Comparative Evaluation of the Photodegradation of Stearic Acid by TiO$_2$ - Modified Cement Under UV Irradiation Through Water Contact Angle and Absorbance Studies

Aniedi Nyong[*], Edet Nsi, Joachim Awaka-Ama, Godwin Udo

Materials Chemistry Research Unit, Department of Chemistry, Faculty of Physical Sciences, Akwa Ibom State University, Akwa Ibom State, Nigeria

Email address:

aniedinyong@aksu.edu.ng (A. Nyong)

[*]Corresponding author

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Abstract: The photodegradation of stearic acid has been studied through evaluation of changes in the contact angles of water and from absorbance measurements. The photodegradation of 0.02 M stearic acid coatings and solutions were initiated by TiO$_2$ nanoparticles of average size of 9.80 ± 2.92 nm embedded in cements in 1.66 wt.%, 3.33 wt.%, 5.0 wt.% and 6.67 wt.% to generate modified cement composites with photocatalytic capability. It was noted that the photodegradation efficiencies increased with the increase in the weight-percent of TiO$_2$ present in the modified cement samples. A modified Cassie-Baxter and the Langmuir-Hinselwood models were used to compute the rate constants, based on changes in the contact angles of water and in the concentration of the stearic acid respectively, on exposure to the UV light source. The modified Cassie-Baxter model successfully provided a route to relate the changes in water contact angle to the rate of photodegradation of a hydrophobic, long-chain stearic acid. The values of the rate constant estimated from both models increased with increase in the amount of TiO$_2$ present in the modified cement samples. However, the rate constant values obtained from the modified Cassie-Baxter model were lower than those obtained from the Langmuir-Hinselwood model. The values of these rate contants were in the range of 0.11-0.50 hr^{-1} and 0.78-1.33 hr^{-1} as btained from the modified Cassie-Baxter and Langmuir-Hinselwood models respectively. This disparity in the values was attributed to a higher mobility of the charge carriers and free-radicals that induced the photodegradation in liquid medium as compared to the solid medium.

Keywords: Photodegradation, UV Irradiation, Stearic Acid, Contact Angle, Absorbance

1. Introduction

Photodegradation and advanced oxidation processes have received a lot of interest from researchers [1]. This is because photodegradation provides a spectacular route for the resolution of environmental problems through the detoxification and mineralization of organic pollutants and organic wastes [2-3].

Beyond the above, photodegradation as a process is gaining prominence due to the low cost for its application, moderate process requirements as well as being residue-free [4].

Prior to now, methods for remediation of waste generally involved thermal procedures, which resulted in the generation of carbon monoxide and other residues that aredeleterious to the environment. It is in this regards that the decomposition of organic molecules, with TiO$_2$ serving as a photocatalyst, has become well-defined [5-6].

TiO$_2$ as a photocatalyst, has been explored for application in anti-fogging and self-cleaning behaviour on the basis of photo-induced hydrophillicity [7-9].

To this end, TiO$_2$ photocatalyst has been introduced into cement materials for self-cleaning purposes [10]. For instance, the self-cleaning and mechanical properties of modified white cementwith nanostructured TiO$_2$ has been studied [11]. X-ray diffraction, transmission

electronmicroscopy (TEM) and BET were used to characterize the TiO$_2$ nanoparticles while the self-cleaning property of the modified white cement wasstudied through calorimetric test in the decolourizationof red dye. The results showed that the self-cleaning ability of the cement increased with increase in the amount of TiO$_2$.

Other workers have also shown the self-cleaning, photodegradation behaviour of TiO$_2$ modifiedcements [12-15]. This include gypsum plaster modified with TiO$_2$, which was studied for the degradation of reactive red 198 dye under UV-Vis light. It was confirmed that the degradation rate of the dye depended on the qualitative and quantitative composition of the materials [16].

In this light, there has been successful incorporation of photocatalysts into bulk materials, mostly cements [17-20]. A majority of such studies have however been restricted to dyes and at high intensity of the UV irradiation. However, the aim of our research is to study the photodegradation of stearic cid, a common organic acid, under low UV irradiation intensity. Beyond using the very traditional methodof absorbance studies in investigating the photodegradation process, we aim to apply a new and novel approach of investigating the photodegradation through the changes in the cotact angles of water on the hydophobic surface coating on cements modified with various quantities of TiO$_2$ nanoparticles

2. Material and Methods

2.1. Materials

The Portland cement used for the experiments was obtained from Larfarge Cement Company, located in Sagamu, Ogun State, Nigeria. The cement was used without further processing. The chemical composition of the cement, based on details obtained from the manufacturers are as stated in Table 1.

The TiO$_2$ nanoparticles was obtained from US Nano-Research, USA and consisted of particles with percentage purity of 99.9%. The other reagents that were used in this work are stearic acid and distilled water, which were all obtained from Sigma-Aldrich, USA. The photodegradation process was carried out in a reactor chamber consisting of a darkened, wooden chamber dimension 50×40×20 cmin which a Stelite UV light bulb rated at 8.0 W was installed and connected to a power source.

Table 1. *The chemical composition of Portland cement obtained from Larfarge cement company, Sagamu, Ogun State, Nigeria.*

Chemical composition	Amount (%)
CaO	51.67 ± 3.84
SiO$_2$	18.02 ± 0.66
Al$_2$O$_3$	1.25 ± 0.25
Fe$_2$O$_3$	10.5 ± 0.76

2.2. Method

Firstly, the form and phase of the TiO$_2$ nanoparticles were determined through scanning electron microscopic and x-ray

diffraction studies. The x-ray diffraction analyses was done at 20° - 60° 2Θ values. The TiO$_2$ modified cements, consisting of specific amounts of cement and TiO$_2$ nanoparticles, were prepared through the physical dispersion method. This consisted of the mixing and stirring of weighed amounts of the Portland cement and TiO$_2$ nanoparticles in a ceramic mortar. The duration of 10 minutes was set for the dispersion and mixing process. The amount of TiO$_2$ nanoparticles added to the cement composites were of the values 0.05g, 0.10g, 0.15g and 0.20g corresponding to 1.67 wt.%, 3.33 wt.%, 5.0 wt.% and 6.67 wt.% respectively. The relationship used in the calculation of the weight percent (wt.%) of the nanoparticles is stated in equation (1).

$$\text{weight percent of TiO}_2 = \frac{\text{weight of nanoparticle (g)}}{\text{Total weight of TiO}_2 \text{ modified cement}} \times \frac{100}{1} \ (1)$$

The total weight of the TiO$_2$ modified cement was set at 3g.

To hydrate the cement-TiO$_2$ nanoparticles mix, a volume ratio of 0.5 for the cement-TiO$_2$ nanoparticles mix-water ratio was used. The hydrated cement-TiO$_2$ nanoparticles mix were then transferred into rubber caps lined with thin aluminum foils, that serve as molds and allowed to dry and set for 48 hours before further characterisation and experimentation.

The photodegradation behaviour of the TiO$_2$ modified cement samples were studied through 2methods, namely: the water contact angle andabsorbance measurements. For the contact angle measurement method, the samples were coated with0.02 M stearic acid solution. This involved

the dip-coating of the samples in solutions of 0.02 M stearicacid prepared by dissolving 2.8g of the stearic acid in 500 ml of ethanol for 1 hour. The coated samples were allowed to dry out in a dessicator placed inside a dark cupboard.

The coated TiO$_2$ modified cement samples were then exposed to the UV light source (8 W) in a dark reactor chamber for 2, 4 and 6 hours respectively. After the exposure, the contact angles measurements, involving placing of water drops of about 5μl on the surfaces of the coated TiO$_2$ modified cement samples using a micro-syringe were carried out. The water drop images were captured using the contact angle goniometer (Rame Hart model 250), updated with the dropimage software, fromwhich the contact angle measurements were done.

For the absorbance measurement method, the various TiO$_2$ modified cement samples were placed in 0.02 M stearic acid solutions which were then exposed to the UV light source inside the reactor chamber for a duration of 2 hours. Equally, standard solution of stearic acid with concentrations of 0.005 M, 0.01 M, 0.015 M, 0.020 M, 0.025 M 0.030 M and 0.035M were also exposed to the ultra-violet light source in the reactor chamber for the same time frame of 2 hours. The absorbance measurements were done using the Helios UV visible spectrophotometer by Thermostatic Spectronic with a wavelength range of 279.4-806.8 nm that was set at 380 nm and 400 nm for the 0.02 M solutions of stearic acid solutions that contained the various TiO$_2$ modified cement samples as

well as the standard solutions after their exposure to ultra-violet light.

3. Results and Discussion

The various results obtained from these experiments based on the absorption studies and water contact angle studies, whose procedures have earlier been stated are as presented below:

3.1. Characterisation of TiO₂ Nanoparticles

The SEM evaluation of the nanoparticles of TiO_2 showed that they were nearly spherical in morphology, with their sizes in the average range of 9.80 ± 2.92 nm, with a maximum size of 18. 33 nm and a minimum size of 6.48 nm. The SEM image, showing the sizes of the nanoparticles, is shown in Figure 1.
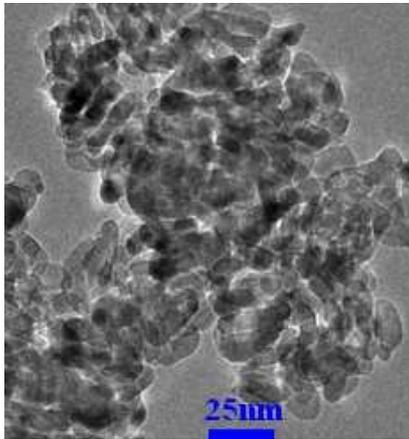

Figure 1. SEM image of TiO₂ nanoparticles used for the preparation of modified cement samples.

The X-ray diffraction studies to determine the phase of the TiO_2 nanoparticles is shown in Figure 2 and the miller indices of the diffraction peaks corresponded to the (101), (004), (200) and (105) planes which were noted at 2Θ values of 25.25°, 37.73°, 47.98° and 53.8° respectively and were similar to those in JCPDS card 21-1272 for anatase phase of TiO_2. The anatase form of TiO_2 is known to show good photocatalytic activity when compared to the other known phasic forms of the oxide.
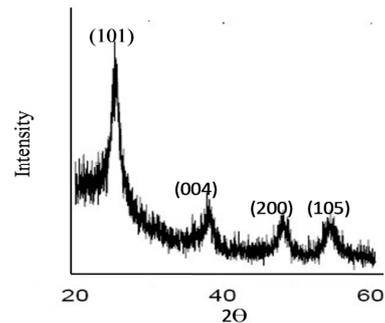

Figure 2. X-ray diffraction for the Miller indexing TiO₂ nanoparticles for phasic determination.

3.2. Contact angle of Water Studies

The contact angle of water on the surfaces of the TiO_2-modified cement samples coated with stearic acid that were evaluated before and after exposure to various time durations of UV light are presented in Table 2.

The images of the water droplets from which these contact angles were measured are also shown in Figure 3.

Table 2. The contact angles of water on surfaces of TiO₂ modified cement samples before and after exposure to UV light.

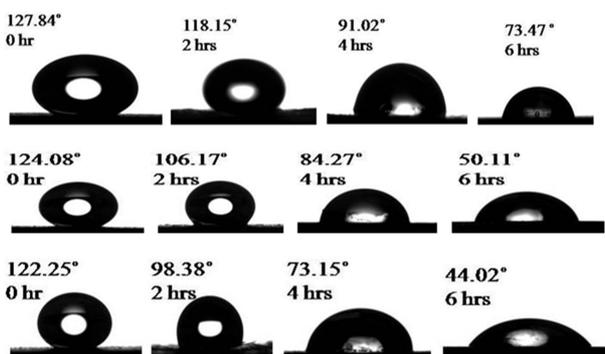| TiO₂-modified cement	Contact Angle of water			
	No Exposure	2 hours	4 hours	6 hours
Cement + 1.67 wt.% TiO₂	124.84 ± 5.28	110.15 ± 3.01	91.02 ± 2.10	73.47±1.54
Cement + 3.33 wt.% TiO₂	124.08 ± 2.35	106.17 ± 1.48	87.27 ± 1.41	50.11±2.72
Cement + 5.00 wt.% TiO₂	122.25 ± 1.43	98.38 ± 1.75	73.15 ± 2.36	44.02±1.30
Cement + 6.67 wt.% TiO₂	124.68 ± 1.58	80.14 ± 2.36	67.73 ± 1.52	43.85±2.51

Figure 3. Images of water droplets from which the contact angles of water were measured.

It was observed that there was a sharp reduction in the values of the water contact angles after such exposures to the UV light. It can be seen, from Table 2 and Figure 2, that the unexposed, stearic acid coated TiO_2-modified cement had values for the contact angles of water above 122°, irrespective of the amount of TiO_2 present in them.

Equally, after 6 hours of exposure to the UV light, the contact angles of water measured were lower than 57° mark, being the water contact angle of unmodified, solid cement paste. This implies that within 6 hours, the TiO_2 in the cement composite matrix had effectively degraded the stearic acid layer, to the extent that it resulted in depreciation of the values of the water contact angles, towards hydrophillicity.

3.3. Absorbance Studies

The absorbance studies of the photodegradation process involved the generation of calibration curves from the standard solutions that were exposed to 2 hours of the UV

light. The calibration curve is based on the principle of the Beer-Lambert's law which states that the intensity of a monochromatic radiation decreasesexponentially with increase in the thickness and the concentration of the absorbing medium [21]. Therefore, from the plots of the variation of the absorbance with known values of concentration of stearic acid, it is possible to determine changes in the concentration values of the stearic acid, if the absorbance values are known. The calibration curves from the absorbance measured at the wavelengths (λ) of 380 nm and 400 nm are shown in Figure 4.

These calibration curves were used to determine the final concentrations of the 0.02 M stearic acid solutions in which the various TiO₂ modified cement samples were placed and exposed to 2 hours of the UV light. The final concentrations (C_T) after the photodegradation of the 0.02 M stearic acid so determined were 0.0033 M, 0.0030 M, 0.0021 M and 0.0014 M as well as 0.0042 M, 0.0035 M, 0.0025 M and 0.0020 M for the cement samples that were loaded with 1.67 wt.%, 3.33 wt.%, 5.00 wt.% and 6.67 wt.% TiO₂ and studied at an absorbance wavelength of 380 nm and 400 nm respectively. The final concentration reduced markedly from the initial 0.02M that was exposed to UV light in the presenceof the various TiO₂ modified cement composites.

4. Discussion

The reduction in the water contact angles and in the values of C_T are due to the degradation of the stearic acid which is both hydrophobic and shows marked absorbance values. The degradation of the acid follows the detailed steps shown by the following equation [22]:

$$UV + TiO_2 \rightarrow TiO_2 \,(h^+ \, e^-)$$
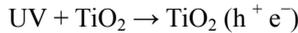
The h^+ and e^- are the positive holes and negative electrons generated within the semiconducting titanium (iv) oxide. The holes (h^+) converts the water molecules present in both the coated layer as well as in the solution of stearic acid used for the contact angle and absorbance studies respectively as follows, [23]:

(i) $h^+ + H_2O \rightarrow H^+ + {}^{\bullet}OH$
(ii) $2\,h^+ + 2H_2O \rightarrow 2H^+ + H_2O_2$
(iii) $H_2O_2 \rightarrow 2\,{}^{\bullet}OH$

These oxidative processes generates a lot of hydroxyl free radicals that extends the photo-degradation in further reductive reactions with oxygen molecules trapped within the coated layer and in the solution of the acid. The oxidation processes facilitated by the hydroxyl free radicals proceeds through the reactions given as follows, [24]:

(iv) $e^- + O_2 \rightarrow {}^{\bullet}O_2^-$
(v) ${}^{\bullet}O_2^- + HO{}^{\bullet}_2 + H^+ \rightarrow H_2O_2 + O_2$
(vi) $HOOH \rightarrow HO^{\bullet} + {}^{\bullet}OH$

The hydroxyl radicals therefore initiated the ultimate chemical deconstruction of the stearic acid chains, by reacting with the high electron-density carboxyl functional group responsible for thehydrophobicity and absorbance [25]. Beyond this, TiO₂ activated by ultraviolet irradiation

from the UV light source progressively increased the surface energy, driving it towards increased wettability by water [26-28].

Increase in the weight percent of TiO₂ in the modified cement samples increased the propensity for the generation of the hydroxyl ions photochemically [29]. This is the reason for the decrease in the water contact-angles, as can be seen in Figure 3 and in the final concentrations (C_T) of stearic acid estimated from the absorbance studies. We believe that the consistent reduction in the water contact angles and in the concentration of stearic

acid on increase in the TiO₂ loading in the modified cement composites imply that the amount of the TiO₂ is not above a threshold that could result in the agglomeration of the TiO₂ as well as a screeningeffect, which would lead to a reduction of the active sites for photoactivity [30-31].
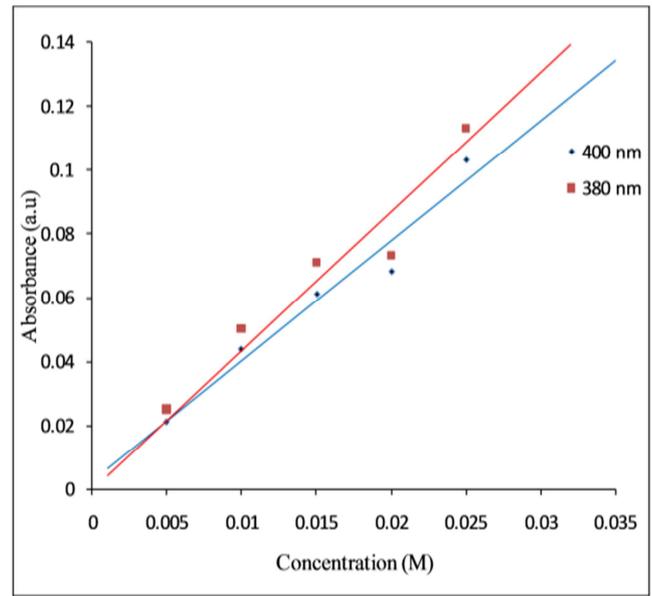

Figure 4. Calibration curve showing the variation of the absorbance with the concentration of variousstandard solutions of stearic acid.

4.1. Efficiency of the Photodegradation Process

The efficiency of the photodegradation process, in the presence of the UV light source, was determined using two approaches. These were based on namely; the changes in the values of the contact angle of water and from the changes in the concentration of stearic acid solution containing the TiO₂ modified cement samples exposed to the UV light source.

It is on this basis that the relationships stated in (2) and (3) were applied to determine the photodegradation efficiency.

$$\frac{\theta_0 - \theta_T}{\theta_0} * 100 = \% \, E \qquad (2)$$

$$\frac{c_0 - c_T}{c_0} * 100 = \% \, E \qquad (3)$$

In equation 2, Θ_o and Θ_T represent the contact angles of water on the TiO₂ modified cement surfaces without exposure and after exposure, for aspecific period, to the UV light respectively. Equally for equation 3, C_o andC$_T$ represent

the initial andconcentrations of the stearic acid solutions containing the various TiO$_2$ modified cementsamples, prior to and after their exposure to the UV light source.

Based on equation 2, the calculated percent photodegradation efficiency (% E) were 7.75%, 14.43%, 19.53% and 35.72%; 28.21%, 29.67%, 38.53% and 45.68%; 48.57%, 59.61%, 63.99% and 64% for the coated samples that were exposed to 2, 4 and 6 hours respectively. And based on equation 3, the obtained values for the percent photodegradation efficiency were 83.5%, 85.0%, 89.5% and 93.0%, after just 2 hours of exposing the 0.02 M of stearic acid solution containing the TiO$_2$ modified cement samples, loaded with 1.67 wt.%, 3.33 wt.%, 5.0 wt.% and 6.67 wt.% of TiO$_2$ respectively, to UV light. The percentage efficiency of the photodegradation process therefore increased with increase in the amount of TiO$_2$ in the cementcomposite samples. However, the higher values of the percent efficiency obtained from equation (3) is ascribed to the nature of the media in which the photodegradation occurred and also due to other factors such as the nature of the surfaces of the TiO$_2$ modified cement composites which influenced the values of the water contact angles [32].

4.2. Kinetics of the Photodegradation Process

The rate of photo-degradation of various organic substrates has often been determined using the Langmuir-Hinshelwood (L-H) kinetic model, which examines the changes in concentration as a function of time and assumes that surfaces are heterogeneous, with a fixed number of sites where chemisorption can occur [33-35].

The Langmuir-Hinshelwood model is stated in equation (4).

$$In \frac{c_T}{c_o} = -k_1 t \tag{4}$$

and here k_1, represents the pseudo - first - order rate constant, for a specific time, t. The values of k_1 evaluated from the values of C$_T$ earlier determined for 2 hours of exposure to the UV light are stated in Table 3.

It can be appreciated that the values of K$_1$ increased with increase in the amount of TiO$_2$ present in thecement matrix of the samples. The implication is simply that with increase TiO$_2$ loading in the cement, the action of the UV light caused a proportional higher number of electrons to be promoted from thevalence band of the semiconducting TiO$_2$ to its conduction band resulting in a higheramount of hydroxyl radicals, which ultimately degraded the stearic acid faster.

However, from the changes in the contact angle of water, the kinetics of the photodegradation was considered on the assumption that TiO$_2$ modified cements were totally coated by the stearic acid, through chemisorption. Consequently, the fractional surface area (f_{sl}) of the stearic acid coated on the TiO$_2$ modified cements that is available for wetting and on which the contact angle of water depends will be dependent on the time of exposure of the samples to the UV light.

Equally, by accepting that the surface degradation of the stearic acid coated on the TiO$_2$ modified cement samples

follows first-order kinetics, we derive herein equations (5-8) a simple relationship representing the behaviour of the fractional surface area on exposure of the stearic acid coated samples to UV light for different time durations.

$$\frac{df_{sl}}{dt} = K_1^c f_{sl} \tag{5}$$

$$\int_{f_{sl(0)}}^{f_{sl(t)}} \frac{df_{sl}}{f_{sl}} = K_1^c \int_0^t dt \tag{6}$$

$$ln \frac{f_{sl(t)}}{f_{sl(0)}} = K_1^c (t - 0) \tag{7}$$

$$f_{sl(t)} = f_{sl(0)} e^{K_1^c t} \tag{8}$$

Equation (8) shows how the fractional surface area ($f_{sl(t)}$) after an exposure for time (t) is related to the rate of the photodegradation of the stearic acid coated of the TiO$_2$ modified cement samples (K_1^c), based on the changes in the water contact angles. Also, the relationship between the fractional surface area available for wetting and the contact angle of water is represented by the Cassie-Baxter model (Cassie and Baxter, 1944). The Cassie-Baxter model relates the heterogeneity of surfaces to the surface energy and therefore to the contact angles. The Cassie-Baxter model is given by the equation in (9-10).

$$\cos \theta_T = f_{sl(t)} \cos\theta_c - 1 + f_{sl(t)} \tag{9}$$

$$\cos \theta_T = f_{sl(t)} (\cos\theta_c + 1) - 1 \tag{10}$$

θ_c in equations (9) and (10) represents the contact angle of water on a smooth surface of unmodified Portland cement solid paste, which was measured as 56°. Introducing equation (8) into (10), we can then set up a relationship that mathematically links the values of the fractional surface area of the stearic acid layer coated on the TiO$_2$-modified cement samples to the contact angles of water as the process of photodegradation proceeds on exposure to the UV light.

Table 3. *Values of K$_1$ estimated fromL-Hmodelfrom absorbance studies at λ = 380 nm and 400 nm.*

TiO$_2$-modified cement	Rate Constant, K hr^{-1}	
	380 nm	400 nm
Cement + 1.67 wt.% TiO$_2$	0.90	0.78
Cement + 3.33 wt.% TiO$_2$	0.95	0.87
Cement + 5.00 wt.% TiO$_2$	1.13	1.03
Cement + 6.67 wt.% TiO$_2$	1.33	1.15

This results in the modified Cassie-Baxter model stated in (11).

$$\cos \theta_T = f_{sl(0)} e^{K_1^c t} (\cos \theta_c + 1) - 1 \tag{11}$$

On the establishment of $f_{sl(0)}$, the modified Cassie-Baxter model as presented in (11) can be used to evaluate the rate constant (k_1^p) for the photodegradation of the stearic acid coated on the TiO$_2$-modified cement samples using the values of the contact angles of water measured on the samples' surfaces after exposure to the UV light. At time (t) equal to zero (t = 0), when there is no exposure of the TiO$_2$-modified

samples to the UV light, equation (11) reverts to the form stated in (12).

$$cos\theta_{T=0} = f_{sl(0)}(cos\theta_c + 1) - 1 \qquad (12)$$

The calculated values of $f_{sl(0)}$ were 0.25, 0.28, 0.30 and 0.27 for the cement samples that were modified with 1.67 wt.%, 3.33 wt.%, 5.0 wt.% and 6.67 wt.% of TiO₂ respectively. The average of these values, which equaled 0.275, was used as that for $f_{sl(0)}$ and subsequently used in equation (11) to estimate the rate constants k_1^c for the photodegradation of the stearic acid coated on the various TiO₂-modified cement samples. The values of k_1^c are as expressed in Table 4. Also, the rate constant k_1^c generally increased with increase in the amount of TiO₂ in the modified cement samples. This trend was quite conspicuous after 2 hours of the exposure to the UV light source. However, between 4 and 6 hours of exposure, the increase in the values of k_1^c were marginal. This can be seen in the plot showing the variation of k_1^c with the amount of TiO₂ in the modified cement samples, as presented in Figure 5.

Table 4. *Calculated values of rate constants for the photodegradation of stearic acid (k_1^c) from equation 11.*

TiO₂-modified cement	Time (in hous) /k_1^c		
	2	4	6
Cement + 1.67 wt.% TiO₂	0.11	0.20	0.18
Cement + 3.33 wt.% TiO₂	0.26	0.23	0.22
Cement + 5.00 wt.% TiO₂	0.35	0.28	0.23
Cement + 6.67 wt.% TiO₂	0.50	0.29	0.23

The values of k_1^c showed that the more the weight percent of TiO₂ the faster the degradation, hence the fast depreciation of the water contact angle values (Θ_t). A comparison of the values of the rates constants, k_1 and k_1^c obtained after two hour showed that k_1 values were greater than k_1^c. It is expected that the photodegradation of the stearic acid will occur at a higher rate when the acid is in the liquid form than when it is in a solid form due to the higher mobility of the free radicals that contribute significantly to structural deconstruction of the stearic acid hydrophobic chain.
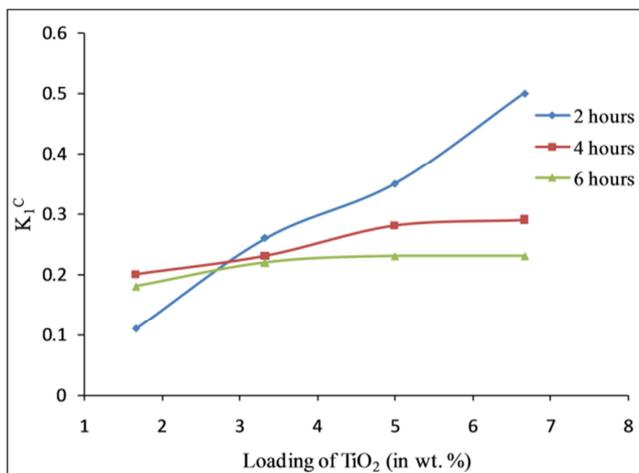

Figure 5. *Plot showing the variation of k_1^c with the amount of TiO₂ in modified cement samples.*

5. Conclusion

Our methods ofinvestigating the photo-degradation showed that weak organic acids, both in solid and liquid forms, can be photodegraded photodegraded in UV lights of low intensities when in contact cementitious materials that have been modified with TiO₂. The changes in the contact angles of water can effectively be used to evaluate the kinetics of the photodegradation processes. The values of the rate constants calculated from themodified Cassie-Baxter model were significantly lower than those obtained the Langmuir-Hinshelwood model. However, the same specific trends in behaviour of k_1 and k_1^c were noted.

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