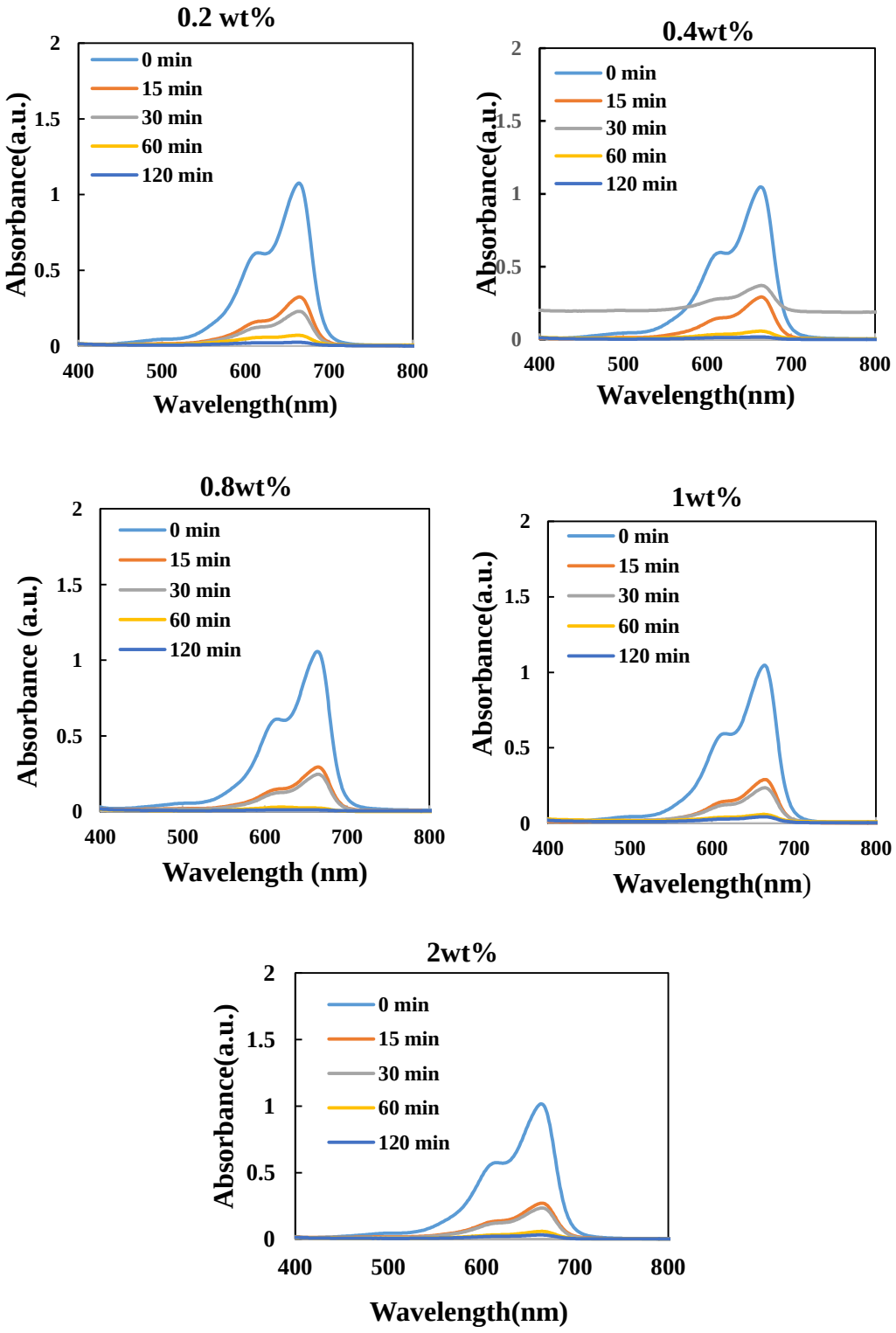


Figure 3: MB (5ppm) UV-Vis absorption spectra catalysed by TiO_2/cement with varying concentrations.

Consider Fig.4, where after 120 min of sunshine irradiation, the degradation of the MB solution increases as TiO_2 contents increase, then reduces at higher TiO_2 contents (1 and 2 wt%). At first, the rise in the amount of catalyst can be explained by the increase in the number of active sites on the surface of the photocatalyst. As mentioned earlier, decreases in degradation after 120 min of sunlight irradiation may be due to (a) a decrease in the specific surface area of the adsorbent due to agglomeration of photocatalytic particles, and (b) a decrease in the quantity of photons reaching the adsorbent active sites because of the screening action of excess catalyst [15]. However, increasing the active material TiO_2 in samples should lead to raise the degradation ratio due to increase the surface area of reaction as well as the concentration of e-h piers.

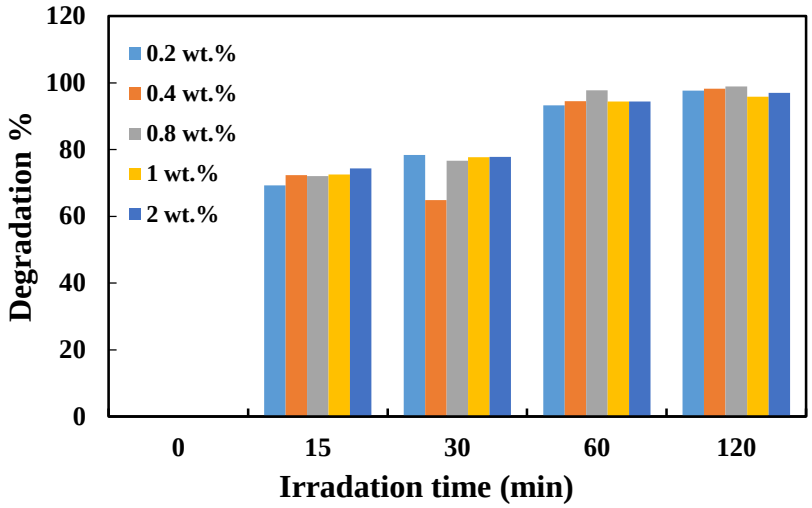


Figure 4: MB degradation % (5ppm) by TiO_2/cement than with solar light irradiation

The decoloration of MB solution at different degradation times is shown in Fig. 5. The color changed from blue to light blue after 120 min under sunlight irradiation.

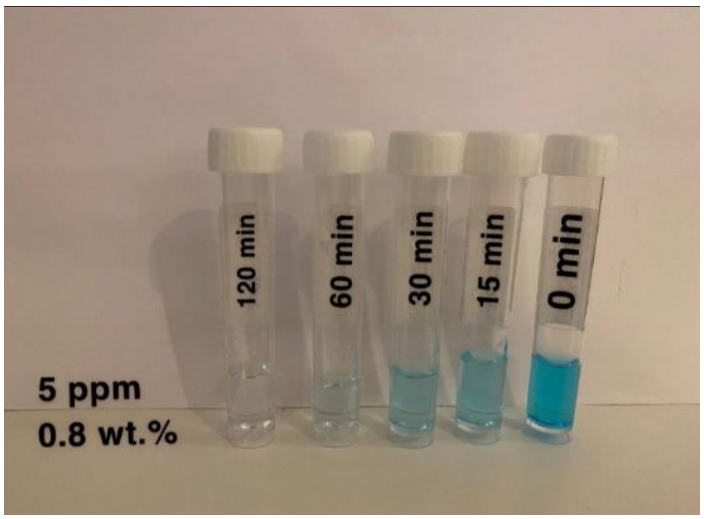


Figure 5: MB decoloration at different photo degradation levels (5ppm).

Fig.6 shows a linear relationship between $ln\,(A_\circ/A)$ and the irradiation time, indicating that the photo degradation of MB follows pseudo-first-order kinetics. The value of k can be directly obtained from the regression analysis of the linear curve in the plot $ln\,A_\circ/A = -kt$.

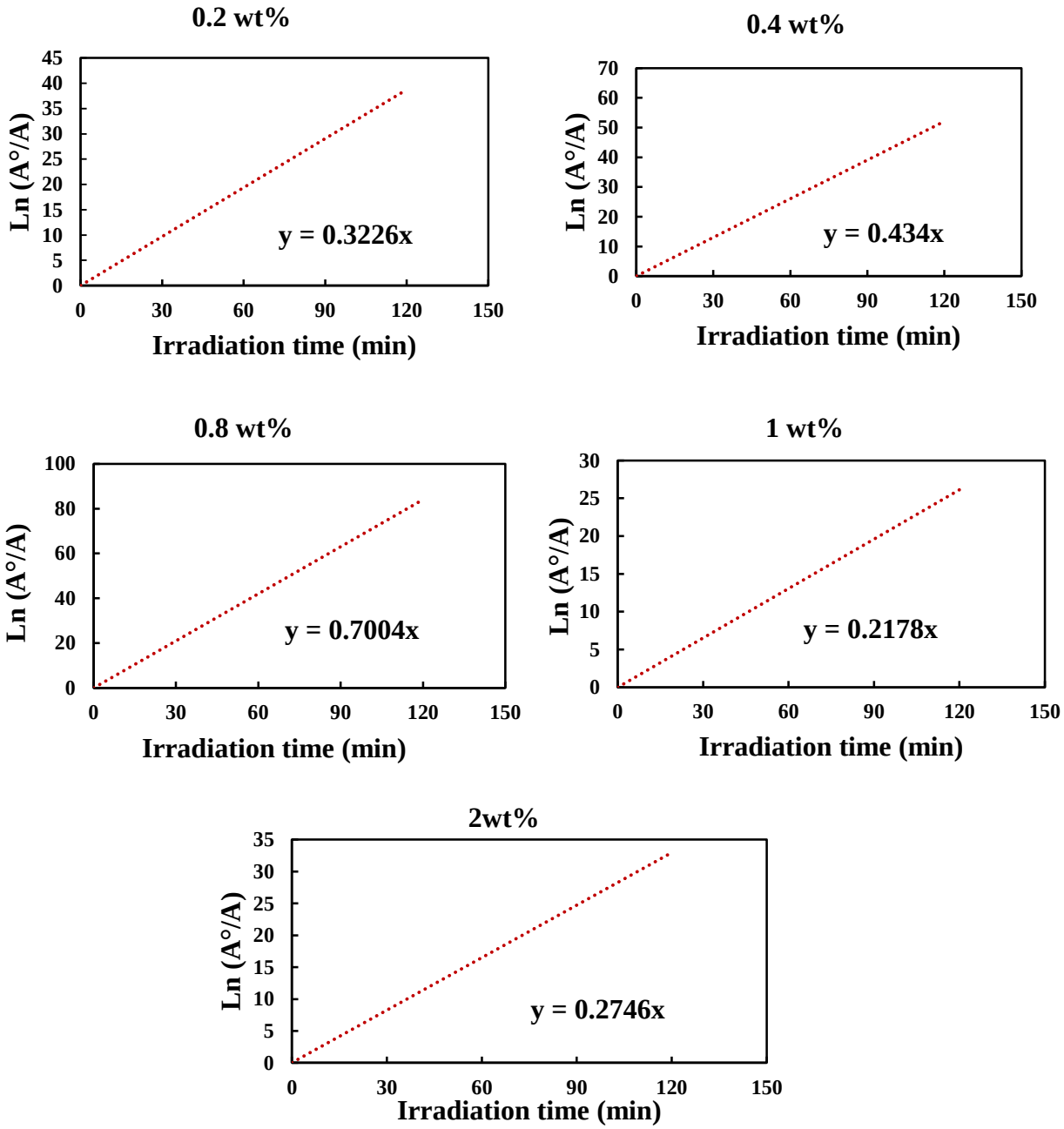


Figure 6: Ln (A_o/A) vs reaction time t of MB (5ppm) decomposition catalyzed by TiO_2/cement under sunlight irradiation.

As shown in Table 1, the rate constants (k) can be calculated from the slope of linear plots between ln($A_\circ$/A) and time. For the best sample 0.8wt%, k = 0.7004 min^{-1} is the value of the (k) constant.

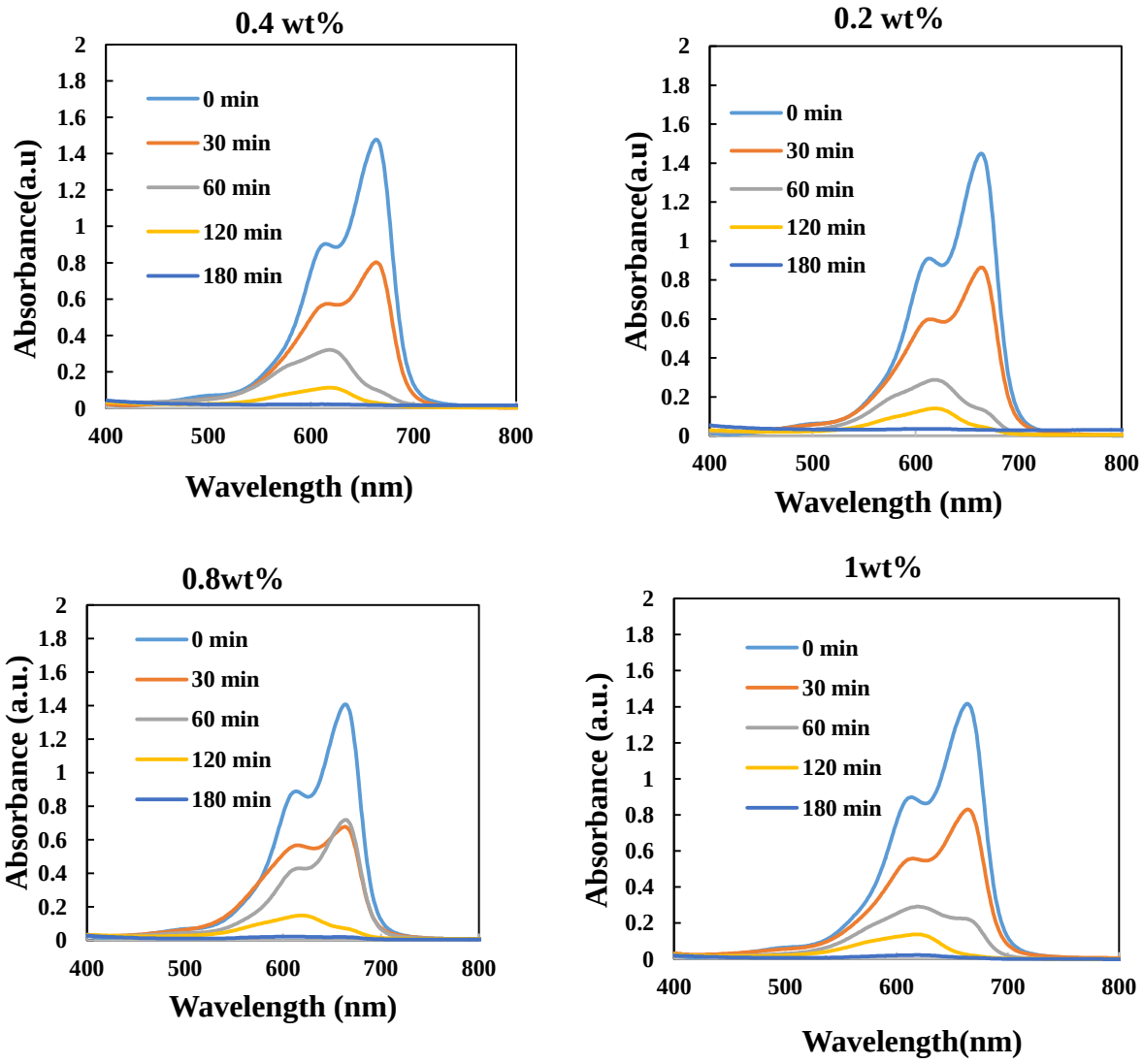
Table 1: Different TiO_2/cement degradation rate constants (5ppm).

TiO_2 wt%	Rate constant (k) min^{-1}
0.2	0.3226
0.4	0.434
0.8	0.7004
1	0.2178
2	0.2746

The absorption spectra of MB (10 ppm) decomposed in the presence of TiO_2/cement photocatalyst when exposed to sunlight, as shown in Fig.7. The characteristic absorption peak intensity of MB increases with decreased degradation time after 180 min of sunlight irradiation. Using optimum TiO_2/cement photocatalyst load (0.2, 0.4, 0.8, 1 and 2 wt%) and Fig. 8 provide graphs of degradation of the dye by photocatalysis as a function of time in percent for varied initial concentrations of 10 ppm MB dye.

When using the optimum TiO_2/cement photocatalytic load (0.8wt%) and varied initial concentrations of MB dye (5 and 10 ppm), it can be noted that dye degradation decreases with increasing concentration, as opposed to Fig.4 at the same TiO_2 content 0.8wt% and 5ppm MB concentration. This is due to the fact that larger dye concentrations (a) shorten the path length of photons entering the dye solution (b) absorbs a large amount of light instead of the catalyst [16].

The slope of linear plots of $ln(A_\circ/A)$ vs. time can be used to determine rate constants (k), and the estimated values of k for the photo degradation by TiO_2/cement are shown in Table 2. According to the apparent slope, the best sample's value of the k constant is 0.8265 min^{-1} at 0.8wt% TiO_2.



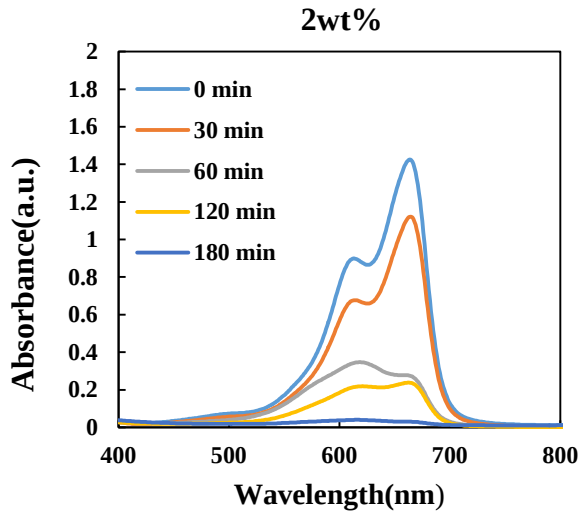


Figure 7: MB (10ppm) UV-Vis absorption spectra catalyzed by TiO_2/cement of varying concentrations.

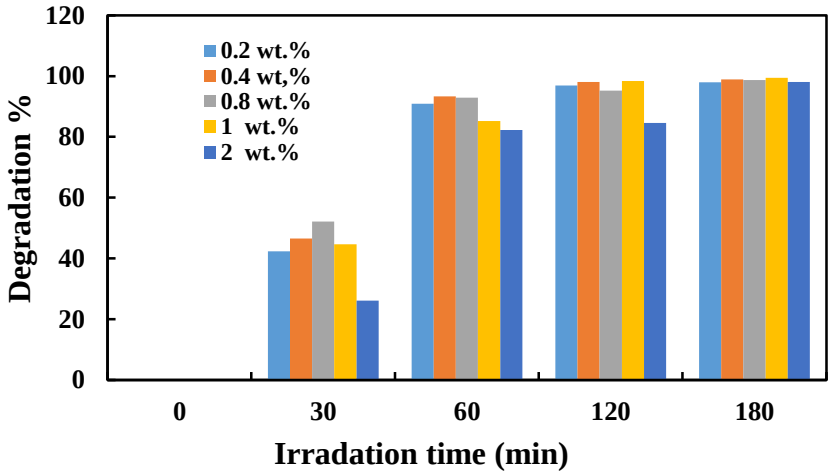


Figure 8: MB degradation % (10ppm) by TiO_2/cement irradiation time than with solar light irradiation.

Table 2: Different TiO_2/cement degradation rate constants (10ppm).

TiO_2 wt%	Rate constant (k) min^{-1}
0.2	0.2622
0.4	0.4591
0.8	0.8265
1	0.3316
2	0.1976

The decoloration of MB solution at different degradation times is shown in Fig. 9. The color changed from blue to light blue after 180 min under sunlight irradiation. The calculated values of k for the photodegradation of TiO_2/cement under sunlight irradiation are shown in Fig.10, which illustrates a linear relationship between ln ($A_\circ$/A) and the irradiation time.

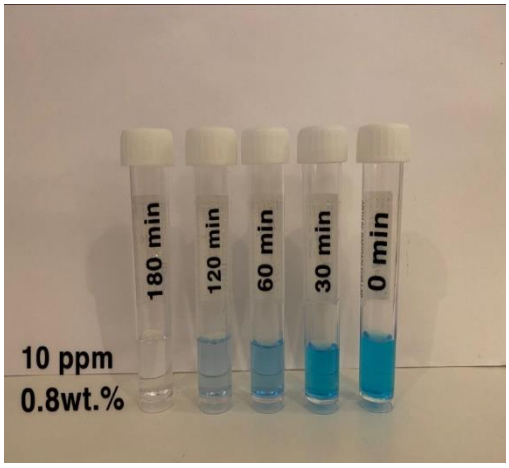


Figure 9: MB decoloration at different photo degradation levels (10ppm).

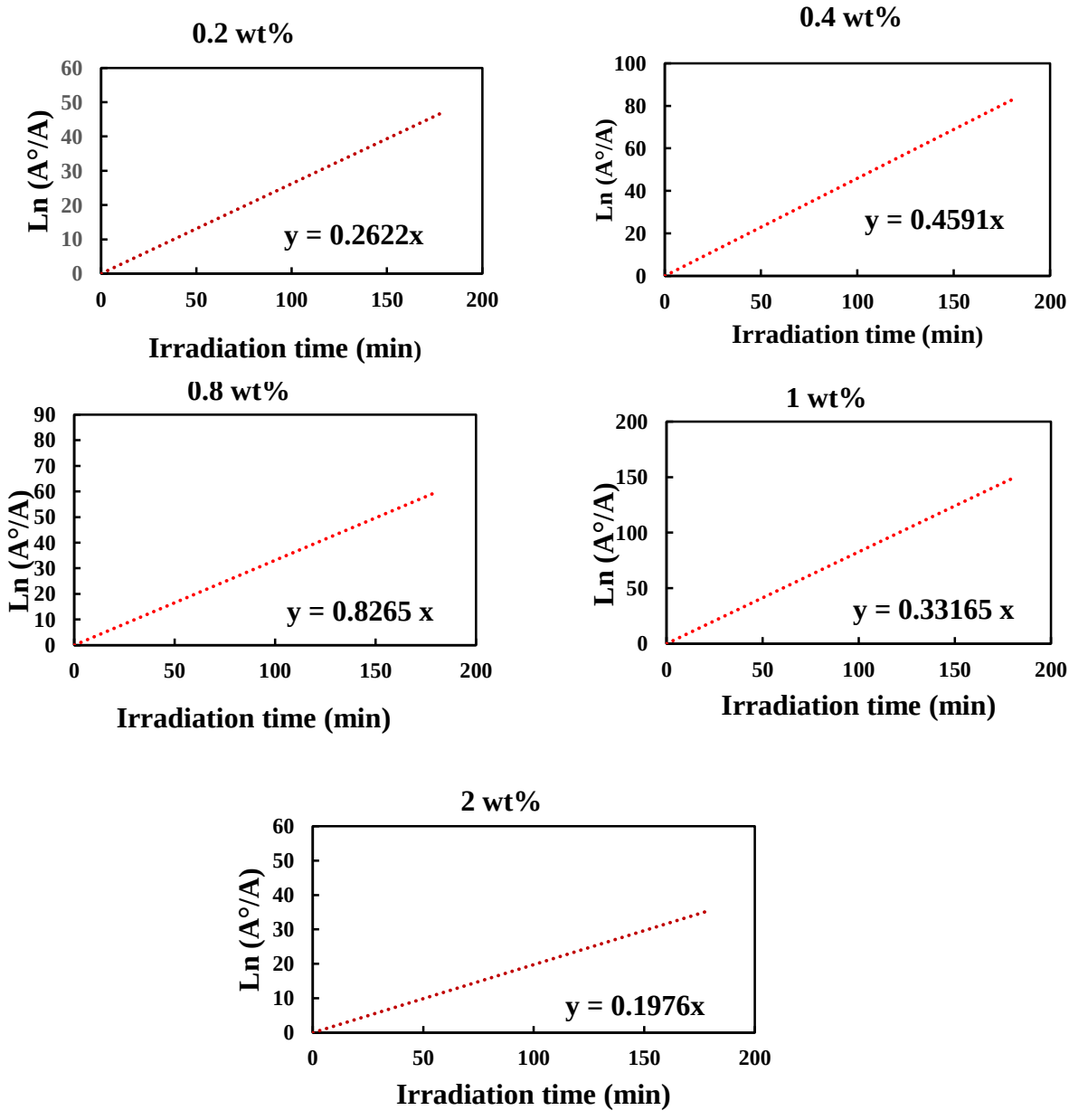


Figure 10: Relationship between Ln (A_o/A) and reaction time t of MB (10 ppm) decomposition catalyzed by TiO_2/cement under sunlight irradiation.

4. Conclusions

Since TiO_2 nanoparticles are added to cement, the cement could remove pollutants by exposing them to visible and UV light by absorbing organic molecules that are present on the cementitious matrix. In the ability of a photocatalytic for a self-cleaning surface, the TiO_2/cement was effectively made, and the results reveal that the MB breakdown rate rises as the dye content in the solution falls. The best results in visible light came from samples made of TiO2, then those with a production concentration of 0.8 wt%. Additionally, samples containing 0.8 wt% TiO_2/cement exhibited the highest photoactivity. TiO_2/cement has shown promise in the creation of photocatalytic systems that can take advantage of most of the available light.

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Conflict of interest

Authors declare that they have no conflict of interest.

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التحلل التحفيزي للميثيل الأزرق بواسطة جزيئات TiO_2 النانوية المدمجة في الاسمنت

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الخلاصة

في هذه الدراسة، تم تحضير عينات من ثاني أكسيد التيتانيوم (TiO_2) النانوية المدمجة مع الأسمنت بطريقة الصب البسيطة بتراكيز مختلفة من TiO_2 (0.2, 0.4, 0.8, 1 and 2 wt%). فحصت العينات المحضرة بتقنية الماسح المجهري الإلكتروني (FESEM) واستخدم مقياس الطيف الضوئي المرئي للأشعة فوق البنفسجية UV-1800 (SHIMADZU) قياس أطياف الامتزاز. تم فحص كفاءة التحفيز الضوئي المرصودة لجسيمات TiO_2 النانوية المدمجة مع الأسمنت عن طريق تحلل صبغة الميثيلين الأزرق في محلول مائي تحت إشعاع ضوء الشمس. وفقًا للنتائج، فإن قيمة ثابت k في أفضل عينة 0.8wt% هي $k=0.8265min^{-1}$. صورة FESEM لثاني أوكسيد التيتانيوم / الأسمنت بمحتوى 0.8wt% تبين أن جزيئات TiO_2 النانوية كانت مرتبطة جيدًا بجزيئات الأسمنت، وكانت تغطي سطح الأسمنت. كانت الزيادة في نشاط التحفيز الضوئي ناتجة عن زيادة تركيز TiO_2 في الأسمنت، والذي يحدث بشكل أفضل بنسبة 0.8wt% من TiO_2 في الأسمنت. كان التحلل في الميثيلين الأزرق (5 جزء في المليون) 98.864٪ بعد 120 دقيقة تحت إشعاع ضوء الشمس. تحضير TiO_2/الأسمنت بسهولة وبساطة يستخدم في التنظيف الذاتي، ويدرس تأثير العوامل المختلفة، بما في ذلك تركيز الصبغة. كان تحضير TiO_2/الأسمنت ناجحًا كمحفز ضوئي لسطح التنظيف الذاتي.