A comparative study on the self-cleaning behavior and antibacterial activity of Portland cement by addition of TiO$_2$ and ZnO nanoparticles

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Abstract
In the present study, the photocatalytic effect of the addition of nano-TiO$_2$/ZnO particles with different molar ratios of polyethylene glycol on the self-cleaning behavior and antibacterial activity of Portland cement was investigated to evaluate its potential for dye decolorization, and inactivation of Escherichia coli and Streptococcus mutans. Moreover, the effect of PEG addition on the hydration and tensile strength properties of the cement samples was evaluated. Furthermore, to study the self-cleaning behavior of the cement samples, an azo dye was selected as an organic pollutant. The modified cement samples were characterized using x-ray diffraction, Fourier-transform infrared spectroscopy, energy-dispersive x-ray spectroscopy, and scanning electron microscopy to assess the pozzolanic reactivity of the cement paste in the presence of TiO$_2$ and ZnO nanoparticles. The results showed that the bactericidal properties of the modified cement specimens were dependent on the hydration time and composition of the samples. Accordingly, the maximum inhibitory effect was observed for the specimens hydrated for 7 d. Additionally, the surface of the samples was able to effectively decompose the azo dye. This novel modified cement has a promising potential to be used as a self-cleaning and antibacterial coating for urban constructions.

1. Introduction
Nanotechnology and the implementation of nanomaterials had the highest impact on the preparation and processing of new materials, which are intended to be modified to show the most optimum properties [1, 2]. Among this achievement, cement is the most applicable construction material, which have not been studied thoroughly especially in the field nanomaterials to maximize their capabilities and simultaneously maintain their cost-effectiveness. For construction applications such as hospitals, cleanrooms, and operating rooms that the antibacterial activity is a critical property, the use of nanotechnology and nanomaterials is inevitable. Hence, it is necessary to exploit the unique antibacterial and self-cleaning properties of nanoparticles in the compositions of mortar and cement [3–5].

Conventional disinfection methods using chemicals e.g. chlorine dioxide and ozone, and UV germicidal irradiation are the most effective and expensive techniques, which are not appropriate for residential constructions. In addition, these compounds lose their antibacterial impacts over time [6]. It is observed that microbial growth occurs on the surface of materials that poses a serious threat to human health. Thus, the application of photo-catalysts as new, inexpensive, simple and efficient coating agents has attracted a lot of attention due to their ability to reduce the number of the microorganisms on the interior surfaces of building.

Many studies have been focused on the application of TiO$_2$ nanoparticles in construction materials to induce novel properties including self-cleaning [7–9], decolorization [10–12], and antibacterial activity [13–18]. Caballero et al [17] studied the photocatalytic inactivation of Escherichia coli (E. coli) deposited on TiO$_2$-loaded
In order to prepare the samples, ZnO and TiO$_2$ nanoparticles were used. The characteristics of the nanoparticles are presented in Table 1. Besides, to increase the strength and stability of the cement samples, PEG with an average molecular weight of 600 g mol$^{-1}$ (purchased from Sigma-Aldrich Co., USA) was added to the cement during the preparation process. Additionally, white Portland cement, (with the specification presented in Table 2), was used for as the main composition of the mixture. Table 3 shows the present phases within the white cement.

### 2. Experimental procedure

#### 2.1. Materials

In order to prepare the samples, ZnO and TiO$_2$ nanoparticles were used. The characteristics of the nanoparticles are presented in Table 1. Besides, to increase the strength and stability of the cement samples, PEG with an average molecular weight of 600 g mol$^{-1}$ (purchased from Sigma-Aldrich Co., USA) was added to the cement during the preparation process. Additionally, white Portland cement, (with the specification presented in table 2), was used for as the main composition of the mixture. Table 3 shows the present phases within the white cement.

### Table 1. Physical properties of ZnO and TiO$_2$ nanoparticles used in this study.

| Manufacturer       | US Nano. | Degussa (Evonik) P25, TiO$_2$ Aeroxide P25 |
|--------------------|----------|------------------------------------------|
| Purity (%)         | 99.99    | 99.5                                     |
| Specific area (m$^2$/g) | 4.8 to 6.8 | 50 ± 15                                  |
| Average length of particles | 150–250 nm | —                                        |
| Average diameter of particles | 80–100 nm | 21 nm                                    |

### Table 2. Chemical composition of the white cement used in this study (mass fraction, wt%).

| CaO | SiO$_2$ | Al$_2$O$_3$ | MgO | SO$_3$ | Na$_2$O | K$_2$O | Fe$_2$O$_3$ | L.O.I.$^a$ |
|-----|---------|-------------|-----|--------|---------|--------|-------------|------------|
| 65  | 23.2    | 4.9         | 1.4 | 1.6    | 0.3     | 0.35   | 0.35        | 2.6        |

$^a$ Loss on ignition: the sample were heated to 950 °C.
2.2. Characterization

To prevent the agglomeration of nanoparticles during the sample preparation ZnO and TiO\textsubscript{2} nanoparticles were dispersed using an ultrasonic processor (Hielscher model UIP1000hd, Germany).

To study the photodegradation of the organic dye, UV radiation was employed using four mercury UV lights with a maximum power of 8 W and wavelength of 365 nm. UV–vis spectroscopy (Shimadzu model UV-2700, Japan) was used for determination of dye decomposition during the self-cleaning experiments. An autoclave was used for sterilization of laboratory glassware and an incubator was used for the cultivation of \textit{E. coli} (PTCC 1399) and \textit{Streptococcus mutans} (S. mutans) (PTCC 1112). To measure the weight of chemicals, a high precision electronic balance (Escaletec model SBA 32, Germany) was utilized. A digital pH meter (Metrohm model 827, Switzerland) was employed for measuring the pH of the solutions during the sample preparation.

The phase characterization of the samples were performed by x-ray diffraction (XRD) (Philips model PW3040, Netherlands) at the working voltage and current of 40 kV and 25 mA using Cu \( k\alpha \) radiation (\( \lambda = 1.54184 \) Å), respectively. Furthermore, to assess the morphology of the samples the scanning electron microscopy (SEM) (TESCAN model Mira3, Czech Republic) was carried out. Moreover, Fourier-transform infrared spectroscopy (FTIR) was carried out to assess the functional groups of the cement samples containing ZnO and TiO\textsubscript{2} nanoparticles.

| Name          | Abbreviation | Chemical formula         |
|---------------|--------------|--------------------------|
| Alite         | C\textsubscript{3}S | Ca\textsubscript{3}SiO\textsubscript{5} |
| Belite        | C\textsubscript{2}S | Ca\textsubscript{2}SiO\textsubscript{3} |
| Aluminate     | C\textsubscript{2}A | Ca\textsubscript{2}Al\textsubscript{2}O\textsubscript{6} |
| Portlandite   | P            | Ca(OH)\textsubscript{2} |
| Ettringite    | E            | [Ca\textsubscript{6}(Al(OH)\textsubscript{2})\textsubscript{4}24H\textsubscript{2}O] |
|               |              | [SO\textsubscript{4}\textsubscript{3}•1.5H\textsubscript{2}O] |
| Calcite       | CaO          | CaO                      |
| Calcium       | CSH          | (CaO\textsubscript{x}SiO\textsubscript{-x}2H\textsubscript{2}O\textsubscript{y}) |

Table 3. Chemical phases present in the white cement.

| Table 4. Cement samples with various ZnO and TiO\textsubscript{2} nanoparticles contents. |
|-----------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Symbols | White cement (wt%) | TiO\textsubscript{2} nanoparticles (wt%) | ZnO nanoparticles (wt%) | Polyethylene glycol (wt%) |
| M-xd | 100 | 0 | 0 | 0 |
| T1-xd | 98.5 | 1 | 0 | 0.5 |
| T2-xd | 96.5 | 3 | 0 | 0.5 |
| T3-xd | 94.5 | 5 | 0 | 0.5 |
| Z1-xd | 98.5 | 0 | 1 | 0.5 |
| Z2-xd | 96.5 | 0 | 3 | 0.5 |
| Z3-xd | 94.5 | 0 | 5 | 0.5 |
| C1-xd | 98.5 | 0.5 | 0.5 | 0.5 |
| C2-xd | 96.5 | 1.5 | 1.5 | 0.5 |
| C3-xd | 94.5 | 2.5 | 2.5 | 0.5 |

\( x \) represents the number of days for hydration process (\( x = 7 \) or 14 d).

2.3. Sample preparation

To assess the antibacterial activity of samples in the presence and absence of ZnO and TiO\textsubscript{2} nanoparticles, the samples were prepared in a sphere-like morphology by adding 0.5 wt% PEG as the stabilizer. The hydration times of 7 and 14 d were selected. Table 4 represents the nanoparticle concentration and hydration time of the samples. To prepare the samples, 20 g cement was mixed with 8 g deionized water with pH = 7, the cement-to-water ratio was kept constant during the entire process. The stirring was kept on at 500 rpm for 3 h. Afterward, the stirring was stopped for 2 min and then restarted at 2000 rpm for 2 h. Then, the mixture was introduced to a disk mold with a height of 3 mm and a diameter of 42 mm. The mixture was preserved at the place with a relative humidity of 95% for 24 h. The pastes were taken out of the mold and soaked into the water to start the hydration process. For the samples containing ZnO and TiO\textsubscript{2} nanoparticles, the ultrasonic homogenization was carried out to the 8 g suspension of water/ZnO and water/TiO\textsubscript{2}.
2.4. Bacteria culture test
In this study, *S. mutans* and *E. coli* bacteria were purchased from Agriculture Biotechnology Research Institute of Iran and they were revitalized by using the liquid culture media of Nutrient Broth (NB) and Nutrient Agar (NA). A simple sugar such as glucose and an enriched nutrient source of succinic acid, phosphor, and sulfur were employed as the carbon source for the growth of the bacteria and synthesis of protein, respectively. For the bacterial culture, 50 ml of NB was added to 100 ml deionized water and 800 ml NA was added to 1000 ml deionized water. Afterward, a sample of bacterial culture were prepared in NA medium and transferred to a vial containing 5 ml NB medium using a sterile loop. Finally, the sample was maintained in an incubator at 37 °C for 24 h. Then 5 drops of bacterial culture was added to 5 ml deionized water. It should be noted that the transparency of the culture fluid was checked according to 0.5 McFarland standard [24]. For this purpose, the sample containing bacteria was kept adjacent to the McFarland standard vial in the presence of sufficient background light. Then, the sample was compared to the standard fluid and it was used for the rest of the experiment, when it had the transparency similar to that of the standard.

2.5. Photocatalytic experiments
The photocatalytic effect of TiO2 and ZnO nanoparticles on the decolorization and antibacterial activity of the cement disks was evaluated. In addition, to investigate the effect of irradiation on the photocatalytic experiments, control sample were evaluated in the absence of irradiation. Moreover, an 8-watt high pressure mercury vapor lamp with the wavelength of 365 nm was used as the radiation source during the photocatalytic experiments.

2.6. Decolorization experiments
To analysis the decolorization properties of the cement specimens, 80 ml of the organic dye solution with pH = 6 was added to a 15-cm diameter flask. Then the cement containing ZnO and TiO2 nanoparticles was soaked into the solution while stirring condition at 200 rpm and 37 °C. The flask was inserted at a dark place to reach the absorption/desorption equilibrium. Additionally, for assessing the effect of nanoparticles the same experimentation was carried out on the samples without the nanoparticles.

2.7. Counting techniques and data acquisition
To determine the numbers of *S. mutans* and *E. coli* bacteria, a sample was obtained from each experiment. Then, ten-fold serial dilutions were prepared and 200 µl of each diluted solution was spread on NA plate and maintained in the incubator for 24 h at 37 °C. The numbers of colonies were finally counted on the plate and the values of colony forming units per milliliter (CFU/ml) were estimated.
3. Results and Discussion

3.1. XRD Characterization

The results of XRD analysis for samples containing various concentrations of ZnO and TiO$_2$ nanoparticles are shown in figure 1. Moreover, XRD spectra of the samples hydrated for 7 and 14 d of hydration process are presented in the figure. The phases of anatase, rutile, and zinc oxide with the structures of rhombohedral, orthorhombic, and hexagonal, respectively, were determined for samples C3-14d and C3-7d. Due to the larger surface area, higher porosity, and more facile formation of free radicals anatase phase shows the highest photocatalytic activity [11, 25]. In addition, it is remarkable that Ca(OH)$_2$ peak decreased for sample C3-7d,
which was modified by ZnO nanoparticles, while for sample C3-14d the peak increased due to the prolongation of the hydration time.

3.2. Microstructure observation

Figure 2 display the SEM micrographs of cement samples prepared and hydrated for 7 d. According to the micrographs, the crystalline platelets of Ca(OH)₂ are seen in the figure 2(a), which contained no nanoparticle. While for those, which contained ZnO and TiO₂ nanoparticles with cauliflower morphologies and C–S–H phase was were formed during the hydration process. It has been mentioned in the previous studies that by adding nanoparticles to the cement, the porous structure of the cement declines because of decrease in the crystalline distance and prevention the formation of Ca(OH)₂ large crystals. According to the cauliflower morphology crystals that are formed in modified cement, it can be concluded that the aggregation decreases due to the presence of ZnO and TiO₂ nanoparticles.

3.3. EDS analysis

The EDS results obtained from samples M-7d, T3-7d, Z3-7d, and C3-7d are shown in figure 2. The presence of TiO₂ and ZnO nanoparticles in the modified samples confirmed the stability of the cement microstructure. According to the results obtained by EDS analysis, the ratios of Ca/Si and Si/Ca can be used as an important criterion for formation of the CH and C–S–H phases. Table 5 demonstrates the Ca/Si and Si/Ca ratios for all samples. According to these results, the Ca/Si ratio increased for sample C3-7d, which was attributed to the pozzolanic reaction between the CH and C–S–H phases in the presence of the added nanoparticles. The rate of pozzolanic reaction directly depends on the specific surface area, chemical compounds and active phase content. Although TiO₂ is not considered as a pozzolanic material, adding nanoparticles with high surface area causes a severe need for water and shorten the cement setting time.

3.4. FTIR spectroscopy

The FTIR results for samples T3-7d, M-7d, C3-7d, and Z3-7d are shown in figure 3. The peak in the wavenumber range of 500-700 cm⁻¹ was attributed to bending vibrations of Ti-O-Ti groups. In the modified samples the peak with high intensity at the wavenumber of 1800–1900 cm⁻¹ was removed. This peak was related

Table 5. Kinetic results of photocatalytic degradation of Chrome Intra Orange G with the initial concentration of 15 ppm.

| Sample     | Apparent kinetic constant (K_{app}) | Degradation efficiency (%) |
|------------|-------------------------------------|-----------------------------|
| Z2-7d      | 0.0029                              | 32                          |
| Z3-7d      | 0.0060                              | 60                          |
| T2-7d      | 0.0046                              | 46                          |
| T3-7d      | 0.0038                              | 38                          |
| C2-7d      | 0.0048                              | 48                          |
| C3-7d      | 0.0091                              | 70                          |
to symmetric stretching and bending vibrations of the O–H bonds within the CSH, CAH, and CASH hydrates. The reduction of intensity of the broadened peak in the range of 3550–3650 cm\(^{-1}\) was assigned to formation of –OH groups within the Ca(OH)\(_2\) phase. It can be deduced that formation of C-A-S gel and the progression of pozzolanic reaction was due to existence of the nanoparticles. Moreover, a peak in the range of 1000–1150 cm\(^{-1}\) was attributed to C–O–H bond, which was related to PEG molecular structure and the bending vibration of –OH groups [26–30].

### 3.5. Antibacterial activity

Figure 4(a) shows the bacterial survival rate (colony forming units per volume [CFU/ml]) of E. coli at different time for samples of T2-7d and T3-7d. The survival rates of the mentioned samples decreased over time and for the durations shorter than 60 min the decrease was significant, while for the durations longer than 80 min the reduction in survival rate was insignificant. According to the results, for the sample containing 1 wt% TiO\(_2\) nanoparticles (T1-d7), the CFU value was not countable, thus no data was reported for this sample.
Figure 4(b) shows the survival rates of S. mutans for various times for samples T2-7d and T3-7d. As can be seen the survival rates reduced over time for samples containing different TiO2 nanoparticles contents. Moreover, the results by prolonging the time from 0 to 60 min the survival rate decreased about 58% for the mentioned samples. In addition, it was observed for sample T1-d7 the survival rate of S. mutans was uncountable. Figure 4(c) also displays the survival rate of E. coli over various periods for samples Z2-7d and Z3-7d. Similar to the results presented in figures 4(a) and (b), it was seen that the survival rates for both samples with different ZnO concentrations declined over time. Moreover, with prolonging the time from 0 to 60 min the survival rates decreased to 75% and 90% for samples Z2-7d and Z3-7d, respectively. However, the survival rate of E. coli reached zero after 140 and 90 min for samples Z2-7d and Z3-7d, respectively. It is evident that the survival rate of E. coli for the sample containing 1 wt% ZnO nanoparticles (Z1-d7) was uncountable. Figure 4(d) also exhibits the survival rate of S. mutans over various periods for samples Z2-7d and Z3-7d. Similarly, the results in figures 4(a)–(c) revealed that the survival rates reduced over time for samples with different ZnO nanoparticles contents. Furthermore, the results exhibited that over time (0–60 min) the survival rate decreased to 71% and 86% for samples Z2-7d and Z3-7d, respectively. On the other hand, the survival rates of S. mutans (similar to that of the E. coli), reached zero after 140 and 90 min and for samples Z2-7d and Z3-7d, respectively. Besides, it is evident that the survival rate of S. mutans for the sample containing 1 wt% ZnO nanoparticles (Z1-d7) was uncountable. Due to the negative charge of the cell membranes of the S. mutans and E. coli, the anions or other molecules with negative charges are repulsed by electrostatic forces; therefore, they cannot enter the bacterial cell membrane. On the other side, other positively-charged molecules such as perhydroxyl radicals can enter the bacterial cell membrane and deactivate the bacteria. Likewise, due to the negative charge of bacterial cell membrane, the ZnO nanoparticles can be easily adsorbed on the membrane surface and deactivate the bacteria [31].

3.5.1. Effect of ZnO nanoparticles

The results of this study indicated that with increasing the ZnO nanoparticles in the presence of PEG as stabilizer the survival rates of both S. mutans and E. coli decreased considerably. The results also showed that after a period of 60 min with enhancing the ZnO content, the survival rate were reduced, which was related to the antibacterial properties of modified cement. It was also shown that the survival rates of both S. mutans and E. coli reduced to zero after 90 and 140 min for samples containing 5 and 3 wt% ZnO nanoparticles, respectively.

3.5.2. Effect of TiO2 nanoparticles

The results of this study exhibited that with increasing the TiO2 nanoparticles in the presence of PEG as stabilizer the survival rate of both S. mutans and E. coli declined noticeably. It is evident in figure 4(c) that after 20 min by increasing TiO2 nanoparticles concentration lower survival rates were resulted, which confirmed the effective antibacterial activity of TiO2 nanoparticles of modified cement (similar to the results obtained for ZnO nanoparticles). According to figure 4(f), the survival rate of S. mutans reached zero after 105 and 165 min for the samples containing 5 and 3 wt% TiO2 nanoparticles, respectively. Moreover, for E. coli the survival rate reached zero after 105 min and 140 min for the samples containing 5 and 3 wt% TiO2 nanoparticles, respectively (figure 4(e)).

3.5.3. Simultaneous effect of ZnO and TiO2 nanoparticles

Figure 4(e) shows the survival rates of E. coli for various times for samples containing nano-TiO2, (T2-7d and T3-7d), nano-ZnO (Z2-7d and Z3-7d), and a combination of both nanoparticles (C2-7d and C3-7d). All samples were prepared by adding 0.5 wt% PEG as a stabilizer with hydration time of 7 d. The figure indicates that with prolonging the test time from 15 min to 135 min the survival rate decreased for all samples and this decrease was more significant during 15–60 min. The results also implied that the effect of ZnO nanoparticles on the antibacterial activity of the cement samples were more significant than those containing TiO2 nanoparticles. In addition, by increasing the concentration of nanoparticles for samples containing only TiO2 or ZnO nanoparticles, the antibacterial activity of the samples improved. It should be noted that the mixture of ZnO and TiO2 nanoparticles increased the antibacterial properties of the cement samples in comparison to those containing only one type of the nanoparticles. This results were obtained using E. coli to evaluate the antibacterial properties of the modified cements.

The graphs presented in figure 4(f) show the survival rates of S. mutans after various times for samples containing nano-TiO2 (T2-7d and T3-7d), nano-ZnO (Z2-7d and Z3-7d), and the mixture of ZnO and TiO2 nanoparticles (C2-7d and C3-7d). All samples were prepared by adding 0.5 wt% PEG as the stabilizer and hydration time of 7 d. These results indicated that by prolonging the test time from 15 to 165 min the survival rates of S. mutans were decreased for all samples and similar to the graphs in figure 4(e) this reduction was significant after 45 min. It can be deduced that the effect of ZnO nanoparticles on antibacterial activity of the cement samples was more remarkable than those containing TiO2 nanoparticles. Nevertheless, the antibacterial
properties of samples T3-7d and Z2-7d were similar, which showed the greater efficiency of ZnO nanoparticles on deactivation of *S. mutans*. Moreover, it was concluded that the mixture of ZnO and TiO2 nanoparticles enhanced the antibacterial activity of cement samples in comparison to ones containing only one type of the nanoparticles, (similar to the results obtained for *E. coli*). Besides, the bacterial survival rates showed that by rising the TiO2 and ZnO contents (with the ratio of 1:1) from 3 to 5 wt%, the antibacterial properties enhanced significantly. Also for sample C3-7d the survival rate reached zero after 90 min suggesting that the highest efficiency was obtained by simultaneous addition of ZnO and TiO2 nanoparticles.

### 3.5.4. Effect of hydration time

The effect of hydration time on the antibacterial activity is shown in figure 5. The samples containing a mixture of both ZnO and TiO2 nanoparticles were used to modify the cement samples and UV irradiation was implemented during the experiments. The results exhibited that with increasing the test time, the survival rates of all samples declined significantly, which was more noticeable during the first 45 min. Accordingly, it was concluded that with prolonging the hydration time, the antibacterial activities of samples decreased. Therefore, the sample, which contained the highest nanoparticles content and hydrated for 7 d showed the highest antibacterial activity. This declination is because by increasing the hydration time, more Ca(OH)2 crystals and C-S-H phase are formed that cover the nanoparticles, which leads to reduction of the nanoparticles at the surface and lowering the antibacterial activity of the samples. The experiments were carried out by adding *E. coli* bacteria on the surface of samples. As can be seen in the figure both samples C3-14d and C2-7d showed a similar trend for the deactivation of *E. coli*. On the other side, the survival rate of *E. coli* reached zero for sample C3-7d after 60 min.

Figure 5(b) shows the effect of hydration time on the antibacterial properties of the samples containing both ZnO and TiO2 nanoparticles under UV irradiation light in the presence of *S. mutans*. The results confirmed that by prolonging the hydration time, the survival rates of the samples C2-7d, C3-7d, C2-14d, and C3-14d declined considerably, which was more noticeable during the first 45 min of the antibacterial test, which was consistent with the results obtained for *E. coli*. According to the figure, it could be concluded that with increasing the hydration time, the antibacterial properties of samples decreased. Thus, for the sample containing the highest nanoparticle concentration, the hydration time was selected 7 d, which resulted in the highest antibacterial properties. Moreover, it can be deduced that both samples C3-14d and C2-7d had a similar efficiency on the inactivation of *S. mutans*. On the other hand, for sample C3-7d the survival rate of *S. mutans* reached zero after 90 min.

Figure 6 compares the survival rates of *E. coli* and *S. mutans* for sample C3-7d under UV irradiation. In other words, it was confirmed that the inactivation of *E. coli* was much higher than that of *S. mutans*. The outer membrane of gram negative bacteria such as *E. coli* is covered by peptidoglycan and lipopolysaccharide, which is much thinner than that of gram positive bacteria such as *S. mutans*, which is made of peptidoglycan and teichoic acid. The gram negative bacteria have a thin layer of peptidoglycan with 2–3 nm thickness, while the outer surface of *S. mutans* is made of an impenetrable structure of teichoic acid, which makes the bacteria more resistance to ZnO and TiO2 nanoparticles and radicals.
3.6. Azo dye degradation

Figure 7(a) reveals the absorption spectrum of Chrome Intra Orange G during the photocatalytic reaction by sample C3-7d at pH = 4 and initial concentration of 15 ppm. The figure shows that after 120 min a wide peak, which was marked by the arrow disappeared. This peak was attributed to the azo bond of the dye and over time the intensity of this peak decreased due to degradation of $N \equiv N$ bond by the added nanoparticles. Moreover, the reduction of the wide peak in the UV region indicated the degradation of the aromatic compound of the dye and production of inert molecules such as H$_2$O and CO$_2$ over time. The results also implied that by addition of TiO$_2$ and ZnO nanoparticles a self-cleaning cement sample was obtained.

In previous studies, it is mentioned that decomposition rate of organic dyes via photocatalysts and exposure to UV irradiation follows the Langmuir–Hinshelwood kinetics model. Based on Langmuir–Hinshelwood equation the photocatalytic reactions occur at the surface of the particles, which are covered the surface of sample [32, 33]. To simplify the equation, low concentration of Chrome Intra Orange G was considered so the equation could be modified as a first-order equation (equation 1).

$$ r = -\frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (1) $$
Equation 1 the equation can be rewritten to determine the dye concentration at various times (equation 2).

\[
\ln \left( \frac{C}{C_0} \right) = k K_t = K_{app} \cdot t
\]

Where \( r \) is the reactant oxidation rate (mg/L.min), \( C_0 \) is the reactant initial concentration (ppm), \( C \) is reactant concentration at any given time (ppm), \( t \) is the irradiation time (min), \( k \) is the reaction rate constant (mg/L.min), which is dependent on the solute properties and reaction conditions such as temperature and pressure, \( K \) is the dye adsorption coefficient (l/mg), and \( K_{app} \) is the apparent first-order rate constant (L/min) [25, 34].

To determine the kinetics of degradation of Chrome Intra Orange G using TiO2 and ZnO nanoparticles in the cement samples, the term \( \ln \left( \frac{C}{C_0} \right) \) was plotted versus irradiation time in figure 7(b). The linear relationship of \( \ln \left( \frac{C}{C_0} \right) \) versus irradiation time indicates that the Chrome Intra Orange G decomposition follows first-order kinetics and the apparent rate constant equals to the slope of the line. According to the figure, sample C3-7d displayed a higher degradation rate over the irradiation time, while sample Z2-7d had a lower degradation efficiency, which approved the decolorization process by ZnO and TiO2.

The values of \( K_{app} \) and the degradation efficiency are reported in table 5. This table indicates that the degradation efficiency ranged from 32% to 70% after exposure to UV irradiation for 2 h. Furthermore, it is evident that the maximum degradation efficiency was obtained when the sample containing both TiO2 and ZnO nanoparticles (2.5 wt% TiO2 and 2.5 wt% ZnO) in the presence of PEG. On the other hand, the minimum degradation efficiency was obtained for the sample containing 3 wt% ZnO nanoparticles. In addition, the maximum value of apparent kinetic constant was attained using sample C3-7d while the minimum value was observed for sample Z2-7d.

4. Conclusions

In this study the effect of addition of ZnO and TiO2 nanoparticles with different contents on the antibacterial activity of white Portland cement was investigated. Furthermore, to enhance the stability of the cement samples, PEG was used as a stabilizer to inhibit the growth of two types of bacteria i.e. S. mutans and E. coli as the most common bacteria. For this reason, to study the self-cleaning properties of the cement samples, an azo dye was selected as an organic pollutant. Microstructural characterization techniques such as XRD, FTIR, EDS, and SEM were carried out to assess the pozzolanic reactivity of the cement samples in the presence of nano-TiO2 and ZnO additives. The antibacterial activity of the cement specimens containing ZnO and TiO2 nanoparticles was evaluated as a function of chemical composition and hydration time. The results demonstrated that the maximum antibacterial activity was attained when a combination of 5 wt% ZnO and TiO2 nanoparticles (1:1) was added to the cement sample and hydrated for 7 d. It was shown that the surface of the photocatalytic cement could effectively degrade the azo dye. Similarly, the optimum results were obtained for the sample, which contained both ZnO and TiO2 nanoparticles and hydrated for 7 d. This novel cement type showed promising potential for self-cleaning finishes for urban constructions and protective coatings against bacterial biofilm formation and biodeterioration.

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