Improved Photodegradation of Organic Contaminants Using Nano-TiO₂ and TiO₂–SiO₂ Deposited on Portland Cement Concrete Blocks

Hoda Jafari* and Shahrara Afshar

Department of Inorganic Chemistry, Iran University of Science and Technology, Narmak, Tehran, Iran Received 14 August 2015, revised 7 October 2015, accepted 13 October 2015, DOI: 10.1111/php.12554

ABSTRACT

The photocatalytic activity of TiO₂ nanoparticles (nano-TiO₂) and its hybrid with SiO₂ (nano-TiO₂-SiO₂) for degradation of some organic dyes on cementitious materials was studied in this work. Nanohybrid photocatalysts were prepared using an inorganic sol-gel precursor and then characterized using XRD, SEM and UV-Vis. The grain sizes were estimated by Scherrer's equation to be around 10 nm. Then, a thin layer was applied to Portland cement concrete (PCC) blocks by dipping them into nano-TiO₂ and nano-TiO₂-SiO₂ solution. The efficiency of coated PCC blocks for the photocatalytic decomposition of two dyes, Malachite Green oxalate (MG) and Methylene Blue (MB), was examined under UV and visible irradiation and then monitored by the chemical oxygen demand tests. The results showed that more than 80% and 92% of MG and MB were decomposed under UV-Vis irradiation using blocks coated with nano-TiO2-SiO2. TiO2/PCC and TiO₂-SiO₂/PCC blocks showed a significant ability to oxidize dyes under visible and UV lights and TiO2-SiO2/PCC blocks require less time for dye degradation. Based on these results, coated blocks have increased photocatalytic activity which can make them commercially accessible photocatalysts.

INTRODUCTION

Effective treatment of toxic pollutants is a required part of water treatment applications. Organic contamination in water and industrial wastewater is a significant pollution problem to people worldwide (1).

One of the main sources of these contaminants is the textile industry and its dye-containing wastewater, which is sometimes directly discharged as aqueous effluent into the environment. However, without adequate treatment, these dyes may remain in the environment for a long time, which is undesirable not only because of their color, but also because several dyes and their precursors act as human carcinogens by transforming into toxic aromatics (2–4).

Traditional physical techniques or chemical and biological treatment methods are usually employed for removing these pollutants (5–10). In some of these methods, the contamination remains without destruction and is transferred from water into other phases and subsequently forms secondary pollutants or is

simply absorbed into the sludge; thus, requiring further treatment for degradation.

 TiO_2 semiconductor nanoparticles are known to be important photocatalysts and have found wide applications in contamination removal. The efficiency of this semiconductor is due to the form of its crystalline structure (11–13), particle size (12,14–16) and preparation methods (17,18).

Of Anatase, rutile and brookite, three common crystalline forms of TiO_2 , Anatase shows the highest photoactivity industrially and can be employed as an effective photocatalyst, which results from a band gap of *ca* 3.2 eV, corresponding to radiation of wavelength around 380 nm (19).

In general, for photocatalytic oxidation, UV light of wavelength shorter than 380 nm is required to excite an electron from the valence band to the conduction band, leaving a hole in the valence band (h^+). The electron-hole pairs are thus produced and serve as oxidizing and reducing agents. Photodegradation of water pollutants proceeds with the formation of the 'OH radicals, the key active species, formed either through the interaction of water molecules with holes or through the interaction of O₂ with the host electrons (20,21).

However, this practical application in aqueous media is limited because of the difficulty of filtration and recovery of small TiO₂ particles. Furthermore, because TiO₂ has a polar surface, it is not a good absorbent for nonpolar organic molecules and adding support material may improve its catalytic activity. Other reasons that prevent TiO₂ from being an appropriate choice are its low surface area, particularly when compared with industrial catalysts such as Degussa P-25 (surface area of approximately 50 m² g⁻¹) (22), and its charge recombination (23), which, together, decrease the efficiency of a photocatalyst. Thus, considerable effort is required to overcome these difficulties.

Recent studies have shown that hybridization of SiO_2 with TiO_2 increases the acidity of the composite oxide and improves the surface area. Thus, new catalytic active sites are formed on the surface because of the interactions between TiO_2 and SiO_2 , which improve the photocatalytic activity and the hydrophilicity of the composite (24–26).

Moreover, the deposition of TiO_2 on several supports such as stainless steel, quartz, Pyrex, paper, fiberglass, clothes, monolith and other building materials to avoid filtration has attracted a considerable attention (27–33).

It is important to have as much TiO_2 as possible at the surface of these substances without increasing the risk of losing it by abrasion or washing. Until now, the most efficient way to do so was to apply TiO_2 as a thin layer on the surface of cementitious

^{*}Corresponding author email: hoda.jafari@gmail.com (Hoda Jafari)

^{© 2015} The American Society of Photobiology

materials to increase the surface area, making it suitable to be applied to concrete tiles.

Many physical and chemical methods for the deposition of nano-TiO₂ and TiO₂–SiO₂ have been reported so far (6,34–38). Among them, the sol–gel process, including dip/spin/spray and paint coating, is most appropriate owing to its low cost, simplicity and easily controllable conditions (39). Dip coating is a common method for deposition of the solution on a plate, cylinder or irregular surface. The method involves immersing a substrate into a reservoir of solution, ensuring complete wetting of the substrate and subsequently withdrawing the substrate from the solution bath. The liquid film formation is achieved mainly by two mechanisms: gravity draining off the liquid solution and evaporation of the solvent (40,41).

The use of this photocatalyst in building materials was first introduced in the early 1990s and many studies have been performed on the effect of cementitious supports for degradation atmospheric pollutants (42–44). The complete removal process of pollutants is constrained by natural energy (sunlight, atmospheric moisture and rain) and presence of the photocatalyst. Nano-TiO₂ can be employed as a photocatalytic material and a structural material as well. As such, it can be used efficiently in exterior construction materials, interior furnishing materials and rod construction materials such as cement mortar, exterior tiles, paving blocks, glass and PVC fabrics (42,45–48). Despite the extensive use of concrete in the construction industry and the possibility of nano-TiO₂ utilization in concrete infrastructure, few studies have been performed on the degradation of organic dyes with these materials.

The main aim of this study was to investigate the enhancement of the photocatalytic efficiency of immobilized TiO_2 and TiO_2 –SiO_2 nanoparticles embedded in Portland cement concrete (PCC) blocks for the removal of dyes such as Methylene blue (MB) and Malachite Green oxalate (MG) as organic pollutants under ultraviolet and visible light irradiation. As the sol–gel methods based on organic precursors generate pollution due to use of organic solvents, an inorganic precursor such as titanium tetrachloride (TiCl₄) has been used to synthesize the nano-TiO₂. The use of inorganic precursors instead of organic precursors reduces the cost of synthesis and eliminates the use of organic solvents which can lead to significant environmental issues.

MATERIALS AND METHODS

Materials. Titanium tetrachloride (TiCl₄, 99%), nitric acid (HNO₃, 65%), ammonia (NH₃, 25%), tetraethylorthosilicate (TEOS, 98%), deionized water and dyes including MG oxalate and MB were purchased from Merck Co. and used as received. The ordinary Portland cement type (II), which is commercially available, was used for making the PCC blocks.

Preparation of samples. The method employed for the synthesis of TiO₂ and TiO₂–SiO₂ nanoparticles in this work is similar to that reported elsewhere, in which the TiO₂ and TiO₂–SiO₂ nanoparticles were prepared using the sol–gel method (49–53). An Ammonium solution (2.5%) was dropped into the TiCl₄ solution and a white precipitant was obtained at pH = 7 at room temperature. The resulting precipitant was washed with deionized water until the complete removal of Cl⁻ and NH₄⁺ ions. Then, HNO₃ (0.5 M) was added to 500 mL of suspension, including 10.7 moles of titanium, until pH = 1.5 with strong stirring and, then, the slurry was refluxed at 343 K for 24 h to create a stable TiO₂ sol. Subsequently, the appropriate amount of TEOS was slowly added into this sol until a TiO₂–SiO₂ molar ratio of 30/70 was obtained and, then, this mixture was heated to 343 K for 1 h with strong stirring and later cooled to room temperature.

Portland cement concrete blocks were produced by mixing cement, sand and water with a sand/cement weight ratio equal to 3. The resulting paste was molded into $20 \times 10 \times 10 \text{ mm}^3$ dimensions and dried at room temperature for 72 h. Then nano-TiO₂ and TiO₂–SiO₂ photocatalysts were immobilized on these cubic blocks by dip coating (three times) in a solution of 26.5 and 88.4 g L⁻¹ of nano-TiO₂ and TiO₂–SiO₂, respectively. The coated blocks were dried in an oven at 343 K and at 373 K for 30 and 60 min and calcined in a programmable furnace at 673 and 723 K for 3 h by rate of 2 °C min⁻¹ for TiO₂ and TiO₂–SiO₂, respectively. Calcination allows nano-TiO₂ and TiO₂–SiO₂ powder to adhere more strongly to the pore walls of the concrete blocks. The amount of photocatalyst deposited on the concrete blocks is calculated by the difference of weights before and after the deposition and are approximately 0.5 g L⁻¹ in the dye solution. Scheme 1 presents the sequential steps of sample preparation.

Photodegradation of organic contaminants. To evaluate the photocatalytic activity, complete oxidation of MB and MG oxalate in aqueous solutions into CO₂ and H₂O was investigated under UV and visible light irradiation. UV-Vis spectroscopy and chemical oxygen demand (COD) methods were utilized to measure dye concentration, which remained in the solution after irradiation. The reaction was performed in 40 mL of dye solution (10 mg L^{-1}) and 20 mg of catalyst at a pH of approximately 5 by using HNO3 on quartz cells, at room temperature. For the irradiation process, a UV lamp (125 W, UVA, $\lambda_{\text{max}} = 365 \text{ nm}$) and a high-pressure mercury-vapor lamp (300 W, $\lambda_{\text{max}} = 546.8$) without cut-off filter were applied as ultraviolet and visible light sources, respectively, whereas the distance between the lamp and the dye solution was kept at 20 cm. Before the irradiation process, to study the adsorption process, the dye-containing solution (10 mg L^{-1}) coated on PCC blocks was aerated and maintained in the dark for 40 min to set up the absorption-desorption equilibrium among the dyes, photocatalyst and dissolved oxygen. It was observed that 18-38% of MB and MG dyes was absorbed by samples very quickly and saturated in 40 min. This result pointed out that the photocatalytic reaction should start after completion of the adsorption process to eliminate the effect of adsorption on the reaction. Then, the irradiation process was started and at a predetermined time, 2 mL of the solutions were taken from the system and, if needed, centrifuged to remove the catalyst. These dye concentrations in aqueous solutions were measured every 5 and 15 min for UV and visible light irradiation. The UV-Vis spectrophotometer (Shimadzu, UV-1700) was used to record variations of dye absorption at their characteristic wavelengths ($\lambda = 617$ nm for MG and 663 nm for MB). The degradation ratio of dye C/C_{0} (concentration/initial concentration of dye) can be simply calculated from the ratio A/A_o where A_o is the solution's absorbance at time zero, and A is the solution's absorbance at time t after



Scheme 1. Preparation of nano-TiO₂ and TiO₂-SiO₂.

irradiation. For comparison, PCC blocks, commercial TiO_2 (P25 Degussa) in PCC blocks, nano TiO_2 powder and TiO_2 -SiO₂ powder were also examined as control groups.

Characterizations. The samples were characterized using an X-ray diffractometer (SIEMENS D5000) at room temperature. The pattern was recorded over the angular range $5-70^{\circ}$ (2 θ), using a scan rate of 1.2° min⁻¹ and CuK α radiation ($\lambda = 0.154056$) with working voltage and current of 35 kV and 20 mA. The particle sizes were calculated by the Debye–Scherrer equation (Eq. (1)):

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where λ is the X-ray wavelength (1.54 Å), β is the full-width at halfmaximum intensity of the diffraction line (1.423) and θ is the diffraction angle (54). Moreover, the Power Surface areas were determined from N2 gas adsorption data using the Brunauer-Emmett-Teller technique (MICRO MERITICS-Gemini). The UV-Vis diffuse reflectance absorption spectra (DRS) was recorded with a Shimadzu (MPC-2200) spectrophotometer and SEM/EDX analysis of the sample was recorded on a Philips-X130 to observe the morphology and characterize the elemental composition of the coatings. The COD method is commonly used to observe the mineralization process of dyes. The measurement of COD was performed using direct photometer systems in the measuring range 0-1500 mg L⁻¹. Typically, 2 mL of various dye solutions before and after irradiation were mixed with COD reagents and then were digested in a COD RD125 Thermoreactor for 2 h at 423 K. After digestion, the mixture was cooled to room temperature and its COD value was determined using the photometer.

RESULTS AND DISCUSSION

Catalyst characterization

The XRD pattern of the samples (Fig. 1) revealed the presence of a diffraction peak at $2\theta = 25.3^{\circ}$, which is the characteristic peak of the Anatase phase from titanium oxide according to PDF21-1276. Detection of other TiO₂ diffraction peaks was difficult because of the small amount of TiO₂ loading of PCC blocks. For comparison, the XRD pattern of the PCC was also recorded. The average particle size of TiO₂ and TiO₂–SiO₂ loaded on the blocks was determined using Scherrer's equations (54,55) on the Anatase (101) diffraction peak for the same solution used for depositing on PCC blocks was found to be 11 and 7 nm, respectively (Fig. 2). The diffraction peaks of TiO₂–SiO₂ were broader than TiO₂ (Fig. 2b). Besides, the addition of SiO₂ increased the specific surface area of nano-TiO₂ powder from 81 to $555 \text{ m}^2 \text{ g}^{-1}$ for nano-TiO₂/SiO₂ photocatalysts.

Homogeneous distribution of TiO2 particles on a PCC surface can be achieved by using SiO₂ particles and this prevents particles sintering, which causes the smaller size of deposited particles by inhibiting enlargement of titania particles and resulting the higher specific surface area for adsorption of big organic molecules for photocatalytic degradation (56-59). It is also confirmed that the titania-silica mixture has high thermal stability, and the Anatase form of the TiO2 remains preserved in TiO₂-SiO₂ composite even at high temperatures (60,61). In our study, it is notable that the calcination temperatures for nano-TiO₂ and nano-TiO₂-SiO₂ were 673 and 723 K, respectively, and Anatase phase was identified for both (Fig. 2a,b). Moreover, SiO₂ particles can act as a cohesion factor and stick TiO2 particles to the support substrate; its Si-O bond increases the mechanical stability of TiO₂ particles on the PCC surface under ultraviolet and visible light irradiation.

Figure 3 demonstrates the SEM images of TiO₂ and TiO₂– SiO₂ species distributed over the blocks at various magnifications. The images show the surfaces of the PCC blocks covered by the spherical TiO₂ and TiO₂–SiO₂ nanoparticles. Without any mechanical polishing process some cracks due to surface roughness were observed. The resulting cracks are likely due to the dipping process and larger surface available for photocatalyst immobilization. It could be noticed that exerting SiO₂ in the initial sol leads to the homogeneous distribution of nano-sized TiO₂ particles loaded on the concrete surface.

EDX analysis was performed to determine the elemental composition of the coatings (Fig. 4). Because of the large penetration depth of the electron beam required for EDX analysis and the small thickness of TiO₂ and TiO₂–SiO₂ (<15 μ m) layer, this result is related to both the substrates (PCC blocks) and the thin layer of nanoparticles. Therefore, the EDX patterns confirmed the existence of some impurities. These impurities, which may have been diffused from the concrete blocks into the layers caused by the calcination process, consisted of Al, Ca, K and Fe ions leading to an increase in photocatalytic activity of coatings (62). Higher specific surface in loaded photocatalysts due to the porous structure of the concrete support, on one hand, and to the



Figure 1. XRD pattern of Portland cement concrete (PCC) blocks, TiO₂/PCC blocks and TiO₂-SiO₂/PCC blocks (star denotes Anatase).



Figure 2. XRD pattern of (a) nano-TiO₂ and (b) nano-TiO₂-SiO₂ (30:70) (A = Anatase).



Figure 3. SEM images of TiO₂/Portland cement concrete (PCC) blocks [panels (a), (b)] and TiO₂–SiO₂/PCC blocks [panels (c), (d)] with different magnifications [panels (b), (c) = 15 000 × and panels (a), (d) = 30 000×].



Figure 5. Elemental mapping and SEM images of TiO_2 -SiO₂ photocatalyst distribution on the concrete blocks.



Figure 6. UV–Vis diffuse reflectance spectra of (A) photocatalyst powders and (B) TiO_2 –SiO₂ and coated blocks: (a) TiO_2 –SiO₂, (b) TiO_2 /Portland cement concrete (PCC) blocks, (c) PCC blocks and (d) TiO_2 –SiO₂/PCC blocks.

other elements as impurities (especially iron) in the concrete materials, on the other hand, improves the photocatalytic activity of concrete-supported catalysts.

According to the elemental mapping analysis shown in Fig. 5, the distribution of the titania–silica particles and metal ions over the concrete blocks is homogeneous. The presence of silica can facilitate the uniformity of the photocatalyst distribution and increase its efficiency.

The optical absorption properties of TiO2, TiO2-SiO2, TiO2/ PCC blocks, TiO2-SiO2/PCC blocks and bare PCC blocks were studied using their UV-Vis DRS, and the representative results are shown in Fig. 6. As shown, the absorption edge in the nano-TiO2-SiO2, nano-TiO2/PCC and TiO2-SiO2/PCC are about 390, 500 and 720 nm, respectively. The Band gap (E_g) can be calculated using the equation: $E_{\rm g}$ (eV)= 1240/ $\lambda_{\rm g}$, where $\lambda_{\rm g}$ is an intersection value for the vertical part and horizontal part of the spectrum (63). The $E_{\rm g}$ is calculated to be about 3.2, 2.48 and 1.7 eV for nano-TiO2-SiO2, nano-TiO2/PCC and nano-TiO2-SiO2/PCC blocks, respectively. Thus, the shorter absorbance for the TiO₂-SiO₂ photocatalyst can be attributed to the accepted quantum size effect (64,65). The existence of SiO₂ decreased the particle size which was ascertained by XRD analysis making the band edge shift to a shorter wavelength that was reflected in an increase in the band gap of TiO2 (Fig. 6A).

The TiO₂–SiO₂/PCC blocks displayed a remarkable redshift of absorption edge and a significant enhancement of light absorption at wavelength of 400–750 nm which may be attributed to the effect of different metal oxides on the surface of coated blocks (Fig. 6B). This broadening of absorption bands has been attributed to electron excitation from 3d orbital of the metal ions to the conduction band of TiO₂ (66).

Photodegradation of organic contaminants under UV and visible light irradiation

The photocatalytic activity of samples was considered to understand their ability to degrade MG oxalate and MB solutions at pH = 5 under ultraviolet and visible light irradiation at room temperature. These most common dyes were selected as model pollutants in industrial wastewater.

The UV–visible absorbance spectra during the photodegradation process of MG dye under UV and visible lights are illustrated in Figs. 7 and 8. The results showed that the characteristic absorption band of the MG dye around 617 nm corresponding to the $\pi \rightarrow \pi^*$ transitions of aromatic rings reduced rapidly without appearance of hypsochromic shifts. A decrease in the absorption maximum of the TiO₂/PCC blocks and TiO₂–SiO₂/PCC blocks implies the complete removal of the conjugated structure of the dye. It suggests that the degradation mechanism involves



Figure 7. UV-visible absorption spectra of Malachite Green dye by (a) TiO₂–SiO₂/Portland cement concrete (PCC) blocks and (b) TiO₂/PCC blocks under UV irradiation at different time intervals.



Figure 8. UV-visible absorption spectra of Malachite Green dye by (a) TiO₂–SiO₂/Portland cement concrete (PCC) blocks and (b) TiO₂/PCC blocks under visible light irradiation.

cleavage of the conjugated chromophore structure of MG dye because the hypsochromic shift is referred to as an N-demethylation process (67). In addition, an increase in the irradiation time shows the formation of a new band at 350 nm. It could be concluded that the polyaromatic rings are broken down without the conjugated structure being formed. Significantly, the formation of benzophenone derivatives, p-aminobenzoic acid and aniline as intermediate reaction products from the reaction of triphenylmethane dyes with hydroxyl radicals has been previously reported by Saquib *et al.* (68).

The representative photodegradation curves of MG under UV and visible light irradiation with different samples have



Figure 9. Photocatalytic degradation of 10 mg L^{-1} Malachite Green dye with samples under (a) UV illumination and (b) visible light irradiation.



Figure 10. UV-visible absorption spectra of Methylene Blue dye by (a) TiO_2 -SiO₂/Portland cement concrete (PCC) blocks and (b) TiO_2 /PCC blocks under UV irradiation at different time intervals.

been illustrated in Fig. 9. After 60 min UV illumination on nano-TiO₂, TiO₂–SiO₂ and commercial TiO₂ (P25 Degussa) in Portland concrete blocks (Fig. 8a), the C/C_o ratio (concentration/ initial concentration of MG dye) decreased from 1.0 to 0.40, 0.26 and 0.12, respectively. However, the C/C_o ratio reduced from 1.0 to 0.09 and 0.01 for TiO₂/PCC blocks and TiO₂–SiO₂/PCC blocks, respectively. As it can be also seen, the decreasing trend of the relative concentration of TiO₂/PCC blocks and TiO₂–SiO₂/PCC blocks is approximately higher than other samples, which confirms the effectiveness of coated blocks for photodegradation.

Moreover, these coated concrete blocks were used to decompose MG dye under visible light irradiation. The results showed that after 60 min irradiation, the C/C_0 ratio decreased from 1.0 to 0.28 and 0.08 and complete degradation is obtained at 145 and 80 min for TiO₂/PCC and TiO₂–SiO₂/PCC blocks, respectively (Fig. 9b). In addition, the comparison of the samples revealed an increase in degradation of MG oxalate by TiO₂/PCC blocks and TiO₂–SiO₂/PCC blocks under visible as well as ultraviolet irradiation.

Figures 10 and 11 illustrate the change in the absorption spectra of MB solution by samples under UV and visible light with varying irradiation time. The absorbance band of MB at 663 nm is caused by $n \rightarrow \pi^*$ transition to the azo group (– N=N–), representing the color of dye solution. The other absorbance at 291 nm is attributable to the $\pi \rightarrow \pi^*$ transition in the aromatic ring (69). The decreases in these peaks were observed with an increase in irradiation time, and no extra peak was detected during degradation. Examination of the spectral variations in Figs. 10 and 11 suggest that the destruction of the MB heteropolyaromatic linkage occurred and a benzene ring with formation of several complicated intermediates is formed throughout the degradation of MB that could not be identified (70).

The results are presented as a plot of the concentration ratio of MB (C/C_0) as a function of irradiation time (Fig. 12). A significant decrease in the C/C_0 occurs when coated samples are used instead of nano-TiO₂–SiO₂ powder and commercial TiO₂ (P25 Degussa) in Portland concrete blocks. After 60 min of irradiation, the degradation ratio of MB solution using TiO₂/PCC



Figure 11. UV-visible absorption spectra of Methylene Blue dye by (a) TiO₂-SiO₂/Portland cement concrete (PCC) blocks and (b) TiO₂/PCC blocks under visible light irradiation.

and TiO₂–SiO₂/PCC blocks decreased to 0.04 and 0.03 while this ratio using TiO₂/SiO₂ powder and commercial TiO₂ (P25 Degussa) in Portland concrete blocks are 0.32 and 0.27, respectively. Moreover, the photodegradation of the dyes under visible light was 41% and 52%, and the color of the MB solution faded at 320 and 300 min for TiO₂/PCC and TiO₂–SiO₂/PCC blocks, respectively (Fig. 12b).

The results confirmed that under ultraviolet light irradiation, 38.55% of the MB dye degrades in the first 15 min of reaction and 44.28% degrades in the next 20 min (Fig. 12a). This can be explained by the different steps of destruction of the MB dye. The C–S⁺=C functional group in MB, which is in direct coulombic interaction with photocatalyst's surface, was attacked by the high concentration of OH⁻ radicals on the surface of these blocks coated with nano-TiO₂–SiO₂ and nano-TiO₂. Consequently, the first step of MB degradation can be attributed to opening the central heteroaromatic ring due to the cleavage of the bonds of the C–S⁺=C functional group. The other attack from OH⁻ radicals lead to the production of sulfate ions *via* the formation of a sulfoxide, a sulfone and sulfonic groups (70).

Furthermore, photodegradation of these two dyes was examined under identical conditions that are in the absence and presence of the samples and bare concrete blocks. The results showed that gradual dye degradation occurs under UV and visible light irradiation. After 60 min irradiation, the C/C_o ratio decreases from 1 to 0.95 and 0.99 for MB dye and 0.87 and 0.9 for MG dye by visible and UV light, respectively. While in the presence of coated samples, the degradation ratio of dye solution decreases from 1 to 0.08, 0.26 (MG dye) and 0.04, 0.59 (MB dye) for TiO₂/PCC blocks and 0.01, 0.08 (MG dye) and 0.03, 0.48 (MB dye) for TiO₂–SiO₂/PCC blocks under UV and visible light, respectively.

The photocatalytic degradation of several dyes over titanium dioxide obeys the Langmuir–Hinshelwood kinetics (20,71) model given by the following equation (Eq. (2)):

$$\ln\left(\frac{C}{C_{\rm o}}\right) = -k_{\rm app}t\tag{2}$$

where C_0 is initial concentration (mg L⁻¹), C is the concentration of the reactant at time t (mg L⁻¹) and k_{app} is the apparent



Figure 12. Photocatalytic degradation of 10 mg L^{-1} Methylene Blue dye with samples at pH = 5 under (a) UV illumination and (b) visible light irradiation.



Figure 13. A plot of $\ln (C_o/C)$ versus time for degradation of Malachite Green under (a) UV illumination and (b) visible light irradiation.

rate constant (min⁻¹). The slope of the logarithmic curves of C_o/C versus time suggested pseudo first order kinetic model for the degradation of MG and MB dyes with TiO₂/PCC and TiO₂-SiO₂/PCC blocks under UV and visible light irradiation.

The apparent rate constants (k_{app}) determine with the linear extrapolations. When the concentrations of dyes become very low, this frequently occurs. Figures 13 and 14 show the curves of Ln (C_o/C) versus time for the degradation of dyes on samples. The good linear fittings confirm that the pseudo first order kinetic model accurately describes the degradation behavior of these dyes on TiO₂/PCC and TiO₂–SiO₂/PCC blocks.

The apparent pseudo first order rate constants (k_{app}) and the values of the coefficient of determination (R^2) are presented in Table 1. The R^2 was greater than 0.9 in all tests, and the catalyst supported on Portland concrete blocks provided superior degradation of the dyes under UV as well as visible light irradiation.

Estimation of COD

Chemical oxygen demand is widely employed as an effective technique to assess the organic strength of wastewater (72,73). The



Figure 14. A plot of $\ln (C_o/C)$ versus time for degradation of Methylene Blue under (a) UV illumination and (b) visible light irradiation.

test involves the estimation of the total amount of oxygen required for oxidation of organic substances to CO_2 and water. COD of the dye solutions were estimated before and after the reactions. A decrease in COD values of the treated dye solutions implied mineralization of the dye molecules along with color removal. Moreover, the degradation efficiency was determined by the following equation (Eq. (3)) (74,75) and the results are presented in Table 2.

Photodegradation efficiency =
$$\frac{\text{Initial}_{\text{COD}} - \text{Final}_{\text{COD}}}{\text{Initial}_{\text{COD}}} \times 100.$$
 (3)

These results confirmed that the COD values of the photodegraded dye solutions for coated concrete blocks decrease and improve photodegradation efficiencies upon UV and visible light irradiation. Moreover, in this study, a maximum of 98.67% photodegradation efficiency was achieved for MB dye degradation using TiO₂–SiO₂/PCC blocks under UV light. Thus, TiO₂–SiO₂/ PCC and TiO₂/PCC blocks display higher degradation rates under UV and visible light.

The observed enhancement in the photocatalytic performances could be reasoned as:

	UV illumination				Visible light illumination			
	$k (\min^{-1}$	$) \times 10^{-2}$	I	R ²	$k (\min^{-1}$	$) \times 10^{-2}$	F	2 ²
Sample	MG	MB	MG	MB	MG	MB	MG	MB
TiO ₂ /SiO ₂ /PCC blocks	7.79	5.88	0.993	0.988	3.24	1.1	0.996	0.997
TiO ₂ /PCC blocks	4.38	5.46	0.97	0.994	2.53	0.65	0.987	0.993
TiO ₂ /SiO ₂	2.99	1.82	0.985	0.997				
P25 in PCC blocks	3.46	2.87	0.972	0.998				

Table 1. The measured rate constants of dye degradation by different samples at room temperature.

PCC = Portland cement concrete; MG = Malachite Green; MB = Methylene Blue.

Table 2. Photodegradation efficiency of organic contaminants with TiO_2/PCC blocks and TiO_2-SiO_2/PCC blocks under UV and visible light irradiation.

	Photodegradation efficiency (%)						
	UV illumi	nation	Visible illumi	Visible light illumination			
Samples	MB	MG	MB	MG			
TiO ₂ /SiO ₂ /PCC blocks TiO ₂ /PCC blocks	98.67 92	93.19 92.31	94.67 82.22	87.73 84.16			
PCC = Portland cement MB = Methylene Blue.	concrete;	MG =	- Malachite	Green;			

1 The existence of Si in PCC and on the TiO₂–SiO₂ composite and formation of Ti–O–Si bonds, leading to the formation of a large number of Lewis acid sites on the surface, along with added adsorption sites. This may cause an enhancement in the adsorption of hydroxide ions and facilitate the adsorption of organic contaminants on the photocatalyst surface. These ions act as the hole traps that prevent electron-hole recombination and oxidize adsorbed molecules. Therefore, with the creation of more absorption sites, more species are degraded on the photocatalyst surface (76,77). Besides, according to previous works (49,52), the presence of SiO₂ leads to more Anatase phase *versus* rutile phase of TiO₂ for which the Anatase phase has a better photocatalytic activity.

2 It was deduced that the highest photocatalytic performance could be related to the abundance of metallic oxides in the concrete support. Some of these metal oxides, such as those comprising iron ions, are transferred to the semiconductor surface where they may improve the lifetime of the electron-hole pairs and enhance the photocatalytic activity. It was assumed that these metal oxides introduce impurity levels between the conduction band and the valence band of TiO₂ leading to a narrower band gap and consequently, increases the visible light absorption.

Our research reveals that the use of high-pressure mercuryvapor lamps (300 W, $\lambda_{max} = 546.8$) as a visible light source



Figure 15. Degradation time for Malachite Green and Methylene Blue dyes with different samples under (a) UV illumination and (b) visible light irradiation.

without any cut-off filter may cause similar photodegradation mechanism under UV and visible light.

A photon with lower wavelength ($\lambda < 400 \text{ nm}$) that has an energy greater than the band gap energy of Anatase TiO₂ ($E_g = 3.2 \text{ eV}$) generates an electron/hole pair. The electron may reduce the dye or react with electron acceptors such as O₂ that are adsorbed on the surface or dissolved in the water and generate radicals (O₂⁻⁻, 'OH). The resulting 'OH radical, being a strong oxidizing agent, can oxidize most of the dyes to their mineralized end-product. The substrates that do not react with hydroxyl radicals are degraded with TiO₂ photocatalysis at high decomposition rates which are influenced by the position of the semiconductor valence band edge.

Our data ascertained that degradation of dyes under UV illumination is faster compared to visible light. Ultraviolet light source is not only harmful but also expensive because of the large input of electric power in generating UV irradiation. Therefore, it is not feasible to use it under all conditions. Besides, our results show that the nanocatalysts deposited on PCC blocks express photocatalytic activity under visible light, as well as UV light, for the degradation of these dyes. Visible light is thus a suitable source as it is easily accessible and economically affordable.

A practical approach toward the set goal involves the use of adsorbents with a large surface area as support material for TiO_2 loading. SiO_2 and Portland concrete blocks are good absorbents for contaminants compared to other support materials.

Thus, analysis of the obtained data revealed that both the coated samples demonstrated good photocatalytic activity under visible light; and TiO_2 -SiO_2/PCC blocks displayed a lower degradation time for both the dyes compared to TiO_2 /PCC blocks due to their small grain size and high surface area (Fig. 15). Therefore, using PCC blocks as support for TiO_2 and TiO_2 -SiO_2 nanoparticles could be helpful in the photodegradation of compounds under UV and visible light irradiation.

To investigate the reusability of the photocatalyst, 10 degradation cycles were carried out. After first cycle, the samples were used immediately for more experiments without any treatment. The results show that photodegradation efficiency for decomposition of dyes on nano-TiO₂ and TiO₂–SiO₂ immobilized on concrete blocks decreases by around 8–10% after 10 cycles. This may be due to the deactivation of active sites of photocatalyst by dyes and their intermediates. In other words, the nano-TiO₂/PCC and TiO₂–SiO₂/PCC blocks are reusable and their high photocatalytic activity after several tests is preserved.

CONCLUSION

In summary, COD and UV–Vis spectrograph analyses confirmed that the strongest degradation of MB and MG (organic pollutants) at acidic pH under UV and visible light irradiation was observed for nano-TiO₂ and nano-TiO₂–SiO₂ when they were immobilized on concrete blocks, in comparison to pure nano-TiO₂ and TiO₂–SiO₂. Moreover, TiO₂–SiO₂/PCC blocks required less time and had more photodegradation efficiency for the dyes' degradation and over 87% of dyes were degraded by these coated blocks under UV and visible light irradiation. SEM images showed that the nanoparticles were well-adhered to the concrete surface and distributed homogeneously which resulted in high surface area for the photocatalytic process. Also, the EDX analysis showed that various cations present in the cement

composition facilitated the photocatalytic activity of titania. Moreover, the presence of SiO_2 limits the TiO_2 -particle size on the concrete blocks and consequently enlarges the surface area of the catalyst and increases its activity because of interaction between the nanotitania and the SiO_2 species. XRD results explained that TiO_2 powder is purely Anatase phase which shows the maximum photoactivity and can be employed as an efficient photocatalyst. Utilization of the sample blocks in wastewater treatments is economical, does not require separation or filtration to recover the catalyst and works well under visible light. It is appropriate for industrial wastewater treatment at room temperature and atmospheric pressure within the pH range.

Acknowledgements—Financial support from Iran University of Science and Technology is gratefully acknowledged.

REFERENCES

- Tsiridis, V., E. Bizani, K. Fytianos and I. Poulios (2006) Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide. *J. Hazard. Mater.* 136, 85– 94.
- Levine, W. G. (1991) Metabolism of azo dyes: Implication for detoxication and activation. *Drug Metab. Rev.* 23, 253–309.
- Weisburger, J. H. (2002) Comments on the history and importance of aromatic and heterocyclic amines in public health. *Mutat. Res.* 506–507, 9–20.
- Vineis, P. and R. Pirastu (1997) Aromatic amines and cancer. Cancer Causes Control 8, 346–355.
- Robinson, T., G. McMullan, R. Marchant and P. Nigam (2001) Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.* 77, 247–255.
- Azmi, W., R. K. Sani and U. C. Banerjee (1998) Biodegradation of triphenylmethane dyes. *Enzyme Microb. Technol.* 22, 185–191.
- Ogugbue, C., N. Morad, T. Sawidis and N. Oranusi (2012) Decolorization and partial mineralization of a polyazo dye by Bacillus firmus immobilized within tubular polymeric gel. *3 Biotech* 2, 67–78.
- Nigam, P., G. Armour, I. M. Banat, D. Singh and R. Marchant (2000) Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues. *Bioresour. Technol.* 72, 219–226.
- 9. Marmagne, O. and C. Coste (1996) Color removal from textile plant effluents. *Am. Dyest. Rep.* **85**, 6.
- Forgacs, E., T. Cserháti and G. Oros (2004) Removal of synthetic dyes from wastewaters: A review. *Environ. Int.* 30, 953–971.
- Nishimoto, S., B. Ohtani and T. Kagiya (1985) Photocatalytic dehydrogenation of aliphatic alcohols by aqueous suspensions of platinized titanium dioxide. J. Chem. Soc. Faraday Trans. 1 81, 2467–2474.
- Tanaka, K., T. Hisanaga, A. P. Rivera, D. F. Ollis and H. Al-Ekabi (1993) *Photocatalytic Purification and Treatment of Water and Air*, pp. 169–178. Elsevier, Amsterdam, The Netherlands.
- Fox, M. A. and M. T. Dulay (1993) Heterogeneous photocatalysis. *Chem. Rev.* 93, 341–357.
- Yoneyama, H., S. Yamanaka and S. Haga (1989) Photocatalytic activities of microcrystalline TiO₂ incorporated in sheet silicates of clay. J. Phys. Chem. 93, 4833–4837.
- Zhang, Z., C. C. Wang, R. Zakaria and J. Y. Ying (1998) Role of particle size in nanocrystalline TiO₂-based photocatalysts. *J. Phys. Chem. B* 102, 10871–10878.
- Tsai, S. J. and S. Cheng (1997) Effect of TiO₂ crystalline structure in photocatalytic degradation of phenolic contaminants. *Catal. Today* 33, 227–237.
- Sclafani, A., L. Palmisano and M. Schiavello (1990) Influence of the preparation methods of titanium dioxide on the photocatalytic degradation of phenol in aqueous dispersion. J. Phys. Chem. 94, 829–832.
- Serpone, N., D. Lawless, R. Khairutdinov and E. Pelizzetti (1995) Subnanosecond relaxation dynamics in TiO₂ colloidal sols (particle sizes Rp = 1.0–13.4 nm). Relevance to heterogeneous photocatalysis. J. Phys. Chem. 99, 16655–16661.

100 Hoda Jafari and Shahrara Afshar

- 19. Gratzel, M., N. Serpone and E. Pelizzetti (1989) *Photocatalysis: Fundamentals and Applications*. pp. 123. Wiley, NewYork.
- Al-Ekabi, H., N. Serpone, E. Pelizzetti, C. Minero, M. A. Fox and R. B. Draper (1989) Kinetic studies in heterogeneous photocatalysis.
 Titania-mediated degradation of 4-chlorophenol alone and in a three-component mixture of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,5-trichlorophenol in air-equilibrated aqueous media. *Langmuir* 5, 250–255.
- 21. Turchi, C. S. and D. F. Ollis (1989) Mixed reactant photocatalysis: Intermediates and mutual rate inhibition. *J. Catal.* **119**, 483–496.
- 22. Brezova, V., A. Blazkova, L. Karpinsky, J. Groskova, B. Havlinova, V. Jorik and M. Ceppan (1997) Phenol decomposition using Mn⁺/ TiO₂ photocatalysts supported by the sol-gel technique on glass fibres. J. Photochem. Photobiol. A 109, 177–183.
- Zhang, Y., G. Xiong, N. Yao, W. Yang and X. Fu (2001) Preparation of titania-based catalysts for formaldehyde photocatalytic oxidation from TiCl₄ by the sol–gel method. *Catal. Today* 68, 89–95.
- Hu, S., F. Li and Z. Fan (2012) Preparation of SiO₂-coated TiO₂ composite materials with enhanced photocatalytic activity under UV light. *Bull. Korean Chem. Soc.* 33, 1895–1899.
- Zhang, M., L. Shi, S. Yuan, Y. Zhao and J. Fang (2009) Synthesis and photocatalytic properties of highly stable and neutral TiO₂/SiO₂ hydrosol. J. Colloid Interface Sci. 330, 113–118.
- Guan, K. S. and Y. S. Yin (2005) Effect of rare earth addition on super-hydrophilic property of TiO₂/SiO₂ composite film. *Mater. Chem. Phys.* 92, 10–15.
- Evans, P. and D. W. Sheel (2007) Photoactive and antibacterial TiO₂ thin films on stainless steel. *Surf. Coat. Technol.* 201, 9319– 9324.
- Mellott, N. P., C. Durucan, C. G. Pantano and M. Guglielmi (2006) Commercial and laboratory prepared titanium dioxide thin films for self-cleaning glasses: Photocatalytic performance and chemical durability. *Thin Solid Films* 502, 112–120.
- Park, J. K., J. K. Kim and H. K. Kim (2007) TiO₂–SiO₂ composite filler for thin paper. J. Mater. Process. Technol. 186, 367–369.
- Bozzi, A., T. Yuranova, I. Guasaquillo, D. Laub and J. Kiwi (2005) Self-cleaning of modified cotton textiles by TiO₂ at low temperatures under daylight irradiation. *J. Photochem. Photobiol. A* 174, 156–164.
- Aguedach, A., S. Brosillon, J. Morvan and E. K. Lhadi (2008) Influence of ionic strength in the adsorption and during photocatalysis of reactive black 5 azo dye on TiO₂ coated on non woven paper with SiO₂ as a binder. *J. Hazard. Mater.* **150**, 250–256.
- Yuranova, T., V. Sarria, W. Jardim, J. Rengifo, C. Pulgarin, G. Trabesinger and J. Kiwi (2007) Photocatalytic discoloration of organic compounds on outdoor building cement panels modified by photoactive coatings. J. Photochem. Photobiol. A 188, 334–341.
- Venkata Subba Rao, K., A. Rachel, M. Subrahmanyam and P. Boule (2003) Immobilization of TiO₂ on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants. *Appl. Catal. B* 46, 77–85.
- Ding, Z., X. Hu, G. Q. Lu, P. L. Yue and P. F. Greenfield (2000) Novel silica gel supported TiO₂ photocatalyst synthesized by CVD method. *Langmuir* 16, 6216–6222.
- 35. Kitano, M., K. Funatsu, M. Matsuoka, M. Ueshima and M. Anpo (2006) Preparation of nitrogen-substituted TiO₂ thin film photocatalysts by the radio frequency magnetron sputtering deposition method and their photocatalytic reactivity under visible light irradiation. J. Phys. Chem. B **110**, 25266–25272.
- Guo, D., A. Ito, T. Goto, R. Tu, C. Wang, Q. Shen and L. Zhang (2013) Preparation of rutile TiO₂ thin films by laser chemical vapor deposition method. *J. Adv. Ceram.* 2, 162–166.
- 37. Kern, W. and K. K. Schuegraf (2001) 1 Deposition Technologies and Applications: Introduction and Overview. In *Handbook of Thin Film Deposition Processes and Techniques (Second Edition).* (Edited by K. Seshan), pp. 11–43. William Andrew Publishing, Norwich, NY.
- Augugliaro, V., V. Loddo and M. Pagliaro (2010) Clean by Light Irradiation: Practical Applications of Supported TiO₂, pp. 41–47. RSC Pub./Royal Society of Chemistry, Cambridge, UK.
- Shukla, S., S. Seal, L. Ludwig and C. Parish (2004) Nanocrystalline indium oxide-doped tin oxide thin film as low temperature hydrogen sensor. *Sens. Actuators, B* 97, 256–265.

- Muthukumarasamy, N., N. Gokilamani and M. Thambidurai (2013) Synthesis and characterization of nanocrystalline TiO₂ thin films by sol–gel dip coating method. *Adv. Mater. Res.* 678, 108–112.
- Sonawane, R. S., S. G. Hegde and M. K. Dongare (2003) Preparation of titanium(IV) oxide thin film photocatalyst by sol-gel dip coating. *Mater. Chem. Phys.* 77, 744–750.
- Chen, J. and C.-S. Poon (2009) Photocatalytic construction and building materials: From fundamentals to applications. *Build. Environ.* 44, 1899–1906.
- 43. Strini, A., S. Cassese and L. Schiavi (2005) Measurement of benzene, toluene, ethylbenzene and o-xylene gas phase photodegradation by titanium dioxide dispersed in cementitious materials using a mixed flow reactor. *Appl. Catal. B* **61**, 90–97.
- Ramirez, A. M., K. Demeestere, N. De Belie, T. Mäntylä and E. Levänen (2010) Titanium dioxide coated cementitious materials for air purifying purposes: Preparation, characterization and toluene removal potential. *Build. Environ.* 45, 832–838.
- Demeestere, K., J. Dewulf, B. De Witte, A. Beeldens and H. Van Langenhove (2008) Heterogeneous photocatalytic removal of toluene from air on building materials enriched with TiO2. *Build. Environ.* 43, 406–414.
- Poon, C. S. and E. Cheung (2007) NO removal efficiency of photocatalytic paving blocks prepared with recycled materials. *Constr. Build. Mater.* 21, 1746–1753.
- Watts, M. J. and A. T. Cooper (2008) Photocatalysis of 4-chlorophenol mediated by TiO2 fixed to concrete surfaces. *Sol. Energy* 82, 206–211.
- Ohama, Y. and D. Van Gemert (2011) Application of Titanium Dioxide Photocatalysis to Construction Materials: State-of-the-Art Report of the RILEM Technical Committee 194-TDP, pp. 5–35. Springer, Netherlands.
- Jahromi, H. S., H. Taghdisian, S. Afshar and S. Tasharrofi (2009) Effects of pH and polyethylene glycol on surface morphology of TiO₂ thin film. *Surf. Coat. Technol.* **203**, 1991–1996.
- Amereh, E. and S. Afshar (2010) Photodegradation of acetophenone and toluene in water by nano-TiO₂ powder supported on NaX zeolite. *Mater. Chem. Phys.* **120**, 356–360.
- Afshar, S., H. Samari Jahromi, N. Jafari, Z. Ahmadi and M. Hakamizadeh (2011) Degradation of malachite green oxalate by UV and visible lights irradiation using nanophotocatalyst. *Sci. Iran.* 18, 772– 779.
- Ahmadi, Z., S. Afshar, L. Vafaee and A. Salehi (2008) Photocatalytic degradation of *E. coli* bacteria using TiO₂/SiO₂ nanoparticles with photodeposited platinum. *Int. J. Nanosci. Nanotechnol.* 4, 39–48.
- Jafari, H., S. Afshar, O. Zabihi and M. Naebe (2015) Enhanced photocatalytic activities of TiO₂–SiO₂ nanohybrids immobilized on cement-based materials for dye degradation. *Res. Chem. Intermed.*, doi: 10.1007/s11164-015-2190-3.
- Bessekhouad, Y., D. Robert, J. V. Weber and N. Chaoui (2004) Effect of alkaline-doped TiO₂ on photocatalytic efficiency. J. Photochem. Photobiol. A 167, 49–57.
- Madhusudan Reddy, K., S. V. Manorama and A. Ramachandra Reddy (2003) Bandgap studies on anatase titanium dioxide nanoparticles. *Mater. Chem. Phys.* 78, 239–245.
- Suzuki, N., X. Jiang, L. Radhakrishnan, K. Takai, K. Shimasaki, Y.-T. Huang, N. Miyamoto and Y. Yamauchi (2011) Hybridization of photoactive titania nanoparticles with mesoporous silica nanoparticles and investigation of their photocatalytic activity. *Bull. Chem. Soc. Jpn.* 84, 812–817.
- Li, Y., B. P. Bastakoti, M. Imura, S. M. Hwang, Z. Sun, J. H. Kim, S. X. Dou and Y. Yamauchi (2014) Synthesis of mesoporous TiO2/ SiO2 hybrid films as an efficient photocatalyst by polymeric micelle assembly. *Chemistry* 20, 6027–6032.
- Shimasaki, K., N. Suzuki, N. Miyamoto and Y. Yamauchi (2011) Aerosol-assisted synthesis of nanoporous silica/titania nanoparticles composites and investigation of their photocatalytic properties. *J. Nanosci. Nanotechnol.* 11, 3256–3264.
- Lee, M. S., J. D. Lee and S. S. Hong (2005) Photocatalytic decomposition of acetic acid over TiO₂ and TiO₂/SiO₂ thin films prepared by the sol-gel method. *J. Ind. Eng. Chem.* 11, 495–501.
- Hong, S.-S., M. S. Lee, S. S. Park and G.-D. Lee (2003) Synthesis of nanosized TiO2/SiO2 particles in the microemulsion and their photocatalytic activity on the decomposition of p-nitrophenol. *Catal. Today* 87, 99–105.

- Bahadur, J., D. Sen, S. Mazumder, P. U. Sastry, B. Paul, H. Bhatt and S. G. Singh (2012) One-step fabrication of thermally stable TiO₂/SiO₂ nanocomposite microspheres by evaporation-induced selfassembly. *Langmuir* 28, 11343–11353.
- Neppolian, B., H. Yamashita, Y. Okada, H. Nishijima and M. Anpo (2004) Preparation of TiO₂ photocatalysts by multi-gelation and their photocatalytic reactivity for the degradation of 2-propanol. *Chem. Lett.* 33, 268–269.
- Mills, A., R. H. Davies and D. Worsley (1993) Water-purification by semiconductor photocatalysis. *Chem. Soc. Rev.* 22, 417–425.
- Anderson, C. and A. Bard (1997) improved photocatalytic activity and characterization of mixed TiO₂/SiO₂ and TiO₂/Al₂O₃ materials. *J. Phys. Chem. B* 101, 2611–2616.
- Guo, B., Z. Liu, L. Hong, H. Jiang and J. Y. Lee (2005) Photocatalytic effect of the sol-gel derived nanoporous TiO₂ transparent thin films. *Thin Solid Films* **479**, 310–315.
- Choi, J., H. Park and M. R. Hoffmann (2010) Effects of single metal-ion doping on the visible-light photoreactivity of TiO2. *J. Phys. Chem. C* 114, 783–792.
- Modirshahla, N. and M. A. Behnajady (2006) Photooxidative degradation of Malachite Green (MG) by UV/H₂O₂: Influence of operational parameters and kinetic modeling. *Dyes Pigm.* **70**, 54–59.
- Saquib, M. and M. Muneer (2003) TiO₂-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions. *Dyes Pigm.* 56, 37–49.
- 69. Párkányi, C., C. Boniface, J. J. Aaron and M. Maafi (1993) A quantitative study of the effect of solvent on the electronic absorption and fluorescence spectra of substituted phenothiazines: Evaluation of

their ground and excited singlet-state dipole moments. *Spectrochim. Acta A* **49**, 1715–1725.

- Houas, A., H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J. Herrmann (2001) Photocatalytic degradation pathway of methylene blue in water. *Appl. Catal. B* **31**, 145–157.
- Konstantinou, I. K. and T. A. Albanis (2004) TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A review. *Appl. Catal. B* 49, 1–14.
- Padamavathy, S. (2003) Aerobic decolorization of reactive azo dyes in presence of various cosubstrates. *Chem. Biochem. Eng. Q.* 17, 147–152.
- Guivarch, E., S. Trevin, C. Lahitte and M. Oturan (2003) Degradation of azo dyes in water by Electro-Fenton process. *Environ. Chem. Lett.* 1, 38–44.
- Reutergådh, L. B. and M. Iangphasuk (1997) Photocatalytic decolourization of reactive azo dye: A comparison between TiO₂ and us photocatalysis. *Chemosphere* 35, 585–596.
- Borhade, A. V., D. R. Tope and B. K. Uphade (2012) An Efficient photocatalytic degradation of methyl blue dye by using synthesised PbO nanoparticles. *J. Chem.* 9, 705–715.
- Balachandran, K., R. Venckatesh and R. Sivaraj (2010) Synthesis of nano TiO₂–SiO₂ composite using sol–gel method: Effect on size, surface morphology and thermal stability. *Int. J. Eng. Sci. Technol.* 2, 3695.
- Jafry, H. R., M. V. Liga, Q. Li and A. R. Barron (2010) Simple route to enhanced photocatalytic activity of P25 titanium dioxide nanoparticles by silica addition. *Environ. Sci. Technol.* 45, 1563– 1568.