Photosensitization effect on visible-light-induced photocatalytic performance of TiO₂/chlorophyll and flavonoid nanostructures: kinetic and isotherm studies

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Abstract. Preparation and performance of natural dye-sensitized photocatalysts of TiO₂ are described in this study. Such sensitized nanostructures offer visible-light-reactive systems for the photodegradation of organic pollutants. Natural pigments of chlorophyll and flavonoid extracted from parsley leaves and *Curcuma longa* roots are grafted on TiO₂ nanoparticles as photosensitizers using an incipient wetness impregnation method. The as-prepared samples are structurally characterized by combined techniques, such as X-ray diffraction, scanning electron microscopy and Fourier transform infrared. The diffuse reflectance UV–Vis spectra are also used to investigate band-gap energies. The resultant band-gap energies confirm the ability of visible light absorption and thereby the ability of more efficient generation of photoexcited charge-carriers. The photocatalytic performance of dye-sensitized nanoparticles is tested in terms of decolourization efficiency of MB dye as a function of involved operating parameters including reaction time, amount of catalyst, initial MB concentration and pH. Both samples show the excellent photocatalytic efficiencies relevant to the red shift generated and high absorption of photons in the visible region. However, the highest efficiency is obtained for TiO₂/chlorophyll catalysts (93%) compared to TiO₂/flavonoid samples (91%), which is perfectly in agreement with their band-gap energies and visible-light absorption ability. Photodegradation process kinetics is investigated by the Langmuir–Hinshelwood model, while the adsorption equilibrium is described based on Langmuir and Freundlich isotherms.

Keywords. Decolourization; titanium dioxide; photosensitization; photocatalyst; natural pigments.

1. Introduction

In recent years, there has been an increasing concern over toxic contaminants discharged into water environment due to industrial development. Organic dyes utilized in textile, cosmetic and food industrials, as a class of causative agents of water pollution cannot be degraded using microorganisms in water, leading to disruption of food chains, the death of aquatic animals and human diseases. This is mainly attributed to coloured organic compounds suppressing photosynthetic reactions through inhibiting sunlight penetration into aquatic ecosystems [1,2]. Customary physical and biological remediation techniques have been proven not to be effective in removing organic dye molecules [3]. One of the various strategies considered as emerging water treatment methods is advanced oxidation processes (AOPs) [4]. The AOPs based on photocatalytic mechanisms originated from metal oxide–semiconductor materials, such as MgO, CuO, Al₂O₃, Ag₂O and ZnO have been extensively investigated for treating dye-containing sewage [5].

Titanium dioxide (TiO₂) as a wide band-gap metal oxide semiconductor has attracted considerable research interest

because of its unique ability in many fields including air purification, water treatment, hydrogen production, solar cells and malignant tumour therapy [6,7]. Extensive studies have been carried out on titanium dioxide for photocatalytic applications due to its numerous advantages, such as high chemical and optical stabilities, low cost and low toxicity [8,9]. In this way, the effects of pore size and calcination temperature of mesoporous TiO₂–SiO₂ composites are investigated to improve the photocatalytic degradation of methylene blue (MB) dye [10,11]. However, the poor consumption of solar energy due to large band-gaps of bare-TiO₂ nanostructures (about 3.2 eV) [9], which is only limited to ultraviolet irradiation (covers 5% of the solar energy spectrum compared to 45% huge fraction of visible light [12]) has restricted its practical applications.

Band engineering technology has been applied to extend the absorption spectrum of semiconductors to the visible range (400–700 nm) by employing different controlling methods, such as constructing multi-layered materials [13], functionalizing with photosensitizers and doping with metals and also non-metals [14]. Photosensitizers like dye molecules owning visible light sensitivity are used in photocatalytic systems for separation and also transformation of photoexcited

electron and hole pairs. Many efforts have been taken for the development of visible-light-driven photocatalysts using inorganic sensitizers, including metal complexes because of their high thermal and chemical stabilities [15]. Boyer *et al* [16] have investigated the role of ruthenium photosensitizers in the degradation of phenazopyridine with TiO₂ electrospun fibres.

Compared to inorganic metal complex dyes, synthetic organic dyes show lower toxicity and easier handling in potential practical applications [17]. Eosin Y, as a kind of organic dye, has been studied to prepare solar-light-driven TiO₂ catalysts for the removal of cadmium ions in aqueous solution of triethanolamine [18]. Chowdhury *et al* [19] have employed an eosin Y-sensitized platinum-loaded TiO₂ catalyst for the phenol degradation under visible solar light. Shang *et al* [20] have presented a comparative investigation on the photocatalytic performance of the TiO₂ photocatalyst sensitized with commercial organic pigments including C. I. Pigment Yellow 154 and C. I. Pigment Red 254 (PR) to remove methyl orange under visible light irradiation. This research group has also reported the preparation and enhanced visible light catalytic activity of TiO₂ sensitized with commercial organic pigment benzimidazolone Yellow H3G for the photodegradation of methyl orange, rhodamine B and acid chrome blue K [21].

However, considering the importance of environment protection and avoidance of secondary contaminations, natural dyes extracted from fruits, flowers and beverages have recently attracted increasing particular attention. Natural plant extracts have been considered as viable alternatives to inorganic and organic pigments due to low cost, easy attainability, abundance in supply of raw materials and also no environment threat [22]. In this way, it has been reported to sensitize Mg/P25 catalysts by the chlorophyll plant pigment to degrade rhodamine B [23]. A comprehensive study on natural pigments including flavonoid, betalains, carotenoid, chlorophyll and anthraquinone as TiO₂ photosensitizers has been carried out by Jaafar *et al* [24]. Zyoud *et al* [25] have described anthocyanin as a safe photosensitizer for TiO₂ particles in the photodegradation of organic contaminants in water. Díaz-Urbe *et al* [26] have reported experimental and theoretical investigations on improvement of the photocatalytic activity of TiO₂ using Colombian Caribbean species (*Syzygium cumini*) as natural sensitizers. Visible-light degradation of dyes and phenols over mesoporous titania prepared using anthocyanin from red radish has also been described by Yan *et al* [27]. Anthocyanin-sensitized TiO₂ nanoparticles for phenazopyridine photodegradation under solar simulated light have been prepared by Zyoud *et al* [28].

Although there are reports about successful use of natural plant extracts, such as chlorophyll and anthocyanin pigments in the process of dye-sensitization, it is still a challenge to test new dye derivatives for photocatalytic degradation. In recent years, flavonoid (curcumin) pigments with intense yellow colour have been suggested to shift the photoresponse of semiconductors to the visible region of the

electromagnetic spectrum. Accordingly, flavonoid (hesperidin) has been employed to improve the photocatalytic decolourization of eosin Y dye using titanium dioxide nanoparticles [29]. Buddee *et al* [30] have coated curcumin pigments on P25 TiO₂ using an impregnation method for the enhanced photodegradation of dyes under visible light. Mesoporous TiO₂ catalysts have also been modified by curcumin to investigate the photocatalytic degradation of MB dye [31]. In another study, Vignesh K *et al* [32] have described the photocatalytic performance of Ag-doped SnO₂ nanoparticles modified with curcumin. To the best of our knowledge, there has been no consideration on comparing the visible-light-response of flavonoid pigments with the most successful photosensitizers. In the present work, considering the profitability of such comparative investigations, natural flavonoid and chlorophyll pigments have been extracted from parsley leaves and *Curcuma longa* roots, respectively, to study the optical properties and photocatalytic performance of TiO₂ nanostructures sensitized with such plant extracts.

2. Experimental

2.1 Materials

Commercial anatase TiO₂ powder was procured from US Nano Company. MB, ethanol (C₂H₅OH, 96%), sodium hydroxide (NaOH, 98%) and sulphuric acid (H₂SO₄, 95%) were obtained from Samchun Chemicals. Both distilled and deionized waters were used in the whole experiment. Parsley, dried *C. longa* roots and dishwashing liquid were also purchased from a local market in Iran to extract chlorophyll and flavonoid pigments. All the chemicals were of analytical grade and used without further purification.

2.2 Characterization

X-ray diffraction (XRD) patterns were obtained on a D8-advance Bruker diffractometer with CuK α_1 ($\lambda = 0.15406$ nm) radiation to determine the crystalline phase of samples. X'Pert HighScore Plus Software was used to analyse the long digital data recorded by the diffractometer. Scanning electron microscope (SEM, TeScan-Mira III) was used to study surface morphologies. Particle sizes were also identified from SEM images using microstructure measurement software (ImageJ). Fourier transform infrared (FTIR) measurements were performed on a PerkinElmer BX-II instrument from USA to investigate the chemical structural information of nanoparticle samples. A UV-Vis spectrophotometer (Hach DR 5000) was utilized to identify the absorption features of natural pigments. Band gaps were calculated using an Avantes diffuse reflectance spectroscopy (DRS) (Avaspec-2048-TEC) with an AvaLamp DH-S setup. The data obtained were analysed using Origin Pro 8 software to measure optical band gaps.

Figure 1. Diagram of TiO_2 dye sensitization.

2.3 Preparation of dye-sensitized TiO_2

A three-step process was utilized to prepare dye-sensitized TiO_2 catalysts. The first step was the initial preparation of purchased TiO_2 nanoparticles through eliminating water absorbed on their surface. In this stage, purchased titanium dioxide powder was dried in an oven at a temperature of 100°C for 4 h to achieve nanoparticles, which was identified as pristine TiO_2 . The second step was to prepare the extraction of natural pigments of chlorophyll and flavonoid. In this work, natural pigments were kindly provided by fresh natural products. Chlorophyll was extracted from green leaves of parsley and flavonoids were obtained from long roots of dried *C. longa*. To extract chlorophyll, the fresh parsley leaves were first washed well with distilled water followed by a drop of dishwashing liquid and then, dried at room temperature. The dried parsley leaves were then chopped into smaller pieces using a grinder machine to facilitate the extraction process by increasing the surface area exposed to the solvent. Then, 3 g of the chopped plant tissue was immersed in 96% ethanol and brought to a final volume of 50 ml in a glass beaker covered by black plastic. The dark condition was provided to remove the effect of the background light and also inhibit the evaporation of the solvent. The ethanolic mass prepared was then kept in a refrigerator at 4°C for 7 days and daily stirred for 30 s to homogenate the mixture. To remove any undissolved material, the raw extract was purified by filtering. The remained

green liquid was finally used as the chlorophyll pigment to sensitize the TiO_2 nanoparticles.

A similar preparation process was also used to obtain the extraction of flavonoid pigments from dried *C. longa* roots. In this process, dried *C. longa* roots were milled by a grinder machine and 6 g of the ground *C. longa* were added to 96% ethanol in a 50 ml volumetric beaker. Finally, the obtained mixture was kept at 4°C for 48 h in the dark to further process in accordance with the extraction method mentioned above. The third step was involved in dye sensitization of the semiconductor surface. Dye sensitization methodology for the experiment is presented in figure 1. In a typical dye sensitization process, 2 g of dried TiO_2 powder was added into 50 ml ethanolic dye solution and the final mixture was then kept at room temperature for 12 h in the dark. After the 12 h reaction, the resultant coloured product was washed three times with distilled water and filtered to remove unabsorbed dye molecules from its surface. The dye-sensitized nanoparticles were dried at 70°C for 3 h to immobilize dye molecules on the surface of the prepared catalyst. Finally, the chlorophyll and flavonoid-sensitized TiO_2 nanostructures turned into light green and intense yellow in colour, respectively.

2.4 Adsorption and photocatalytic activity measurement

Photocatalytic activity of dye-sensitized TiO_2 samples was evaluated by monitoring the degradation of MB as a test

pollutant in aqueous solutions under visible light irradiation. The photocatalytic reactor used in present work included a 150-W metal halide lamp (Philips) as a light source illuminating aqueous solutions at a distance of 30 cm from the top. Typically, a suitable UV cut-off filter was used to ensure that the prepared samples were exposed only to the light rays above 410 nm in the visible part of the electromagnetic spectrum. The UV filter had a nearly constant transmission within the visible light range between 410 and 700 nm. All equipments of the photocatalytic reactor were placed inside a box made of medium-density fiberboard to eliminate the effects of the room light and reduce the background light. Since visible light irradiation heated up and evaporated the reactant solution, it was necessary to maintain the reaction temperature constant using a cooling system. Therefore, the reactor was equipped with two fans to move the air to cool the reaction media.

Parameters involved in the photocatalytic reaction, such as irradiation time, dosage of photocatalyst, initial concentration of MB and pH of samples were optimized in the ranges of 0–270 min, 0.05–0.3 g, 5–15 ppm and 4–12, respectively. To investigate photocatalytic tests, 0.01 g of MB powder was first dissolved in 100 ml deionized water to prepare a stock solution of MB with a concentration of 100 ppm. A magnetic stirrer was continuously used to uniform aqueous suspensions in the reactor. Before illumination, all samples were maintained under dark conditions for 30 min to establish an adsorption–desorption equilibrium between the surface of dye-sensitized TiO₂ and MB. Acidic conditions and alkaline phases were achieved by adding sulphuric acid (H₂SO₄, 95%) and sodium hydroxide (NaOH, 98%), respectively. A pH meter system was also used to measure the initial pH of the samples. The characteristic absorption peak of MB was monitored by a UV–Vis spectrophotometer (Hach DR 5000) at $\lambda_{\max} = 663$ nm at certain time intervals. First, a centrifuge with a speed of 3000 rpm for 10 min and then, a syringe filter were used to remove the particles of dye-sensitized TiO₂ from the mixture before monitoring the absorption peak.

The adsorption studies and the photocatalytic activities were investigated by the adsorption capacity and the photodegradation percentage, respectively. The adsorption capacity is determined in the dark by mass balance equation as [33]:

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of MB in mg l⁻¹, respectively. V is the solution volume in l and m is the photocatalyst amount applied in g. The photocatalytic efficiency under visible light was also calculated by the following equation [34]:

$$\text{Degradation efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100, \quad (2)$$

where C_0 and C_t show the initial and the final concentrations at time t and in mg l⁻¹, respectively.

Figure 2. Powder XRD spectra of: (a) pristine TiO₂, (b) chlorophyll- and (c) flavonoid-sensitized TiO₂.

3. Results and discussion

3.1 XRD analysis

The phase structure and crystalline size of the pristine TiO₂ and dye-sensitized TiO₂ nanoparticles with different pigments are investigated by powder XRD. The representative 20–800 scans of XRD for various TiO₂ samples are depicted in figure 2. As illustrated in figure 2a, all twelve detectable peaks in the pattern of the pristine TiO₂ are assigned to (101), (103), (004), (112), (200), (105), (211), (213), (204), (116), (220) and (215) planes of anatase TiO₂ (JCPDS no. 00-021-1272). No impurity peaks or ones originating from other phases are detected, demonstrating high purity of the anatase crystal. As shown in figure 2, comparing the XRD data obtained for dye-sensitized TiO₂ samples and the pristine TiO₂ reveal that there is no fundamental change in the crystal phase of modified TiO₂ due to dye sensitization. In fact, it is found that the surface sensitization to titanium dioxide has no effect on the crystalline phase. The average particle size of the pristine

Table 1. Photocatalytic properties of TiO₂ catalysts.

Sample	Crystallite size (nm) ^a	Particle size (nm) ^b	Absorption edge (nm) ^c	Band gap (eV) ^d	Decolourization efficiency (%)
Pristine TiO ₂	18.98	26	387	3.2	—
Chlorophyll-sensitized TiO ₂	19.52	29	427	2.90	93
Flavonoid-sensitized TiO ₂	19.25	28	418	2.96	91

^aCrystallite size according to the Scherrer equation.^bAverage particle size calculated by microstructure measurement software (ImageJ).^cOptical parameters calculated by the Tauc method.

TiO₂ and dye-sensitized TiO₂ catalysts can be determined by the Scherrer's equation as follows [35]:

$$D = k\lambda / \beta \cos(\theta), \quad (3)$$

where D , λ , θ and k show the average crystal size, the wavelength of the incident beam, angle position of peak and Scherrer's constant, respectively. In addition, β is calculated from the full width at half maximum (FWHM) of the peak as $\beta = \pi \times \text{FWHM}/180$. The average crystallite sizes of all the samples for $k = 0.9$ and $\lambda = 1.54 \text{ \AA}$ are estimated from the largest peak (101) placed at $2\theta \cong 25.36^\circ$ and are listed in table 1. As reported in table 1, after dye-sensitization, the average crystallite sizes of TiO₂ particles are slightly increased from 18.98 to 19.52 and 19.25 nm for chlorophyll- and flavonoid-sensitized TiO₂, respectively. Hence, it can be concluded that dye-sensitization may be responsible for such a slight increase in the particle size [12,36].

3.2 SEM analysis

SEM observations are performed to determine the surface morphology of photocatalysts. SEM analysis can be employed to identify the shape, particle size, distribution and structure of nanoparticles. For this purpose, the SEM images of the pristine TiO₂ and dye-sensitized TiO₂ catalysts at magnification of 200 nm along with particle size histograms, which are obtained using microstructure measurement software (ImageJ), are displayed in figure 3. Figure 3A-a illustrates a spherical-like morphology with a relatively uniform distribution of particles for pristine TiO₂ catalysts. According to the results shown in figure 3B-a, the non-sensitized homogeneous TiO₂ spheres present an average particle size of about 26 nm in diameter. Figure 3A-b and A-c displays the typical SEM images of TiO₂ catalysts after the dye-sensitizing process. As shown in figure 3A-b and A-c, surface morphologies of nanoparticles have not been changed after the dye-sensitization process. Performed calculations based on SEM images of dye-sensitized catalysts, as shown in figure 3B-b and B-c estimate average diameters of about 29 and 28 nm for chlorophyll- and flavonoid-sensitized TiO₂ photocatalysts, respectively. Although the dye-sensitized

TiO₂ samples show a relatively similar surface structure to non-sensitized TiO₂, it should be noted that due to the dispersion of natural pigments on sensitized catalysts [36], the surface of such samples seems slightly rougher as compared to non-sensitized particles.

3.3 FTIR analysis

It is possible to examine the functional groups and the surface characteristics of photocatalysts before and after dye-sensitization by FTIR spectroscopy. Surface groups of the pristine TiO₂ and dye-sensitized TiO₂ samples are detected in the wavenumber range of 400–4000 cm⁻¹ by FTIR spectra and the results are shown in figure 4. As indicated in figure 4a, a relatively wide band in the vicinity of 400–800 cm⁻¹ belonging to the typical Ti–O–Ti vibration is caused by stretching the vibration of hydroxyl groups [12,37]. An absorption peak at 1386 cm⁻¹ suggests that there are groups relevant to functional groups of C–OH in the FTIR spectrum of the pristine TiO₂ [38,39]. Sharp characteristic peaks are also observed at 1610 and 3256 cm⁻¹ for the non-sensitized TiO₂ sample, which can be ascribed to the –OH group and surface-absorbed water. This observation indicates that water molecules can be absorbed on the TiO₂ surface to form the –OH stretching vibration peak [40,41].

As can be seen from figure 4b, after being grated of chlorophyll molecules on the TiO₂ surface, the obtained sample shows new absorption peaks at 1640 and 2930 cm⁻¹, which can be attributed to the C=O bond of aldehyde groups and the stretching vibration of the O–H bond, respectively. The absorption peaks observed in figure 4b at near 3388 and 3440 cm⁻¹ are also ascribed to the stretching vibration of the O–H bond. Apart from the bands mentioned, another absorption peak at 3735 cm⁻¹ corresponds to the interactions between hydroxyl groups and the surface of TiO₂ [42]. By comparing the results obtained from figure 4a and b, it is noted that other characteristic absorptions are approximately similar to the pristine and chlorophyll-sensitized TiO₂.

In addition, comparison of the FTIR spectrum information obtained from figure 4a and c reveals that flavonoid-sensitized TiO₂ shows the appearance of new peaks at 1275 and 1509 cm⁻¹ corresponding to the OCH₃ group and benzene

Figure 3. (A) SEM images and (B) the corresponding histograms of (a) pristine TiO₂, (b) chlorophyll- and (c) flavonoid-sensitized TiO₂.

aromatic rings, respectively. According to figure 4c, in the FTIR spectrum of the flavonoid-sensitized TiO₂, the weak peaks around the positions of 1639 and 3661 cm⁻¹ correspond to the typical C–C bond and hydroxyl groups [43]. Accordingly, the changes obtained in the FTIR spectra of sensitized samples can well describe the successful sensitization of the dye to the semiconductor surface to anchor chlorophyll and flavonoid pigments on dye-sensitized TiO₂ catalysts.

3.4 Optical characteristics of pigments

The absorption features of the extracted natural pigments are investigated using UV–Vis spectrophotometry. Figure 5 displays the absorption spectra of chlorophyll and flavonoid pigments in ethanol between 300 and 600 nm. The absorption spectra of the chlorophyll and flavonoid pigments show the typical absorption bands at about 460 and 410 nm, respectively. It is evident that chlorophyll molecules are able to absorb visible-light photons possessing less energy compared to flavonoid pigments. In addition, the comparison of the UV–Vis profiles presented in figure 5 reveals a stronger absorption pattern for the chlorophyll pigment compared with the flavonoid sample.

3.5 Diffusion reflectance spectra analysis

To understand the optical characteristics of the pristine TiO₂ and TiO₂ sensitized using natural pigments of chlorophyll and flavonoid, it is advisable to use diffuse reflectance UV–Vis spectroscopy (DRS) to analyse absorption regions and detect the band structure of sensitized catalysts. DRS spectra of pristine TiO₂ and dye-sensitized TiO₂ samples in both absorption and reflection modes are displayed in figure 6a and b, respectively. As shown in figure 6, the optical characteristics of all the samples are plotted in the wavelength range of 300–600 nm. The optical data exhibited in figure 6 can be analysed to specify the near-band-edge optical absorption of the prepared samples. The photoresponse characterization illustrated in figure 6a clearly demonstrates the differences in the absorption wavelengths. The absorption spectrum of pristine TiO₂ exhibits a strong absorption profile in the UV region of the electromagnetic spectrum without any absorption in the visible region. It is quite clear that the inability to absorb light in the visible part is attributed to the absorption edge of the anatase phase of TiO₂ nanostructures, which is located at about 387 nm.

According to figure 6a, both dye-sensitized TiO₂ catalysts indicate stronger absorption in the visible region in contrast to the pristine TiO₂. However, the comparison of the

Figure 4. FTIR spectrum of: (a) pristine TiO₂, (b) chlorophyll- and (c) flavonoid-sensitized TiO₂.

absorption spectra of dye-sensitized TiO₂ catalysts shows that chlorophyll-sensitized TiO₂ has higher absorption compared with flavonoid-sensitized TiO₂. It can be clearly attributed to the fact that dye molecules are chemically absorbed onto the surface of sensitized samples. As a result, sensitizers of chlorophyll and flavonoid are successfully coated on the TiO₂ surface and create an enhanced absorption in the visible light region.

The reflectance data plotted in figure 6b can be applied to estimate the band gaps of samples. The optical band-gap energy of the pristine TiO₂ and dye-sensitized TiO₂ nanoparticles can be calculated by the Kubelka–Munk relation as follows [44]:

$$(F(R) \cdot h\nu) = C(h\nu - E_g)^n, \quad (4)$$

where $h\nu$ is the photon energy, C the proportionality constant and E_g the optical band gap of the nanoparticles. Parameter n depends on the nature of transition, which is considered $1/2$, $3/2$, 2 and 3 corresponding to allowed direct transitions, forbidden direct transitions, allowed indirect transitions and

Figure 5. UV-Vis absorption spectra of chlorophyll and flavonoid pigments.

forbidden indirect transitions, respectively. $F(R)$ is also a factor proportional to the reflection coefficient and is calculated using the following equation [6,14]:

$$F(R) = (1 - R)^2 / 2R. \quad (5)$$

Here, R is the reflectivity at a particular wavelength. For TiO₂ materials the Kubelka–Munk equation can be rewritten as [6,14]:

$$(F(R) \cdot h\nu)^{1/2} = C(h\nu - E_g). \quad (6)$$

According to the Tauc method, the band gap can be determined by plotting the optical data $(F(R) \cdot h\nu)^{1/2}$ vs. photon energy ($h\nu$). These plots for the pristine TiO₂ and dye-sensitized TiO₂ catalysts are shown as the inset in figure 6b. As illustrated in the inset of figure 6b, the tangential interceptions to the $h\nu$ -axis determine the optical band-gap energies. Table 1 shows the wavelength of the absorption edge (λ) and the relevant band gap energy (E_g) for the investigated samples. The data obtained from the inset of figure 6b provide smaller optical band gaps equivalent to 2.90 and 2.96 eV for chlorophyll- and flavonoid-sensitized TiO₂, respectively, as compared to the value of 3.2 eV for pristine TiO₂ catalysts. The results obtained from the inset of figure 6b indicate red shifts of about 40 and 31 nm for chlorophyll- and flavonoid-sensitized TiO₂ in contrast to the pristine TiO₂, respectively.

The observed red shifts can be described as a decrease of photon energy required to start photocatalytic performances, which can be achieved by the dye-sensitization process. These results indicate that a decrease in band-gap energy occurs with

Figure 6. (a) UV-Vis diffuse absorption spectra and (b) UV-vis reflectance spectra; inset: plots of $(F(R) \cdot h\nu)^{1/2}$ to obtain optical band gaps of dye-sensitized TiO₂.

a dye-sensitizing technique that is probably related to both the preparation method and parameters involved in the preparation process such as pigment concentrations. A decrease in the band-gap energy with the dye sensitization technique is attributed to the fact that dye molecules coated on the TiO₂ surface absorb visible light photons, which have less energy compared to UV photons, which can be absorbed by pristine TiO₂. Actually, the summation of optical density for dye pigments leads to the less band-gap energy. It can be concluded that such proposed photocatalysts can efficiently be photoactive in the wavelength region, which is >387 nm.

3.6 Adsorption equilibrium studies

It is significant to analyse the adsorption equilibrium data before performing the photocatalytic experiments. It is necessary to understand the adsorption contribution in the photodegradation process to design more efficiently photocatalytic systems [45]. Adsorption isotherm studies can express the adsorption capacity of adsorbents by describing the distribution of adsorption molecules between liquid and solid phases in the equilibrium state. Langmuir and Freundlich methods are considered as the most common isotherm models that can explain the nature of adsorbent-adsorbate interactions [33]. The Langmuir isotherm model quantitatively express the monolayer activity of adsorbents by considering the assumption that adsorbent surfaces include a finite number of active sites having identical energies. However, the Freundlich model suggests a multilayer activity over heterogeneous surfaces having an infinite number of active sites with different energetic distributions [46]. The Langmuir model is valid in which no transmigration takes place in the plane of the adsorbent surface and thereby interactions between adsorbed molecules can be discarded. Whereas the Freundlich isotherm

model includes such interactive behaviours in the presence of solid adsorbents [47].

3.6a Langmuir isotherm equation: The linear form of the Langmuir equation is described as follows [48]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}, \quad (7)$$

where C_e is the equilibrium concentration of MB in solution in mg l^{-1} . q_e is the adsorption capacity or the MB weight per unit of the dye-sensitized TiO₂ weight (mg g^{-1}). Parameters $q_{\max}$ and K_L are the Langmuir constants which can be obtained from the slope and the intercept of the linear curve C_e/q_e vs. C_e . $q_{\max}$ describes the adsorption capacity in mg g^{-1} . K_L shows the affinity between binding sites and the adsorption free energy in l mg^{-1} . The essential features of the Langmuir model can also be expressed by the dimensionless equilibrium parameter R_L referred as the separation factor term [49]:

$$R_L = \frac{1}{1 + (1 + K_L C_0)}. \quad (8)$$

The MB adsorption process based on the Langmuir model is considered favourable if $0 < R_L < 1$, unfavourable if $R_L > 1$, linear if $R_L = 1$ and irreversible if $R_L = 0$.

3.6b Freundlich isotherm equation: The Freundlich equation linearized for heterogeneous surface energy systems is

Figure 7. Linearized (a) Langmuir and (b) Freundlich models for MB decolourization in the presence of dye-sensitized TiO_2 .

Table 2. Adsorption isotherm model parameters for MB decolourization in the presence of dye-sensitized TiO_2 catalysts and without visible light irradiation.

Sample	Langmuir				Freundlich			
	$q_{\max}$ (mg g^{-1})	K_L (l mg^{-1})	R_L^2	R^2	$1/n_f$ (g mg^{-1})	n_f (mg g^{-1})	K_F (mg g^{-1})	R^2
Chlorophyll-sensitized TiO_2	0.97	0.098	0.40–0.67	0.9954	0.55	1.831	0.134	0.9998
Flavonoid-sensitized TiO_2	0.84	0.083	0.44–0.7	0.9689	0.5709	1.751	0.101	0.9962

determined as [46]:

$$\log q_e = \log K_F + \frac{1}{n_f} \log C_e, \quad (9)$$

where the plot of $\log q_e$ vs. $\log C_e$ can be used to obtain the Freundlich constants K_F and $1/n_f$. The dimensionless parameter n_f is calculated from the line slope to be an indication of the MB adsorption intensity. It represents the heterogeneity factor and indicates the variation as the adsorption linearity. The MB adsorption is considered linear if $n_f = 1$, physical if $n_f > 1$ and as a chemical process if $n_f < 1$. However, the MB adsorption can be considered as a favourable process when n_f lies between 1 and 10. The smaller $1/n_f$ represents the greater heterogeneity for dye-sensitized TiO_2 catalysts. The constant parameter K_F obtained from the line intercept can also indicate the MB adsorption capacity in mg g^{-1} or $(\text{l mg}^{-1})^{1/n_f}$. The greater K_F shows the greater adsorption capacity and the easier removal of MB molecules from aqueous solutions [50].

The Langmuir and Freundlich adsorption isotherms of MB onto dye-sensitized TiO_2 samples at different concentrations of 5, 10 and 15 ppm are presented in figure 7a and b, respectively. The experimental adsorption data are given by the

symbols, while the theoretical models are fitted by solid lines in figure 7. The values of Langmuir and Freundlich isotherm parameters calculated from the fitting of the experimental data for chlorophyll- and flavonoid-sensitized TiO_2 are summarized in table 2. The values of the separation factor R_L calculated from Langmuir isotherm analysis at different initial MB concentrations are found to be fall in the range of 0.4–0.67 and 0.44–0.7 for chlorophyll- and flavonoid-sensitized TiO_2 samples, respectively. The R_L values obtained between zero and one indicate an approximately favourable adsorption process based on the Langmuir model before visible-light irradiation.

Freundlich isotherm analysis also reveals a normal adsorption with the n_f values estimated in the range of 1–10 for both the dye-sensitized TiO_2 samples. However, the Langmuir adsorption coefficient K_L and Freundlich adsorption coefficient K_F for chlorophyll-sensitized TiO_2 nanoparticles are 2.57 and 1.33 times bigger than those of flavonoid-sensitized nanoparticles, respectively. Thus, it can be concluded that the adsorption strength of MB onto the chlorophyll-sensitized TiO_2 sample is greater compared to the flavonoid-sensitized TiO_2 sample. A comparison of the resulted correlation coefficients R^2 shows that the Freundlich equation yields greater R^2

Figure 8. Influence of irradiation time on the photocatalytic activity of pristine and dye-sensitized TiO₂.

values as compared to the Langmuir relation suggesting the multilayer coverage of MB on the surface of dye-sensitized TiO₂ nanoparticles. However, the closeness of all the correlation coefficients to one indicates that both investigated isotherm models can be applied to describe the equilibrium condition of the photocatalytic systems prior to the presence of visible light.

3.7 Photocatalytic studies

The photocatalytic performance of visible-light-driven TiO₂ based on the dye-sensitization method is evaluated via decolourization of MB aqueous solutions. The validity of the visible light irradiation time on decolourization efficiency is investigated in the solution with 10 ppm dye concentration and pH 7 containing 0.1 g catalyst. The rate of MB degradation is periodically recorded in different time intervals (each 30 min) up to 270 min at room temperature. The resultant data for pristine TiO₂ and dye-sensitized TiO₂ samples are presented in figure 8. As shown in figure 8, both sensitized photocatalysts indicate an increase in the rate of degradation of pollutants as time prolongs. It can be clearly observed from figure 8, the samples sensitized by chlorophyll and flavonoid molecules exhibit much better photocatalytic activities for MB degradation under visible light irradiation, compared with the pristine TiO₂ photocatalyst. Comparison of reported data in figure 8 reveals that photocatalytic activity of chlorophyll-sensitized TiO₂ is somewhat higher compared to the flavonoid-sensitized catalyst. For example, for an exposure time of 120 min, the flavonoid-sensitized TiO₂ indicates a decolourization percentage of about 15%, while the chlorophyll-sensitized sample reveals a bigger amount

of about 28% for the same time. Such a difference between the decolourization ability of dye-sensitized catalysts can be explained in terms of difference created between the band gaps of two photocatalysts during the dye-sensitization process as shown in the inset of figure 6b. As previously reported, by photosensitization, band-gap engineering technology has created a band-gap value equivalent to 2.90 eV for chlorophyll-sensitized TiO₂ compared with the value of 2.96 eV for flavonoid-sensitized TiO₂. It is accepted that based on photosensitization technology, semiconductors with narrower band gaps can extend the light absorption range and as a result, improve the photocatalytic performance. However, it must be mentioned that considering the irradiation period, there is no remarkable difference between enough times to reach an optimal decolourization time for both catalysts. According to data plotted in figure 8, an optimal contact time of about 210 min can be estimated to decolourize MB solutions with a reaction rate equal to 30.16 and 19.97% in the presence of chlorophyll and flavonoid-sensitized TiO₂, respectively.

To achieve the highest photocatalytic efficiency and also avoid excessive use of catalysts, it is necessary to determine the optimum photocatalyst concentration. For this purpose, a series of experiments are carried out by employing different concentrations ranging from 0.05 to 0.3 g in pH 7 aqueous solutions. Experiments are performed for solutions with 10 ppm MB concentration over an optimum time of 210 min under visible light irradiation. Figure 9a and b present the decolourization percentage of MB as a function of irradiation time in the presence of different amounts of chlorophyll- and flavonoid-sensitized TiO₂, respectively. It is clear from figure 9a and b that the decolourization rates of chlorophyll- and flavonoid-TiO₂ increase with an increase in the catalyst dose from 0.05 to 0.2 g. The explanation of this behaviour can be the fact that an increase in the amount of photocatalysts up to a certain amount causes an increase in the number of active sites on the semiconductor surface and in turn an increase in the number of electron-hole pairs generated during irradiation [51].

However, as illustrated in figure 9a and b, more increment in catalyst amounts from 0.2 to 0.3 g shows a negative effect on decolourization efficiency, because the higher concentration of photocatalysts leads to two significant effects. The first effect is a large aggregation of catalyst particles, which causes a decrease in the availability of active sites and as a result, a decrease in photocatalytic activity. The second effect can be described based on an increase in turbidity and thereby an increase in the number of scattered light rays, which finally leads to a decrease in the photon penetration and thus, a decrease in the degradation rate [52]. Therefore, data obtained from figure 9a and b indicate the optimum amount of 0.2 g under the experimental conditions reported with the degradation percentage of 59.57 and 28.88% for chlorophyll- and flavonoid-sensitized catalysts, respectively.

Another significant parameter for controlling the rate of decolourization is initial MB concentration, which is studied

Figure 9. Influence of the photocatalyst concentration on the MB decolourization for: (a) chlorophyll- and (b) flavonoid-sensitized TiO₂.

Figure 10. Influence of the initial MB concentration on the MB decolourization for: (a) chlorophyll- and (b) flavonoid-sensitized TiO₂.

by altering the initial concentration in the range of 5–15 ppm under optimum conditions obtained in previous steps. Figure 10a and b demonstrates the decolourization efficiency for pH 7 and a catalyst amount of 0.2 g at a contact time of 210 min for chlorophyll- and flavonoid-sensitized TiO₂, respectively. The data results from figure 10 clearly reveal that the rate of decolourization is severely decreasing by increasing the initial concentration of MB in the presence of both dye-sensitized catalysts. The photodegradation rate decreases from 67.99% (37.10%) at an optimum concentration of 5 ppm to 38.83% (22.8%) at an initial concentration of 15 ppm in the presence of chlorophyll (flavonoid) pigments.

The occurrence can be attributed to two remarkable effects involved in the process of generating electron–hole pairs. The first effect may be due to the fact that at high MB concentrations, dye molecules of MB are absorbed on the surface of photocatalysts and reduce the number of active sites to

generate hydroxyl radicals, because MB molecules do not permit the desire light intensity to reach surface active areas of nanoparticles. In addition, another effect can be ascribed to incapability of incident photons to reach the photocatalyst surface at a high MB concentration because of the action of MB molecules in the aqueous phase as a filter against incident light. In fact, an increase in the initial MB concentration decreases the path length of photons by penetrating aqueous solutions and as a result, a number of OH[•] and O₂[•] radicals are generated to attack the coloured pollutants [51,52].

The wastewater purification efficiency in the process of photocatalytic treatment is strongly dependent on pH of aqueous environments. Since wastewater released from industries may have various acidic or alkaline conditions, the final step to reach the highest photocatalytic activity is to investigate the dependence between pH of solution and the photodegradation rate. In the study, H₂SO₄ (95%) and NaOH (98%) are

Figure 11. Influence of pH on the MB decolourization for: (a) chlorophyll- and (b) flavonoid-sensitized TiO_2 .

used to adjust the initial pH of the MB solution in acidic and alkaline phases, respectively. All solutions with an initial MB concentration of 5 ppm and a catalyst dose of 0.2 g are visible light-irradiated over 210 min. The effect of pH values on the decolourization efficiency in the pH range of 4–12 in the presence of chlorophyll- and flavonoid-sensitized TiO_2 are displayed in figure 11a and b, respectively.

According to the data plotted in figure 11a and b, both photocatalysts show a fast increase in the decolourization rate of MB as the pH value increases from 4 to 11, followed by a sudden decrease in the decolourization rate of MB at pH 12. For example, for pH 4, the decolourization efficiencies are about 28.4 and 12.5% for chlorophyll- and flavonoid-sensitized TiO_2 , while they are enhanced to about 93.01 and 91.10%, respectively at pH 11. Then, they drop to about 79.83 and 78.49% at pH 12. Thus, the highest rate of photodegradation occurs at the optimum pH value of 11 for such an experiment. Considering the obtained results for such photocatalysts sensitized under optimal conditions, there is an overall degradation efficiency of about 93% for the chlorophyll-sensitized catalyst compared to the efficiency of about 91% for flavonoid-sensitized TiO_2 after 210 min visible-light irradiation.

This behaviour may be explained on the basis of the surface characteristic of TiO_2 nanoparticles which is a limiting factor for pH values and surface charge properties. The surface charge of photocatalysts depends on the point of zero charge (pzc) which is defined as the pH value for a situation in which proton charge is equivalent to zero. Parameter pzc for dye-sensitized TiO_2 is estimated about 6.7, similar to pristine TiO_2 [53]. Therefore, the surface charge of dye-sensitized catalysts is positive under acidic conditions ($\text{pH} < \text{pH}_{\text{pzc}}$) and negative in the alkaline phase ($\text{pH} > \text{pH}_{\text{pzc}}$). Benjamin *et al* [54] explained that since the protonation of MB molecules takes place at the more acidic phase (lower pH), the dye molecules experience a strong force of repulsion from the positively charged semiconductor surface. This event

induces a decrease in the rate of the photodegradation process. However, when the pH value becomes higher than pH of zero point charge, the sensitized- TiO_2 surface provides the higher number of OH^- ions which are effective to form more hydroxyl radicals to enhance the decolourization efficiency [52]. Nevertheless, with an increase in the pH value from 11, the OH^- ions absorbed on the surface of semiconductor severely make it negatively charged. Consequently, the electrostatic repulsion created between the MB anion and the oxide surface abruptly increases and the rate of decolourization decreases.

3.8 Kinetic rate expressions and reaction mechanism

To develop the systems dependent on wastewater treatment technologies, it is necessary to describe the degradation rate of pollutants based on kinetic terms. The kinetic expressions relevant to dye-sensitized TiO_2 photocatalysts can be explained by the Langmuir–Hinshelwood equation in concentration terms as follows [55]:

$$d[C(t)]/dt = k_n[C(t)]^n, \quad (10)$$

where $C(t)$ is the MB concentration at a certain time t and in mg l^{-1} . The parameter n is the order of kinetic in which k_n represents the decolourization rate constant for n -order. After substituting $n = 0, 1$ and 2 in equation (10) and applying boundary conditions: $C(t) = C_0$ at $t = 0$ and $C(t) = C_t$ at $t = t$, the integrated form of the equation becomes as:

$$(C_0 - C_t) = k_0 t, \quad (11)$$

$$-\ln\left(\frac{C_t}{C_0}\right) = k_1 t, \quad (12)$$

$$\left(\frac{1}{C_t} - \frac{1}{C_0}\right) = k_2 t. \quad (13)$$

The equations obtained as equations (11)–(13) represent the linearized forms of zero-, first- and second-order kinetics,

Figure 12. (a) Zero-, (b) first- and (c) second-order kinetic curves of MB decolourization for: (A) chlorophyll- and (B) flavonoid-sensitized TiO_2 .

Table 3. Kinetics for MB decolourization at different initial concentrations in the presence of dye-sensitized TiO_2 catalysts (catalyst amount, 0.2 g; pH, 7 and irradiation time, 210 min).

Sample	Concentration (ppm)	Zero-order		First-order		Second-order	
		K_0 ($\text{mg l}^{-1} \text{min}^{-1}$)	R_0^2	K_1 (min^{-1})	R_1^2	K_2 ($\text{l mg}^{-1} \text{min}^{-1}$)	R_2^2
Chlorophyll-sensitized TiO_2	5	0.0029	<u>0.9956</u>	0.0052	0.9901	0.0105	0.9587
	10	0.0039	0.9959	0.0036	<u>0.9964</u>	0.0034	0.9871
	15	0.0038	<u>0.9979</u>	0.0024	0.9942	0.0015	0.9845
Flavonoid-sensitized TiO_2	5	0.0015	0.9751	0.0021	0.9845	0.0030	<u>0.9899</u>
	10	0.0020	0.9872	0.0016	0.9909	0.0013	<u>0.9911</u>
	15	0.0020	0.9867	0.0011	<u>0.9900</u>	0.0007	0.9898

respectively, where C_0 is defined as the MB concentration immediately after the adsorption–desorption equilibrium. k_0 , k_1 and k_2 are the rate constants of zero-, first- and second-order models in $\text{mg l}^{-1} \text{min}^{-1}$, min^{-1} and $\text{l mg}^{-1} \text{min}^{-1}$, respectively. The rate constants k_0 , k_1 and k_2 are obtained from the slope of the corresponding lines when $(C_0 - C_t)$, $-\ln\left(\frac{C_t}{C_0}\right)$ and $\left(\frac{1}{C_t} - \frac{1}{C_0}\right)$ are plotted vs. time t , respectively.

Kinetic curves of zero-, first- and second-order are shown in figure 12a–c, respectively. Experimental data at different concentrations assigning to chlorophyll- and flavonoid-sensitized

TiO_2 based on the governing experimental conditions in figure 10, accompanied by theoretical fitted lines are illustrated in figure 12A and B, respectively.

The linear regression method based on the correlation coefficients R^2 is applied to select the best model. The quantities of the rate constants (k_0 , k_1 and k_2) and the correlation coefficients (R_0^2 , R_1^2 and R_2^2) were calculated and are tabulated in table 3. To identify better, the highest values of R^2 are underlined in table 3. A careful observation at data relevant to chlorophyll-sensitized TiO_2 samples reveals that the values of correlation coefficients for zero-order kinetic are on

Table 4. Dimensionless term of $k_{\text{Chlorophyll}}/k_{\text{Flavonoid}}$ in the presence of dye-sensitized TiO_2 .

Parameter	Concentration (ppm)	Zero-order	First-order	Second-order
$k_{\text{Chlorophyll}}/k_{\text{Flavonoid}}$	5	1.93	2.47	3.5
	10	1.95	2.25	2.61
	15	1.9	2.18	2.14

Figure 13. Charge-transfer mechanism of dye-sensitized TiO_2 under visible light illumination.

an average higher as compared to first- and second-order kinetics. However, it can be observed that the R^2 values in the case of second-order kinetics for flavonoid-sensitized TiO_2 samples are on an average greater as compared to the R^2 values for zero- and first- order kinetics. It can be concluded that resultant data suggest that zero- and second-order kinetics as the prominent reaction models in the presence of chlorophyll- and flavonoid-sensitized samples, respectively.

The rate constants of kinetics are obtained to describe the photocatalytic reaction speeds. The greater k values indicate the better photocatalytic performances. The results summarized in table 3 show that the k values in the case of all kinetic orders and also for all flavonoid-sensitized TiO_2 samples are less as compared to the corresponding k values for chlorophyll-sensitized TiO_2 samples. In a comparative study, the dimensionless parameter, $k_{\text{Chlorophyll}}/k_{\text{Flavonoid}}$ is defined to quantitatively identify the photocatalytic difference between dye-sensitized TiO_2 catalysts. The results calculated for the corresponding samples and kinetics are listed in table 4.

It is noteworthy to mention the effective roles of chlorophyll and flavonoid pigments extracted from parsley leaves and *C. longa* roots in the process of photocatalytic degradation of MB under visible light irradiation. Both chlorophyll and flavonoid pigments coated on the TiO_2 semiconductor surface can be excited under visible light and transfer photoexcited electrons from a ground level to an excited energy level. In such a situation, photoexcited electrons migrate from

the highest occupied molecular orbital to the lowest unoccupied molecular orbital (LUMO) of pigment molecules.

The presence of TiO_2 nanostructures as suitable electron acceptors alongside dye molecules can lead to the migration of photoexcited electrons from the LUMO of chlorophyll and flavonoid pigments to the conduction band (CB) of TiO_2 to participate in the process of MB photodegradation according to the basic photocatalytic mechanism illustrated in figure 13. Based on the above analysis, the mechanism of the photocatalysis can be described as the following equations [56]:

Here, P is considered as the representative of the pollutant and S is selected as a subscript sign for the word of sensitizer (chlorophyll and flavonoid). Molecules of surface sensitizers

can be excited in the presence of visible light photons (equation (14)). Upon irradiation, dye molecules absorbed on the TiO₂ surface release electrons to the CB of TiO₂ (equation (15)). In this situation, free organic pollutant molecules such as methylene blue tested in the investigation can reduce the oxidized form of the dye absorbed by the surface as outlined in equation (16). According to equation (17), free electrons available in the CB of TiO₂ can also participate to reduce molecular O₂ to superoxide radicals O₂^{•−}. Finally, the repeated generation of superoxide/hydroperoxide (O₂^{•−}/HO₂[•]) radicals leads to degraded pollutant molecules (equations (18 and 19)).

4. Conclusion

The photocatalytic performance of visible-light-responsive TiO₂ nanostructures for decolourization of MB dye has been reported in this study. Photosensitization technology has been utilized to improve the photocatalytic performance of TiO₂ nanoparticles. Two natural dyes, chlorophyll and flavonoid have been extracted from parsley leaves and *C. longa* roots to investigate their visible light harvesting capabilities and also photocatalytic performances. The data obtained from analytical techniques of XRD and SEM have been revealed that any fundamental changes in the crystal phase and also surface morphologies have not been observed after the surface sensitization process. However, the results obtained from FTIR studies have indicated that dye molecules have successfully been grafted on the surface of sensitized-TiO₂ samples. The excellent visible-light-driven photocatalytic performance of chlorophyll- and flavonoid-sensitized-TiO₂ in the degradation of aqueous MB solution has mainly been attributed to the red shift of the absorption edge and the visible light response which have been a result of photosensitization by the natural pigments. Changes in band-gap energies and the obtained onset maximal wavelength have been estimated by the diffuse reflectance UV–Vis spectra.

Chlorophyll-sensitized samples have exhibited a photocatalytic activity with a MB decolourization rate as high as 93% which has been slightly better compared to flavonoid-sensitized photocatalyst particles with a degradation rate of about 91%. It has been found that the occurrence is because of lower band-gap energy belonging to chlorophyll-sensitized samples. Adsorption equilibrium studies have been investigated by Langmuir and Freundlich isotherms. The Langmuir–Hinshelwood method has also been used to evaluate photodegradation kinetics. There are various applications, which benefit from a visible light harvesting pigment such as dye-sensitized solar cells and photocatalysts. Our results suggest that it is promising to use a flavonoid pigment extracted from *C. longa* as a suitable candidate sensitizer accompanied by or as an alternative to other common dye-sensitizers, such as chlorophyll and anthocyanin.

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References

- [1] Johar M A, Afzal R A, Alazba A A and Manzoor U 2015 *Adv. Mater. Sci. Eng.* **2015** 1
- [2] Chen J, Liao W, Jiang Y, Yu D, Zou M, Zhu H *et al* 2016 *Nanomater. Nanotechnol.* **6** 9
- [3] Rakkesh R A and Balakumar S 2013 *J. Nanosci. Nanotechnol.* **13** 370
- [4] Koseira V S, Cruz T M, Chaves E S and Tiburtius E R 2017 *J. Photochem. Photobiol. A: Chem.* **344** 184
- [5] Behzadnia A, Montazer M and Rad M M 2015 *Ultrason. Sonochem.* **27** 10
- [6] He Q, Zhang Z, Xiong J, Xiong Y and Xiao H 2008 *Opt. Mater. (Amsterdam, Neth.)* **31** 380
- [7] Ramírez-Ortega D, Meléndez A M, Acevedo-Peña P, González I and Arroyo R 2014 *Electrochim. Acta* **140** 541
- [8] Wang Q, Yun G, Bai Y, An N, Chen Y, Wang R *et al* 2014 *Int. J. Hydrog. Energy* **39** 13421
- [9] Yin J, Huang S, Jian Z, Wang Z and Zhang Y 2015 *Mater. Sci. Semicond. Process.* **34** 198
- [10] Haghighatzadeh A, Mazinani B, Asl M S and Bakhtiari L J D 2017 *Desalin. Water Treat.* **80** 156
- [11] Haghighatzadeh A, Mazinani B, Shokouhimehr M and Samiee L 2017 *Desalin. Water Treat.* **92** 145
- [12] Jiang D, Xu Y, Wu D and Sun Y J 2008 *Solid State Chem.* **181** 593
- [13] Singleton J and Rabe K M 2002 *Phys. Today* **55** 61
- [14] Khan M M, Ansari S A, Amal M I, Lee J and Cho M H 2013 *Nanoscale* **5** 4427
- [15] Chowdhury P, Gomaa H and Ray A K J S N 2013 in *Advances and achievements* N Shamim, V K Sharma (eds) (Washington: American Chemical Society) p 231
- [16] Boyer S M, Liu J, Zhang S, Ehrlich M I, McCarthy D L, Tong L *et al* 2016 *J. Photochem. Photobiol. A: Chem.* **329** 46
- [17] Pei D and Luan J 2012 *Int. J. Photoenergy* **2012** 1
- [18] Chowdhury P, Athapaththu S, Elkamel A and Ray A K 2017 *Sep. Purif. Technol.* **174** 109
- [19] Chowdhury P, Moreira J, Gomaa H and Ray A K 2012 *Ind. Eng. Chem. Res.* **51** 4523
- [20] Shang X, Li B, Zhang T, Li C and Wang X 2013 *Procedia Environ. Sci.* **18** 478
- [21] Shang X, Li B, Li C, Wang X, Zhang T, Jiang S *et al* 2013 *Dye. Pigment.* **98** 358
- [22] Yan Z, Gong W, Chen Y, Duan D, Li J, Wang W *et al* 2014 *Int. J. Photoenergy* **2014**
- [23] Phongamwong T, Donphai W, Prasitchoke P, Rameshan C, Barrabés N, Klysubun W *et al* 2017 *Catal. B Environ.* **207** 326
- [24] Jaafar S N H, Minggu L J, Arifin K, Kassim M B and Wan W R 2017 *Renew. Sust. Energ. Rev.* **78** 698
- [25] Zyoud A, Zaatar N, Saadeddin I, Helal M H, Campet G, Hakim M *et al* 2011 *Solid State Sc.* **13** 1268

- [26] Diaz-Urbe C, Vallejo W, Campos K, Solano W, Andrade J, Munoz-Acevedo A *et al* 2018 *Dye. Pigment.* **150** 370
- [27] Yan Z, Gong W, Chen Y, Duan D, Li J, Wang W *et al* 2014 *Int. J. Photoenergy* **2014** 1
- [28] Zyoud A H, Saleh F, Helal M H, Shawahna R and Hilal H S 2018 *J. Nanomater.* **2018** 1
- [29] Vignesh K, Suganthi A, Rajarajan M and Sakthivadivel R 2012 *Appl. Surf. Sci.* **258** 4592
- [30] Buddee S, Wongnawa S, Sriprang P and Sriwong C 2014 *J. Nanopart. Res.* **16** 2336
- [31] Abou-Gamra Z and Ahmed M 2016 *J. Photochem. Photobiol. B: Biol.* **160** 134
- [32] Vignesh K, Hariharan R, Rajarajan M and Suganthi A 2013 *Solid State Sci.* **21** 91
- [33] Chawla S, Uppal H, Yadav M, Bahadur N and Singh N 2017 *Ecotoxicol. Environ. Saf.* **135** 68
- [34] Yoon K H, Noh J S, Kwon C H and Muhammed M 2006 *Mater. Chem. Phys.* **95** 79
- [35] Suresh D, Nethravathi P, Rajanaika H, Nagabhushana H and Sharma S 2015 *Mater. Sci. Semicond. Process.* **31** 446
- [36] Phongamwong T, Chareonpanich M and Limtrakul J 2015 *Catal. B Environ.* **168** 114
- [37] Jia C, Zhang X and Yang P 2018 *Appl. Surf. Sci.* **430** 457
- [38] Kumar K D, Kumar G P and Reddy K S 2015 *Mater. Today: Proc.* **2** 3736
- [39] Pu S, Zhu R, Ma H, Deng D, Pei X, Qi F *et al* 2017 *Appl. Catal. B: Environ.* **218** 208
- [40] Beranek R and Kisch H 2008 *Photochem. Photobiol. Sci.* **7** 40
- [41] Pazokifard S, Mirabedini S, Esfandeh M, Mohseni M and Ranjbar Z 2012 *Surf. Interface Anal.* **44** 41
- [42] Ahmed J K, Amer Z J A and Al-Bahate M J M 2015 *Int. J. Mater. Sci. Appl.* **4** 21
- [43] Maciej Heneczkowski M K, Nowak D and Kuzniar A 2001 *Acta Pol. Pharm Drug Res.* **58** 415
- [44] Thankachan R M, Joy N, Abraham J, Kalarikkal N, Thomas S and Oluwafemi O S 2017 *Mater. Res. Bull.* **85** 131
- [45] Zhang L, Li H, Liu Y, Tian Z, Yang B, Sun Z *et al* 2014 *RSC Adv.* **4** 48703
- [46] Ali A, Mannan A, Hussain I, Hussain I and Zia M 2018 *Environ. Nanotechnol. Monit. Manage.* **9** 1
- [47] Balarak D, Mostafapour F K, Azarpira H and Joghataei A 2017 *J. Pharm. Res. Int.* **20** 1
- [48] El-Moselhy M M and Kamal S M 2018 *Groundwater Sustain. Dev.* **6** 6
- [49] Nekouei F and Nekouei S 2017 *J. Alloys Compd.* **701** 950
- [50] Gunasundari E and Kumar S 2017 *J. Ind. Eng. Chem.* **56** 129
- [51] Chamjangali M A, Bagherian G, Javid A, Boroumand S and Farzaneh N 2015 *Spectrochim. Acta: Part A* **150** 230
- [52] Wang H, Xie C, Zhang W, Cai S, Yang Z and Gui Y 2007 *J. Hazard. Mater.* **141** 645
- [53] Umh H N and Kim Y 2014 *J. Ind. Eng. Chem.* **20** 3175
- [54] Benjamin S, Vaya D, Punjabi P and Ameta S C 2011 *Arab. J. Chem.* **4** 205
- [55] Sivakumar P, Kumar G G and Renganathan S 2014 *J. Nanostruct. Chem.* **4** 107
- [56] Chatterjee D and Mahata A 2001 *Appl. Catal. B* **33** 119