

DEIVANAI SURESH KUMAR¹, KANMANI SELLAPPA¹

PHOTOCATALYTIC DEGRADATION OF REACTIVE DYES AND REAL TEXTILE COMPOSITE WASTEWATER USING TiO₂/MWCNT NANOCOMPOSITE UNDER UVA AND UVA-LED IRRADIATION. A COMPARATIVE STUDY

Nano TiO₂ and TiO₂/MWCNT nanocomposite synthesized by the sol-gel method were characterized by XRD, BET, SEM, EDAX and FTIR techniques. These nanoparticles were used for photocatalytic decolorisation and degradation of three different reactive dyes such as Reactive Orange 16 (RO 16), Reactive Yellow 145 (RY 145) and Reactive Red 195 (RR 195) and real textile composite wastewater under the UVA and UVA-LED irradiation at room temperature. The maximum color removal of 96% and COD removal of 72% were achieved after 5 h in the presence of TiO₂/MWCNT and H₂O₂ under UVA-LED irradiation. The kinetic studies obey pseudo-first order kinetics which is discussed in terms of the Langmuir–Hinshelwood kinetic model. The maximum degradation of 50% was achieved after 5 h in the presence of H₂O₂ using TiO₂/MWCNT/UVA-LED for real textile composite wastewater. This study revealed that TiO₂/MWCNT has improved the photocatalytic activity when compared to that of bare TiO₂ under similar conditions. UVA-LED could be an alternative light source for the replacement of the conventional UV light for the photocatalytic treatment of reactive dyes.

1. INTRODUCTION

Conventional treatment technologies, namely physical, chemical, biological and thermal methods have been widely applied in the treatment of domestic and industrial wastewaters for many decades. These technologies consume much energy, require high operating cost and convert the target pollutant from one form to another one, which requires further treatment for disposal [1]. To overcome these difficulties, economically viable and environmentally friendly advanced oxidation process viz., photocatalysis using semiconductor materials are an impending alternative technique for the degradation

¹Centre for Environmental Studies, Anna University, Chennai – 600025, Tamil Nadu, India, corresponding author D.S. Kumar, e-mail address: deivanai.k@gmail.com

of recalcitrant pollutants in wastewater. Generally, semiconductors such as TiO_2 , ZnO , Fe_2O_3 , CdS , ZnS and ZrO_2 with suitable band gaps may be used as photocatalysts [2]. Many studies on dye degradation using TiO_2 have been reported because of its high chemical resistance, low costs, high catalytic activity and non-toxicity [3, 4]. However, there are still many limitations that are to be met before TiO_2 become economically viable, including the challenges for prevention of recombination of photogenerated electron-hole pairs [5].

Extensive research studies have been carried out to improve the photocatalytic activity of TiO_2 by doping various metals (Fe, Pt, Ag, Cr), non-metals (N, S, C) and dye sensitisation. In recent times, a huge concern has been dedicated to synthesizing efficient catalyst with carbon nanotubes (CNTs) [6]. Amongst various materials available for modifying TiO_2 , CNTs are considered a good alternative due to their high mechanical strength, large specific surface area, good electronic properties and excellent chemical stability. Many researchers reported that the addition of CNTs increased the adsorption ability and photocatalytic activity of TiO_2 [7]. Multi-walled carbon nanotubes (MWCNTs) play a major role as a good electron acceptor for TiO_2 by aiding the separation of electron-hole pairs and modifying its optical band gap, which may enhance the photocatalytic efficiency [8].

Studies on photocatalytic degradation of pollutants were conducted with broad spectral UV light sources, namely low- and medium-pressure mercury-vapour lamps and TiO_2 as a catalyst. As the bandgap of CNTs is smaller than that of TiO_2 , the photo-excitation is high under irradiation of UV light. However, the following are the drawbacks associated with the use of UV light sources which impede the commercialization of photocatalytic technologies: (i) use of toxic mercury metal, (ii) low photonic efficiency, (iii) long exposure time for complete mineralisation of recalcitrant pollutants, (iv) need for cooling the system due to overheating lamps, (v) necessity of application of high voltage at the initial phase and (vi) short lifetime [2]. To overcome the limitations with the conventional irradiation sources, safer and energy efficient ultraviolet light emitting diodes (UV-LEDs) are now being given much attention. They possess high robustness, long lifetime, less heat production and enable one to develop compact size reactor systems [9].

At present, cutting edge technology is also available for the development of compact, cheap and eco-friendly light emitting diodes (LEDs). An LED is a semiconductor light source with a narrow spectrum that releases energy in the form of photons called electroluminescence. Modern LEDs are available in different wavelengths (infrared, visible, or near ultraviolet) depending on the composition and condition of the semiconducting materials. Many researchers reported the development of LED-based photocatalytic reactors for the degradation of dyes and organic pollutants [10]. Both homogeneous and heterogeneous catalysts are being used in UV-LED based photoreactors [11]. Jo and Tayade [12] developed a simple UV-LED photocatalytic reactor to study the degradation of dyes viz., Methylene Blue (MB), Malachite Green (MG), Direct Blue-15 (DB)

and Amaranth (AM) in the presence of impregnated TiO₂ on mosquito net. UV-LEDs are emerging as an alternative light source over conventional UV irradiation for photocatalytic processes. The advantages of UV-LED increase the flexibility in the design of a photocatalytic reactor [13]. Nowadays, the development of UV-LED based photocatalytic reactors for the degradation studies has gained more attention considering them good and environmentally friendly alternative to conventional UV mercury lamps for the degradation of the organic pollutant.

In this research, TiO₂/MWCNT nanocomposite with UVA-LED reactor system was developed for photocatalytic degradation of reactive dyes such as Reactive Yellow 145 (RY 145), Reactive Orange 16 (RO 16) and Reactive Red 195 (RR 195), and compared with conventional UVA system under batch recirculation mode. Degradation experiments were conducted at laboratory scale for understanding the system for real-time applications.

2. MATERIALS AND METHODS

Materials. Titanium tetraisopropoxide (TTIP, 97%, Sigma Aldrich), isopropanol (RANKEM), multi-walled carbon nanotubes (MWCNT, purchased from Nanoshell) and deionised water were used as received without any further purification. RO 16, RY 145 and RR 195 were procured from a textile unit in Perundurai SIPCOT, Tamil Nadu, India and used as received. The UVA (16 W, 365 nm) was purchased from Heber Scientific, Chennai. 25 UVA-LEDs (Nos. 25, 10–12 mW, 365 nm) were procured from Electroncomponents.com, India, and Bytech Electronics Co., Ltd., China, and the resistors of 100 ohms were procured from the local market. The UVA-LED is a p-n junction device made of indium gallium nitride (InGaN). The diameter of UVA-LED was 3.5 mm. The operating temperature range of UVA-LED was from –25 to 85 °C. The radiant flux was in the range of 10–12 mW at 20 mA. The chemical composition and molecular formula of the dyes selected for the present work are presented in Table 1.

Table 1

Chemical composition and maximum of absorbance of the selected reactive dyes

Dye	Molecular weight [g/mol]	Molecular formula	λ_{\max} [nm]
Reactive Red 195	1136.32	C ₃₁ H ₁₉ ClN ₇ Na ₅ O ₁₉ S ₆	516 nm
Reactive Orange 16	617.54	C ₂₀ H ₁₇ N ₃ Na ₂ O ₁₁ S ₃	414 nm
Reactive Yellow 145	1026.26	C ₂₈ H ₂₀ C ₁ N ₉ O ₁₆ S _{5.4} Na	384 nm

For details cf. www.pubchem.ncbi.nlm.nih.gov/compunds.

Textile composite wastewater used in this study was collected from a textile industry located in SIPCOT Perundurai (Tamil Nadu, India). The composite wastewater was

stored at room temperature before further use for experiments. The textile composite wastewater was analysed for some initial parameters.

Synthesis of nano TiO₂. Nano-sized titanium dioxide was prepared by the sol-gel method [14]. TTIP was mixed with isopropanol in the volume ratio of 1:7 and the solution was kept under constant stirring for 10 min. 10 cm³ of deionized water was added to the above solution and stirred continuously for 2 h. The resulting yellowish gel was then dried at 80 °C for 4 h and calcination was carried out at 450 °C for 2 h to obtain TiO₂ nanopowders.

Synthesis of TiO₂/MWCNT nanocomposite. TiO₂/MWCNT nanocomposite was synthesized by the sol-gel method [5, 8]. A known amount of MWCNT was added to ethanol and distilled water and treated ultrasonically for 10 min to achieve homogeneity. A mixture of TTIP and acetic acid were subjected to stirring for 1 h to form a clear solution. Ammonia solution was then added slowly to the above solution to form a uniform TiO₂ glazing on the surface of MWCNTs. Then the solution was dried in the hot air oven at 90 °C. Thus the prepared TiO₂/MWCNT nanocomposite was calcinated using muffle furnace at 350 °C for 3 h.

Textile wastewater characteristics. The textile composite wastewater was characterised for the following parameters color absorbance, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS) and total dissolved solids (TDS). The characteristics of textile industry wastewater (IWW) are given in Table 2 which reveals that there is an insignificant extent of variation from sample to sample. In most cases, BOD/COD ratio of the composite textile wastewater was in the range of 0.08–0.13 that implies that the wastewater contained a large amount of non-biodegradable organic matter.

Table 2

Characteristics of textile industry wastewater

Parameter	IWW 1	IWW 2	IWW 3
Absorbance, m ⁻¹			
at 436 nm	58.3	79.4	63.2
at 525 nm	11.5	60.5	32.6
at 620 nm	4.6	8.6	19.2
pH	9.2	9.4	8.7
TDS, mg/dm ³	6240	6720	6440
TSS, mg/dm ³	210	290	280
COD, mg/dm ³	1520	1040	760
BOD ₃ , mg/dm ³	130	102	98
BOD ₃ /COD	0.08	0.09	0.13

Measurements of absorbance were carried out at three wavelengths of 436 nm, 525 nm and 620 nm by the German standard method DIN 38 404 [15]. The color absorbance, m^{-1} , was calculated as:

$$\text{Color absorbance} = \frac{\text{absorbance} \times \text{dilution factor}}{\text{path length}} \quad (1)$$

Characterization of the catalysts. Nano TiO_2 and $\text{TiO}_2/\text{MWCNT}$ nanocomposite were characterized by X-ray diffraction (XRD) technique with a Bruker-D8 advanced diffractometer using Ni-filtered CuK_α radiation ($\lambda = 1.54439 \text{ \AA}$) in the range of $5\text{--}90^\circ$. The morphology and elemental composition were analysed by the scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX, C. Zeiss EVO 18 microscope (at an accelerating voltage of 15 keV). The band gap of the photocatalysts was determined with a Shimadzu UV-2450 UV-Vis spectrometer in the spectral range of 200–800 nm. The functional group was identified by the Fourier transform infrared spectroscopy (FTIR) using an ABB MB 3000 model FTIR spectrometer. The surface area using conventional BET model from the pore volume, and pore size were determined using a Micromeritics ASAP 2020 porosimeter.

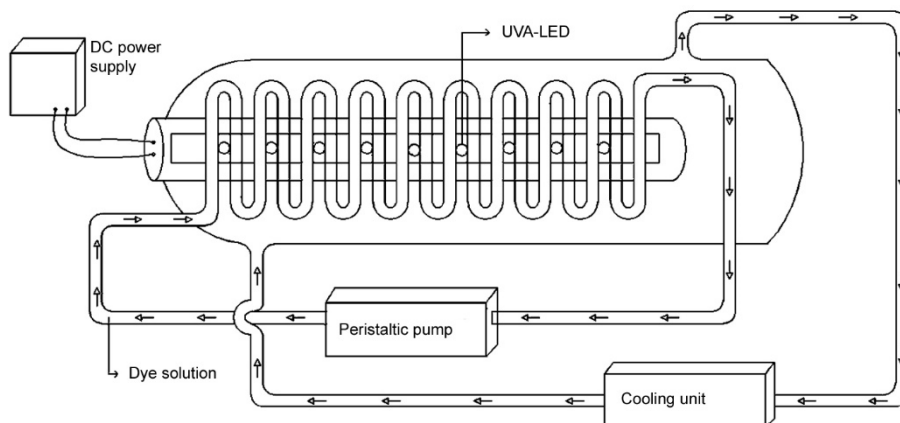


Fig. 1. Schematic representation of the UVA and UVA-LED system

UVA and UVA-LED based photocatalytic reactor. Figure 1 represents the schematic diagram of the photocatalytic reactor. It consists of a spiral glass coil made from a glass tube 150 cm long with the inner diameter of 1.8 cm. The spiral glass coil 35 cm long is placed inside a glass tube with an inner diameter of 10 cm with an inlet and outlet ports through which cooling unit is connected with recirculating water to remove the heat generated by the conventional UV lamp. The spiral glass tube is connected with the inlet and outlet port using silicon rubber tubes for the recirculation of the dye solution using

a peristaltic pump. The recirculation arrangement prevents the settling of photocatalyst in the tube. A quartz tube 25 cm long is kept in the centre of the spiral coil so as to place the UVA-LED arrangement and conventional UVA lamp for the irradiation reaction. The UV LEDs were connected in series with resistors in the PVC flat channel to the length of 20 cm and the same was placed inside the quartz tube and inserted into the centre of the spiral tube. The lamp was placed in such a way that the spiral tube with the dye solution was coiled over the quartz tube with UV-LED lamp. In the outer zone, cooling water was recirculated using a cooling unit to maintain room temperature. All the experiments were carried out under the atmospheric condition and lasted for 5 h. Dark experiments were conducted to investigate the performance of the photocatalysts. The simulated textile dye solution of 400 cm³ was mixed with a known amount of catalyst and purged into the reactor. Samples were drawn at regular intervals every 30 min and centrifuged at 3500 rpm for 30 min to separate the photocatalysts from suspension, prior to analysis. Degradation by-products were determined by the gas chromatography (GC).

The experiments were carried using nano bare TiO₂, bare MWCNT and TiO₂/MWCNT nanocomposite under UVA and UVA-LED irradiation. The operating parameters affecting the decolorisation efficiency were as follows: pH (3, 5, 7, 9 and 11), catalyst dosage (1, 2, 3, 4 and 5 mg/dm³), initial concentration of dye (10, 20, 30, 40 and 50 mg/dm³) and oxidant (H₂O₂) concentration (100, 200, 300 and 400 mg/dm³). A similar set of lab-scale experiments were conducted for the real textile composite wastewater.

The decolorisation efficiency was calculated from

$$\text{Decolorisation efficiency} = \frac{A_0 - A'}{A_0} \times 100\% \quad (2)$$

where, A_0 and A' are the absorbances of the reactive dye solutions at the initial and final sampling times for every 30 min, respectively.

The degradation efficiency was calculated from:

$$\text{Degradation efficiency} = \frac{C_0 - C'}{C_0} \times 100\% \quad (3)$$

where, C_0 and C' are the COD values of the reactive dye solutions at initial and final sampling times for every 30 min, respectively.

GC-MS analyses. The intermediates formed were identified using a gas chromatography-mass spectrometry (GC/MS) system. The GC (Agilent Technologies) was equipped with a DB-1MS capillary column. The initial temperature of the GC column was 50 °C held for 2 min, ramp at 80 °C/min till it reached 280 °C/min held for 5 min. The

injector temperature was 250 °C with helium serving as the carrier gas at the flow rate of 1 cm³/min. The intermediate products were identified by comparing the GC/MS spectra patterns with those of standard mass spectra in the National Institute of Standards and Technology (NIST) library. The samples for GC/MS analyses were prepared by extraction of a part (20 cm³) of the irradiated solution after centrifuging the solution for the removal of the catalyst with ethyl acetate (20 cm³). The extracted sample was then analysed by GC/MS.

3. RESULTS AND DISCUSSION

3.1. CHARACTERISATION OF NANO TiO₂ AND TiO₂/MWCNT NANOCOMPOSITES

Figure 2 illustrates the XRD spectra of nano TiO₂, MWCNT and TiO₂/MWCNT nanocomposites. The photocatalytic property of the catalyst greatly depends on the crystal structure and crystal phase [16].

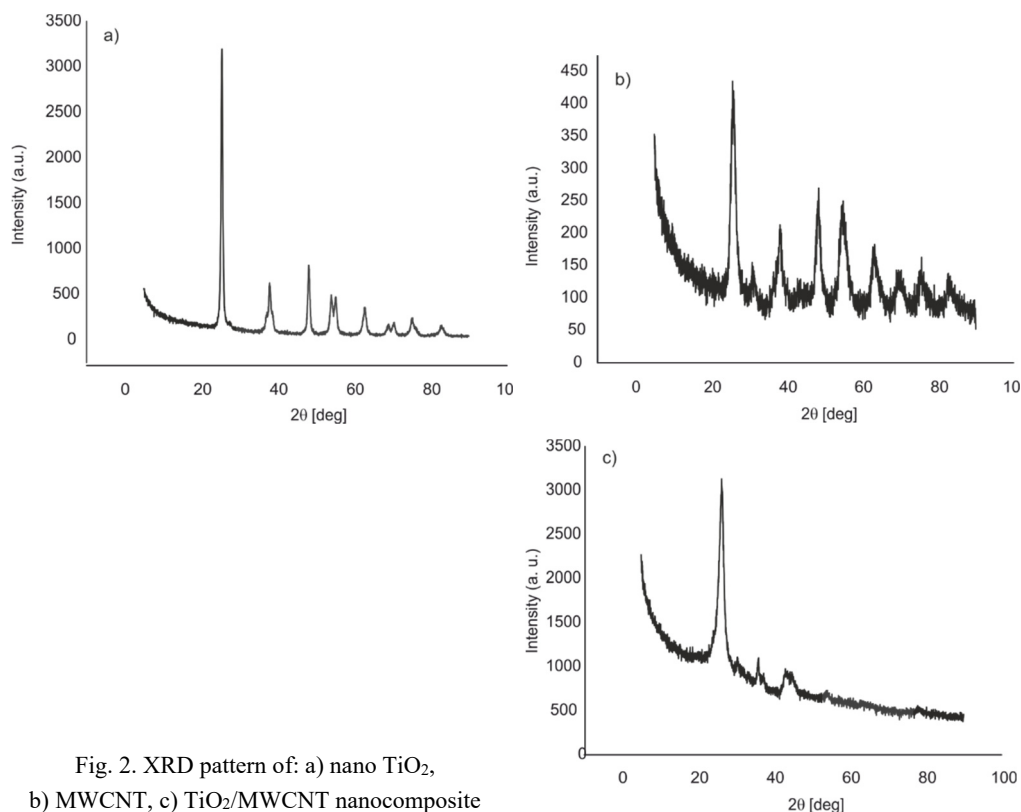


Fig. 2. XRD pattern of: a) nano TiO₂,
b) MWCNT, c) TiO₂/MWCNT nanocomposite

The crystallite sizes of the photocatalyst crystals were determined using the Debye–Scherrer’s formula given by the equation $D = K\lambda/(\beta\cos\theta)$, where D denotes the size of the crystal, λ – the wavelength of the X-ray radiation (0.15406 nm) for $\text{CuK}\alpha$, K is taken as 0.9 and β is the line width at its half-maximum height. The crystalline size of nano TiO_2 ($2\theta = 25.4201^\circ$), MWCNT ($2\theta = 26.2055^\circ$) and $\text{TiO}_2/\text{MWCNT}$ ($2\theta = 25.6933^\circ$) nanocomposites were found to be 14.60 nm, 16.80 nm and 15.03 nm respectively. MWCNT plays an auxiliary role in the development of the crystalline phase [8]. The broad peaks show the crystalline nature of the particles. Smaller the crystalline size, higher the photocatalytic activity is.

Table 3

BET analysis. Surface area, pore volume and pore size of TiO_2 , MWCNT and $\text{TiO}_2/\text{MWCNT}$

Photocatalyst	Surface area [m^2/g]	Pore volume [cm^3/g]	Pore size [\AA]
TiO_2	163	0.033	76.17
MWCNT	105	0.152	85.91
$\text{TiO}_2/\text{MWCNT}$	289	0.126	40.70

Table 3 presents the surface area, pore volume and pore size of three nanophotocatalysts. It was observed that smaller the crystalline size, larger the surface area is. The nitrogen sorption measurements revealed the surface area and porosity of the TiO_2 , MWCNTs and $\text{TiO}_2/\text{MWCNT}$ nanocomposite. The integration of nano TiO_2 on the surface of the MWCNTs increased the surface area to $289 \text{ m}^2/\text{g}$, which enhanced the pollutant adsorption capability. Since carbon-based photocatalyst increases the surface properties, MWCNTs may be considered as a support and robust material for improving the photocatalytic activity of TiO_2 . The surface area of the $\text{TiO}_2/\text{MWCNT}$ is higher than the bare TiO_2 and MWCNT which may exhibit higher photocatalytic activity. The pore sizes and pore volumes of the MWCNT are higher than those of TiO_2 and $\text{TiO}_2/\text{MWCNT}$.

In Figure 3, the SEM micrographs of TiO_2 , MWCNTs and $\text{TiO}_2/\text{MWCNT}$ s are shown. They confirm a successful preparation of photocatalysts by the sol-gel method. The $\text{TiO}_2/\text{MWCNT}$ s image shows that the cluster of TiO_2 nanoparticles is uniformly decorated on the surface of the MWCNTs due to the presence of copious hydroxyl groups and carboxyl groups [17]. TiO_2 nanoparticles are spherically agglomerated due to decomposition shrinkage and densification phenomena [18]. Figure 4 presents the EDX spectrum of $\text{TiO}_2/\text{MWCNT}$ s nanocomposite, which clearly reveals the presence of Ti, O and C atoms and confirms the successful preparation of photocatalysts.

UV-Vis absorption spectral analysis was carried out to determine the optical property of the prepared TiO_2 and $\text{TiO}_2/\text{MWCNT}$ s composite which is shown in Fig. 5. The

absorbance of TiO_2 and $\text{TiO}_2/\text{MWCNTs}$ is measured to be 325 nm and 360 nm respectively. Addition of MWCNTs could enhance the light utilization efficiency; as MWCNT act as a light sensitizer, which injects the electrons into the conduction band of TiO_2 [19]. Presence of MWCNTs in the TiO_2 matrix does not shift to visible light range perhaps due to the assimilation of a small amount of MWCNTs [20].

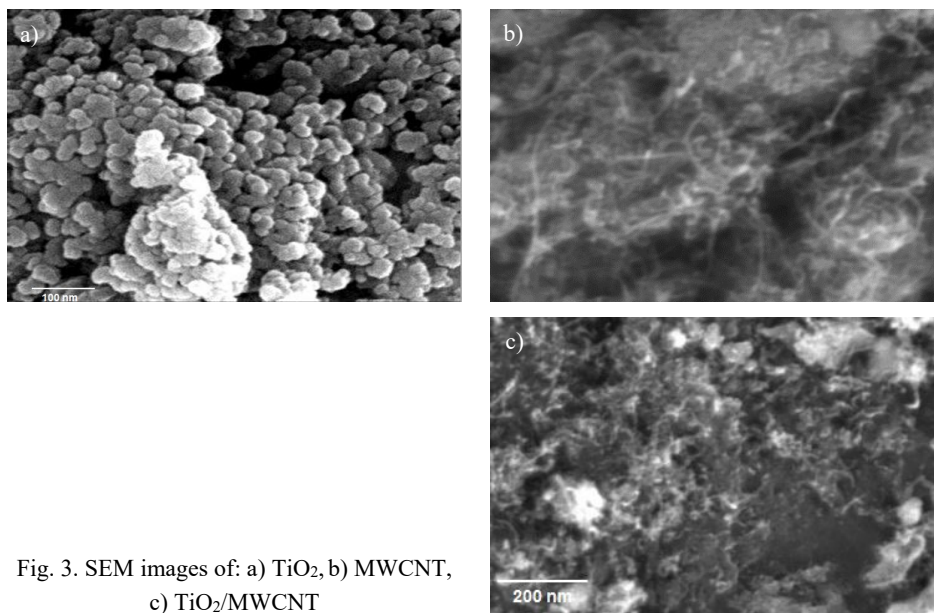


Fig. 3. SEM images of: a) TiO_2 , b) MWCNT, c) $\text{TiO}_2/\text{MWCNT}$

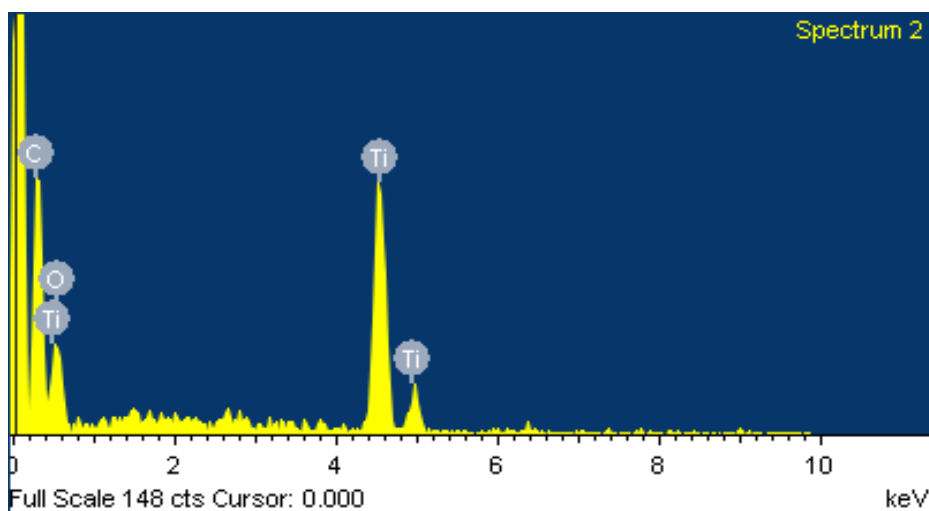


Fig. 4. EDX spectrum of $\text{TiO}_2/\text{MWCNTs}$ nanocomposites

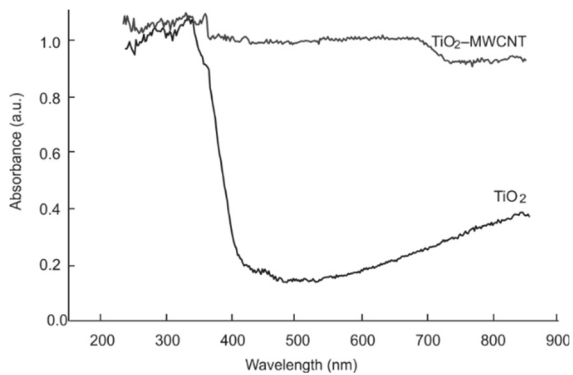


Fig. 5. UV-Vis spectra of $\text{TiO}_2/\text{MWCNT}$ composite and TiO_2

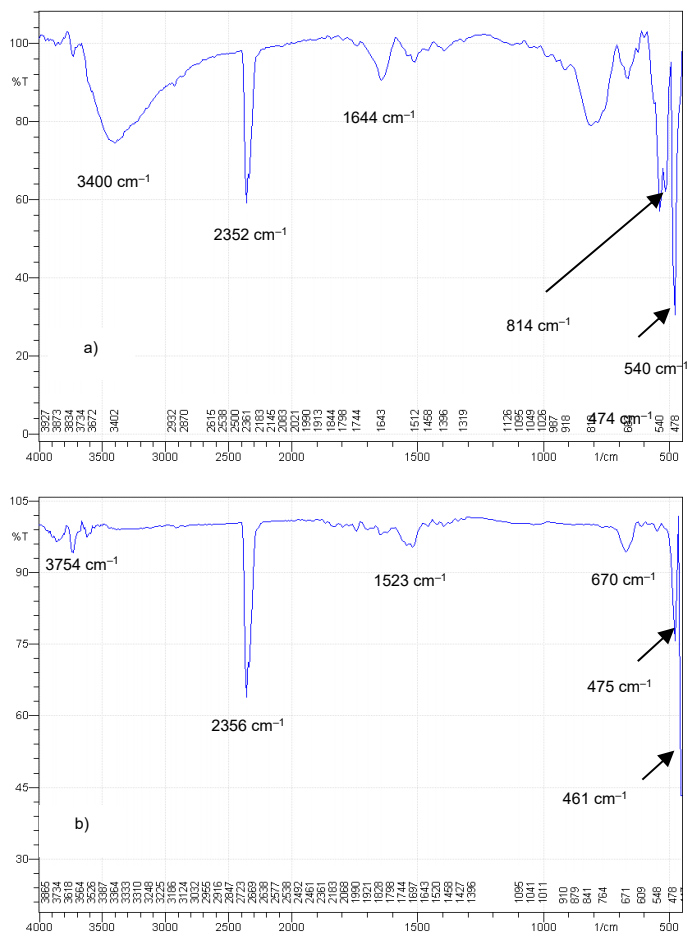


Fig. 6. FTIR spectra of a) TiO_2 , and b) $\text{TiO}_2/\text{MWCNT}$

FTIR spectra of TiO_2 and $\text{TiO}_2/\text{MWCNT}$ nanocomposite are shown in Fig. 6. For TiO_2 spectrum, the absorption peaks at 3400 cm^{-1} and 1644 cm^{-1} correspond to hydroxyl and carbonyl functional groups, respectively. The peak observed at 2352 cm^{-1} in the spectrum of TiO_2 , and at 2356 cm^{-1} in that of $\text{TiO}_2/\text{MWCNT}$ corresponds to CO_2 symmetric stretching mode [21]. In the region of $400\text{--}100\text{ cm}^{-1}$ a characteristic absorption peak of anatase TiO_2 is observed. The peak at 540 cm^{-1} represents the Ti–O–Ti stretching vibration [22].

3.2. PHOTOCATALYTIC EXPERIMENTS

pH plays a significant role in the decolorisation of reactive dyes. Its effect is illustrated in Fig. 7. An increase in pH leads to increase in decolorisation efficiency for all the three reactive dyes under UVA and UVA-LED irradiation.

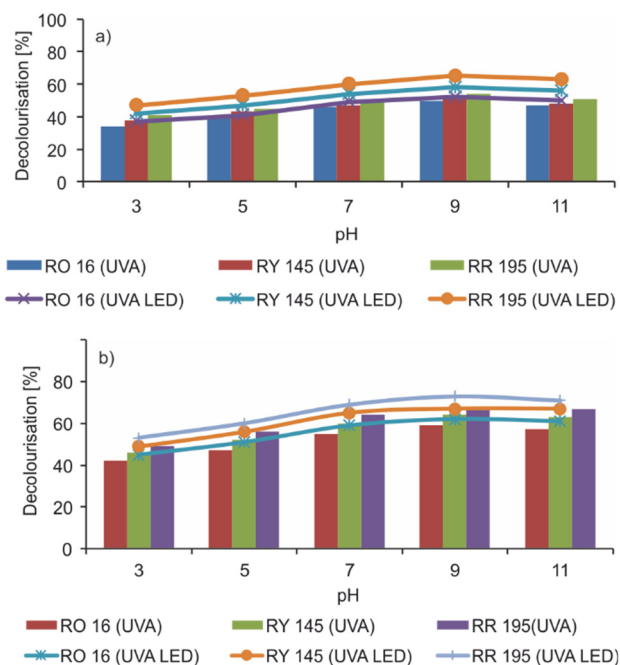


Fig. 7. Effects of pH on: a) UVA/ TiO_2 and UVA-LED/ TiO_2 as well as on b) UVA/ $\text{TiO}_2/\text{MWCNT}$ and UVA-LED/ $\text{TiO}_2/\text{MWCNT}$

A similar result was observed by Giwa et al. [23]. The decrease in decolorisation efficiency in acidic solution may be due to TiO_2 agglomeration resulting in a reduction of dye adsorption and light photon absorption. Also, Giwa et al. [23] reported that the reduction in the electrophilic mechanism is due to the interaction between excess H^+ ions and azo groups thereby retarding the reactivity of hydroxyl radicals at an acidic

solution. Many researchers observed that the generation of hydroxyl radicals are considered to be predominant at neutral and alkaline conditions rather than at acidic solutions; this may be due to diminishing the adsorption of dye in the acidic solution. Upon the increase in pH from 7 to 9, the decolorisation efficiency increases. At pH 9, the maximum decolorisation efficiency was attained under the synergistic effect of UVA-LED/TiO₂/MWCNT process when compared with the UVA/TiO₂ and UVA-LED/TiO₂. This may be due to the reason that carbon nanotubes possess high electrical conductivity and high electron storage capacity. Also, MWCNTs helps in narrowing the band gap of TiO₂ and acts as an adsorbent, support and photogenerated transfer station. Further increase in pH decreases the decolorisation efficiency, since more adsorption of the dye on the surface of a catalyst results in inhibition of penetration of light into the dye solution. The UVA-LED/TiO₂/MWCNT achieves maximum efficiency of 94% when compared to conventional UVA of 89% of decolorisation for RR 195. Hence, UVA-LED may be a good alternative source for conventional UV sources and can be utilized for the development of photocatalytic reactor model for removal of hazardous dye from wastewater.

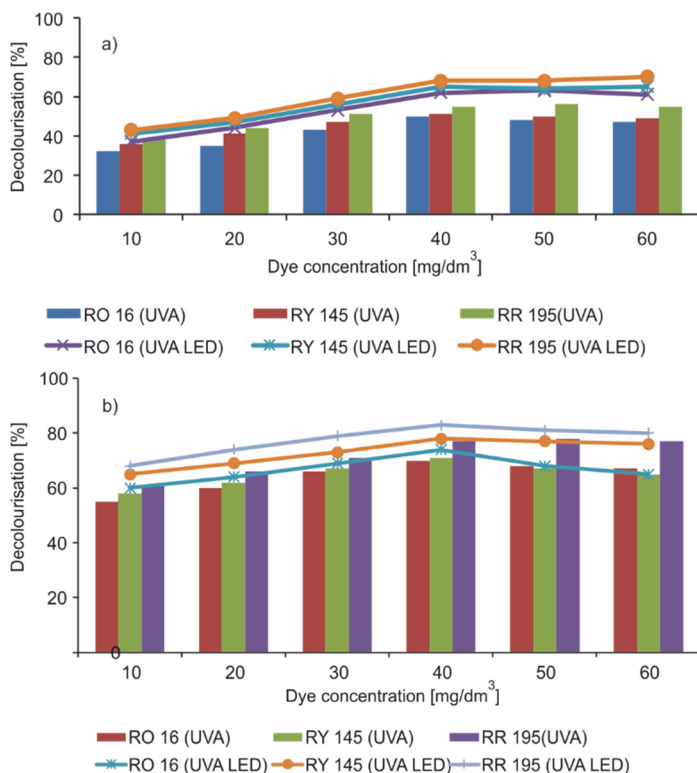


Fig. 8. Effects of dye concentration: a) UVA/TiO₂ and UVA-LED/TiO₂ and b) UVA/TiO₂/MWCNT and UVA-LED/TiO₂/MWCNT

The effect of initial dye concentration on the decolorisation of three reactive dyes is illustrated in Fig. 8. Upon an increase in dye concentration from 10 mg/dm^3 to 40 mg/dm^3 , the decolorisation efficiency increases and further increase results in a decrease of decolorisation efficiency. Increase in initial dye concentration increases the amount of dye adsorbed on the catalyst surface. Hence, only fewer photons will reach at the catalyst surface which results in a decrease of hydroxyl radical ($\bullet\text{OH}$) and superoxide ($\bullet\text{O}_2^-$) radicals thereby decreasing the photocatalytic activity [3]. The highly colored solution is less transparent to the light and the amount of unabsorbed dye molecules increases leading to decrease in penetration of light into the solution and onto the surface of catalyst which in turn reduces the $\bullet\text{OH}$ formation [24]. Since the irradiation time and the catalyst dosage are constant, the amount of $\bullet\text{OH}$ radicals formed on the catalyst surface is also constant. Hence the optimisation of dye concentration is important, as it increases, the catalyst dosage should increase. The maximum decolorisation efficiency of 83% was attained in the presence of $\text{TiO}_2/\text{MWCNT}$ at the dye concentration of 40 mg/dm^3 due to the formation of the Ti–C and Ti–O–C bonds between titania and CNTs and to the formation of the hydroxyl and superoxide radicals [25]. Also, the addition of MWCNTs to photocatalyst increases the interface between the dye molecules and the photocatalyst, increases the surface area and also reduces aggregation of the titania nanoparticles [26].

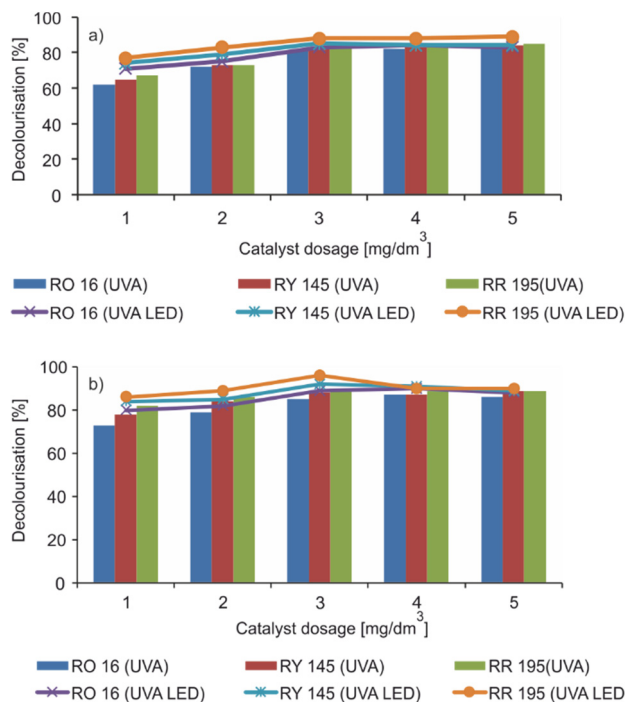


Fig. 9. Effect of catalyst dosage (a) UVA/TiO₂ and UVA-LED/TiO₂ and (b) UVA/TiO₂/MWCNT and UVA-LED/TiO₂/MWCNT

It is important to study the effect of catalyst dosage in order to optimise the amount of catalyst to be added, thereby reducing the addition of unnecessary excess catalyst and to ensure total absorption of light photons for attaining efficient decolorisation. To study the effect of catalyst dosage on the rate of decolorisation, the catalyst dosage was varied while other variables were kept constant. The results are shown in Fig. 9. In the absence of the photocatalyst, the photodegradation of the reactive dyes under UVA and UVA-LED irradiation was very slow and almost no degradation of dye was observed even after 90 min. However, when the catalyst TiO_2 and $\text{TiO}_2/\text{MWCNT}$ composite was added to the dye solution, the decolorisation of dye took place. Upon the increase in $\text{TiO}_2/\text{MWCNT}$ catalyst dosage from 1 to 3 mg/dm^3 , the decolorisation efficiency attains a maximum and a further increase in the catalyst dosage, decreases the dye decolorisation efficiency. $\text{TiO}_2/\text{MWCNT}$ exhibits high photocatalytic performance and UVA-LED/ $\text{TiO}_2/\text{MWCNT}$ shows a synergistic effect in attaining the maximum decolorisation efficiency of 96% with the catalyst dosage equal to 3 mg/dm^3 . Further increase in catalyst dosage, decreases the decolorisation efficiency as the solution becomes turbid and thereby reducing the interaction between the catalyst and the light source. After addition more catalyst to the solution, the UVA-LED energy was not sufficient to irradiate the catalyst and hence high amount of catalyst reduced the photonic efficiency. Therefore, the rate of dye decolorisation depends on the amount of catalyst added to the solution. Also, Kaur et al. [27] reported that the excess amount of catalyst leads to opacity which may be a shield to impede the light penetration. The $\text{TiO}_2/\text{MWCNT}$ demonstrated a considerable higher photocatalytic activity than pure TiO_2 under UVA-LED light irradiation. This effect may be due to that carbon particles absorb UV light and generate photoinduced electrons (e^-) into the conduction band of the TiO_2 which increase the extent of electrons in the solution [28]. The combination of TiO_2 with carbon nanotubes exhibits high photocatalytic efficiency both under UVA and UVA-LED irradiation. This may be due to the presence of MWCNT which stimulates the process even at low concentrations and it acts as an electron sink reducing the probability of electron recombination [29]. Hence the decrease in decolorisation at higher catalyst dosage may be due to the collision of excited electrons in the conduction band with the holes in the valence band. All the above reasons contribute to the escalation of the photocatalytic activity of the $\text{TiO}_2/\text{MWCNT}$ process [19].

To study the effect of oxidant concentration on the decolorisation of the reactive dyes, the oxidant concentration was varied while the other variables were kept constant. In Figure 10, the effect of oxidant concentration using TiO_2 and $\text{TiO}_2/\text{MWCNT}$ under the UVA and UVA-LED irradiation is shown. Under UVA-LED irradiation in the presence of $\text{TiO}_2/\text{MWCNT}$ catalyst, the decolorisation efficiency was increased from 75%, 80% and 86% to 81%, 86% and 88% for RO 16, RY 145 and RR 195 respectively when the oxidant concentration increased from 100 to 200 mg/dm^3 . Further increase in oxidant concentration results in a decrease of decolorisation efficiency. Alahiane et al. [24] reported that the irradiation of TiO_2 with UV under the presence of H_2O_2 results in

a synergistic effect which increases over than 200 mg/dm³ decreases the decolorisation efficiency due to the scavenging effect. H₂O₂ acts as a strong oxidant due to the formation of hydroxyl radicals and also as electron scavengers as excess adsorption of H₂O₂ on catalyst surface hinders the catalytic activity. The UVA-LED/TiO₂/MWCNT shows the synergistic effect and maximum decolorisation efficiency of 96% was achieved after 5 h. Similar results were reported by Mahmoodi [30], that the UV/CNT/*n*-TiO₂/H₂O₂ was the most efficient method to degrade dyes because of the synergistic effect of CNT/H₂O₂ on *n*-TiO₂ photocatalytic activity.

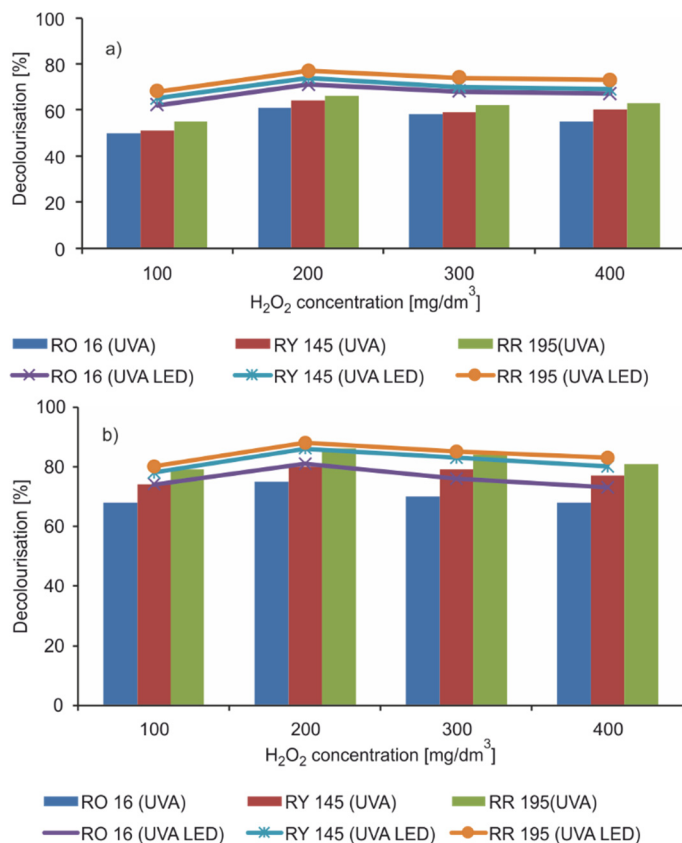


Fig. 10. Effects of oxidant concentration: a) UVA/TiO₂ and UVA-LED/TiO₂ and b) UVA/TiO₂/MWCNT and UVA-LED/TiO₂/MWCNT

3.3. DEGRADATION KINETICS

Based on the kinetic studies of the degradation of the reactive dyes, the photocatalytic degradation efficiency could be related to the Langmuir–Hinshelwood model:

$$r = -\frac{dC}{dt} = \frac{k_r k_a C}{1 + k_a C} \quad (4)$$

where k_r and k_a represent the rate constant and adsorption constant, respectively. The simplified form of the above equation to an apparent first order equation is as follows:

$$\ln \frac{C}{C_0} = k_r k_a t = -kt \quad (5)$$

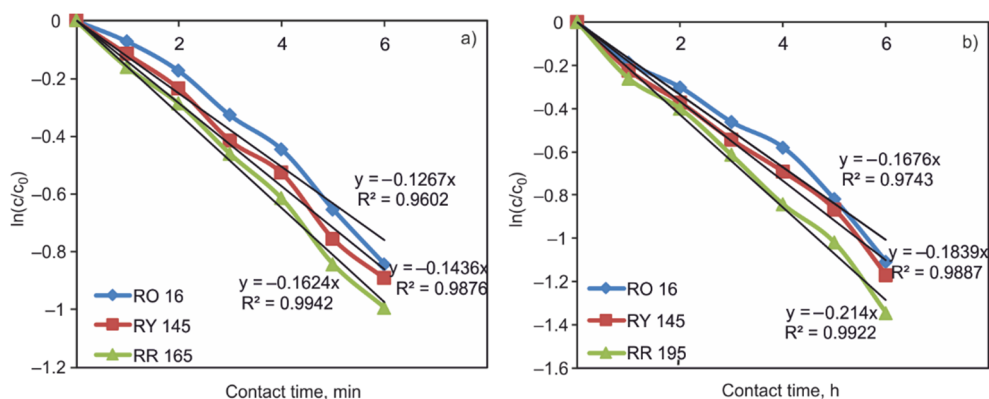


Fig. 11. Effects of contact time UVA/TiO₂/MWCNT and UVA-LED/TiO₂/MWCNT

Plots of $\ln(C/C_0)$ vs. t for degradation are shown in Fig. 11. The plots represent linear time dependences of the dye concentration. The values of k and the linear regression coefficients (R^2) of photodegradation of reactive dyes under optimised conditions are given in Table 4.

Table 4

First order constants (k) and linear regression coefficients (R^2) for UVA/TiO₂/MWCNT and UVA-LED/TiO₂/MWCNT

Dye	UVA		UVA-LED	
	k [min ⁻¹]	R^2	k [min ⁻¹]	R^2
Reactive Red 195	0.126	0.960	0.167	0.974
Reactive Orange 16	0.143	0.987	0.183	0.988
Reactive Yellow 145	0.162	0.994	0.214	0.992

3.4. IDENTIFICATION OF INTERMEDIATES

The GC-MS peaks confirmed the presence of benzene 1-chloro-4-trifluoromethyl, diethyl phthalate, naphthalene, Bis (2-ethylhexyl) phthalate, toluene, benzyl ethyl ketone, naphthionic acid, 1-amino-2-naphthol as intermediates in the photocatalysis of

RO 16, RY 145 and RR 195. These intermediates can be mineralised further to form CO_2 and H_2O .

3.5. DEGRADATION OF REACTIVE DYES USING UVA AND UVA-LED

A photocatalytic reactor based on the combined use of TiO_2 , $\text{TiO}_2/\text{MWCNT}$ photocatalyst and UVA-LED light irradiation was employed for the degradation of reactive dyes. The comparison was made with the earlier studies based on conventional UVA and UVA-LED light as a source for photocatalytic degradation of dyes. Table 5 presents the comparison of the results with the literature data for different lamps such as solar light UV, UV LED sources with the catalyst of $\text{TiO}_2/\text{MWCNT}$ and TiO_2 . It was observed that the maximum degradation efficiency of 72% was achieved because of the synergistic effect of UVA-LED/ $\text{TiO}_2/\text{MWCNT}$. Many researchers reported the studies in photocatalytic degradation of dyes using UVA-LED as a light source. From this comparison, it resulted that the UVA-LED light source may be a good alternative as a source for light irradiation for photocatalytic wastewater treatment.

Table 5

Comparison of the results with the literature data

Pollutant, its concentration	Source of light	Volume [cm^3]	Time [min]	Degradation [%]	Ref.
Methylene Blue (MB), 10 mg/dm^3	UV, 125 W	100	<100	76	[5]
Erichrome Black T (EBT) Eosin Blue Shade (EBS), 20 mg/dm^3	Solar light, 450 W	100	240	80.4	[18]
Reactive dyes, 40 mg/dm^3	UVA, 365 nm, 16 W	400	300	61	This work
	UVA-LED, 365 nm, 10–12 mW			72	

3.6. DEGRADATION OF REAL TEXTILE COMPOSITE WASTEWATER USING UVA AND UVA-LED

The degradation experiments for textile composite wastewater were conducted in the lab scale so as to evaluate the system for the real-time application. The optimisation study to optimise the catalyst dosage, contact time and oxidant concentration was carried out using the composite wastewater at room temperature. At optimised conditions viz., TiO_2 and $\text{TiO}_2/\text{MWCNT}$ dosage of 3 mg/dm^3 and H_2O_2 concentration 200 mg/dm^3 , the maximum decolorisation efficiency of 60% and 71% at 436 nm using TiO_2 -UVA LED and $\text{TiO}_2/\text{MWCNT}$ -UVA LED was achieved after 5 h of irradiation, respectively. Khan et al. [30] reported that the real textile wastewater was effectively decolorised with titanium dioxide under pH of 9 and the maximum decolorisation was achieved within 150 min of irradiation time. The degradation of 40% and 50% at 436 nm was

achieved using TiO₂-UVA LED and TiO₂/MWCNT-UVA LED in the presence of H₂O₂ after 5 h, respectively.

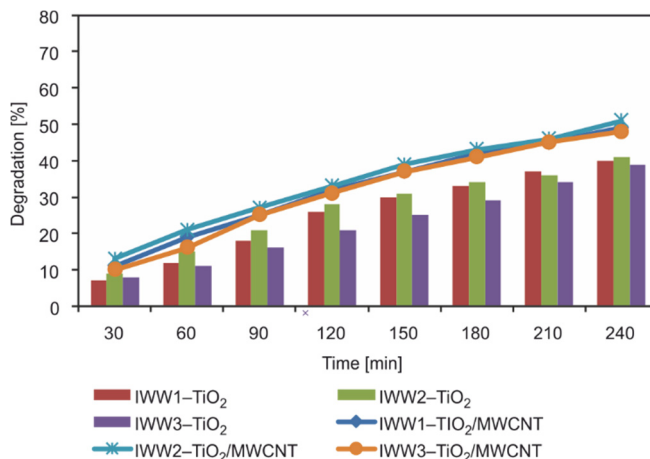


Fig. 12. Degradation of real textile dye waste water using UVA LED; pH 9, catalyst dosage 0.3 g/100 cm³, H₂O₂ dosage 200 mg/dm³

Figure 12 presents the degradation efficiency of real textile composite wastewater using TiO₂-UVA LED and TiO₂/MWCNT-UVA LED. The maximum degradation of the textile wastewater with hydrogen peroxide under UV irradiation is more efficient due to the formation of two •OH which contributes to the reaction of hydroxyl radical with the contaminants [30].

3.7. PHOTOCATALYTIC MECHANISM OF TiO₂/MWCNT FOR DYE DEGRADATION

TiO₂/MWCNT nanocomposite exhibited high photocatalytic activity for the degradation of the reactive dyes. A possible mechanism on the synergistic effect of the TiO₂/MWCNT nanocomposite on the enhancement of the photocatalytic degradation of the reactive dyes is proposed as shown in Fig. 13.

Normally, when the catalyst is irradiated by the light source having equal or higher photonic energy than the band gap energy (E_b), electrons (e^-) are excited from the valence band (V_B) to the conduction band (C_B) creating an electron vacancy or holes (h^+) in the valence band (V_B) (Eq. (6)). These holes have a tendency to quickly recombine without participating in the photo-degradation of the dyes resulting in low efficiency. However, when the nanocomposite (TiO₂/MWCNT) is applied, strong bonding between the CNTs and metal oxide particles (TiO₂) results in the formation of barrier junction wherein reducing the electron-hole recombination by the positioning of an electron into the nanotubes. MWCNTs act as photo-generated electron acceptors to promote interfacial electron transfer process and TiO₂ as an electron donor under UV light irradiation.

Under UV irradiation, the electron (e^-) in the valence band ($\text{CNT}^{e-(\text{CB})}$) is excited to the conduction band and a hole ($\text{TiO}_2^{h+(\text{VB})}$) is formed.

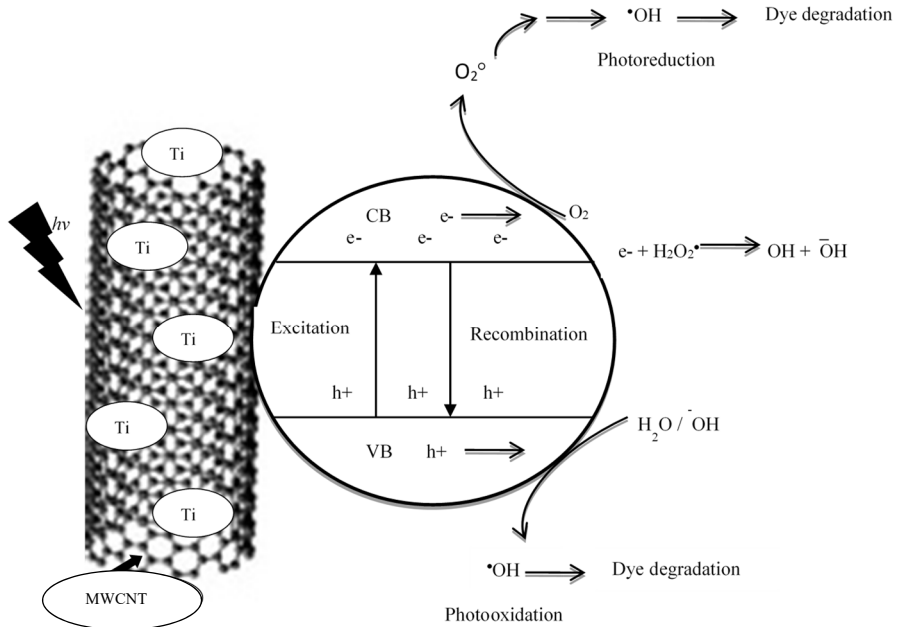
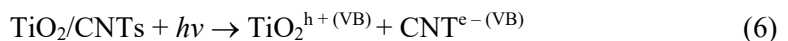
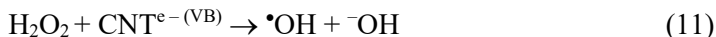


Fig. 13. Schematic representation of the proposed photocatalytic mechanism for dye degradation using MWCNTs/TiO₂ under UV irradiation

Electrons (e^-) in the conduction band may react with O_2 which results in the formation of highly reactive superoxide ($\text{O}_2^{\circ-}$) radical ions which contribute to the direct attack of dyes for complete degradation. The superoxide ($\text{O}_2^{\circ-}$) radicals combine with H^+ from water molecules which results in the formation of hydroperoxyl ($^{\circ}\text{OOH}$) radicals. These radicals combine with H^+ ions and electrons of the valence band forming hydroxyl radicals ($^{\circ}\text{OH}$) and oxidised hydroxyl groups (^-OH). ^-OH anions recombine with holes in the valence band and form hydroxyl radicals ($^{\circ}\text{OH}$). From the above, it is inferred that photoreduction and photo-oxidation reaction takes place for the formation of hydroxyl radicals ($^{\circ}\text{OH}$) which involves in the dye degradation. The proposed mechanism is represented in the following equations.





4. CONCLUSION

The effect of TiO_2 and $\text{TiO}_2/\text{MWCNT}$ on reactive dyes under UVA and UVA-LED irradiation has been examined for effective photocatalytic activity. The characterization results confirmed the assimilation of nano TiO_2 on the surface of MWCNT and clearly revealed a successful preparation of photocatalysts. The photocatalytic degradation of dyes using $\text{TiO}_2/\text{MWCNT}$ is higher than that of bare TiO_2 due to adsorption of dye particles on the porous surface of MWCNT and fast electron transfer between MWCNT and TiO_2 . The rate of degradation increased in the order $\text{RR 195} > \text{RY 145} > \text{RO 16}$. The kinetic studies revealed that the photocatalytic degradation of reactive dyes followed the Langmuir–Hinshelwood kinetics model. The photocatalytic degradation of dyes was confirmed through the GC-MS analysis. From the experimental data, it was observed that the decolorisation efficiency in the range of 89–96% for three reactive dyes was achieved at optimum conditions under UVA-LED/ $\text{TiO}_2/\text{MWCNT}$ system. In the study on degradation of real textile composite wastewater the COD removal of 50% was obtained which is due to the synergistic effect using UVA-LED- $\text{TiO}_2/\text{MWCNT}$ in the presence of H_2O_2 . It is evident that the process UVA-LED/ $\text{TiO}_2/\text{MWCNT}$ may be an alternative technique for the textile dye decolorisation and degradation which could be applied for real-time applications with proper designing and by conducting pilot scale studies.

REFERENCES

- [1] NATARAJAN T.S., NATARAJAN K., BAJAJ H.C., TAYADE R.J., *Energy efficient UV-LED source and TiO_2 nanotube array-based reactor for photocatalytic application*, Ind. Eng. Chem. Res., 2011, 50, 7753.
- [2] TAYADE R.J., NATARAJAN T.S., BAJAJ H.C., *Photocatalytic degradation of methylene blue dye using ultraviolet light emitting diodes*, Ind. Eng. Chem. Res., 2009, 48, 10262.
- [3] NATARAJAN K., NATARAJAN T.S., BAJAJ H.C., TAYADE R.J., *Photocatalytic reactor based on UV-LED/ TiO_2 coated quartz tube for degradation of dyes*, Chem. Eng. J., 2011, 178, 40.
- [4] NATARAJAN T.S., THOMAS M., NATARAJAN K., BAJAJ H.C., *Study on UV-LED/ TiO_2 process for degradation of Rhodamine B dye*, Chem. Eng. J., 2011, 169, 126.
- [5] ZHAO D., YANG X., CHEN C., WANG X., *Enhanced photocatalytic degradation of methylene blue on multiwalled carbon nanotubes– TiO_2* , J. Coll. Int. Sci., 2013, 398, 234.

- [6] CHAUDHARY D., ANSARI M.Z., KHARE N., VANKAR V.D., *Preparation, characterization and photocatalytic activity of anatase, rutile TiO₂/multiwalled carbon nanotubes nanocomposite for organic dye degradation*, J. Nanosci. Nanotechnol., 2017, 17, 1894.
- [7] HSIEH S.-H., CHEN W.-J., *Synthesis and characterization of TiO₂/CNT nanocomposites for azo dye degradation*, Mater. Sci. Forum, 2017, 909, 243.
- [8] HAMID S.B.A., TAN T.L., LAI C.W., SAMSUDIN E.M., *Multiwalled carbon nanotube/TiO₂ nanocomposite as a highly active photocatalyst for photodegradation of reactive black 5 dye*, Chinese. J. Cat., 2014, 35, 2014.
- [9] NATARAJAN K., KURESHY R.I., BAJAJ H.C., TAYADER J., *Photocatalytic degradation of Indigo carmine dye using hydrothermally synthesized anatase TiO₂ nanotubes under ultraviolet light emitting diode irradiation*, Mater. Sci. Forum Online: 2016-05-19 ISSN: 1662-9752, 855, 45.
- [10] YANG C.-C., DOONG R.-A., CHEN K.-F., CHEN G.-S., TSAI Y.-P., *The photocatalytic degradation of methylene blue by green semiconductor films that is induced by irradiation by a light emitting diode and visible light*, J. Air Waste Manage. Assoc., 2018, 69 (1), 29.
- [11] BUITRAGO L.A.B., VASQUEZ C., VEITIA L., ECHEVERRY O.O., VALLEJO J.R., BURGOS J.B., CABRALES N.M., MARTÍNEZ F.M., *An approach to the utilization of artificial high power LED UV-A radiation in photoreactors for methylene blue degradation*, Photochem. Photobiol. Sci., 2017, 16, 79.
- [12] JO W.K., TAYADE R.J., *Facile photocatalytic reactor development using nano-TiO₂ immobilized mosquito net and energy efficient UVLED for industrial dyes effluent treatment*, J. Environ. Chem. Eng., 2016, 4, 319.
- [13] SILVEIRA J.E., CLARO E., PAZ W., OLIVEIRA A., ZAZO J.A., CASAS J.A., *Optimization of Disperse Blue 3 mineralization by UV-LED/FeTiO₃ activated persulfate using response surface methodology*, J. Taiwan Inst. Chem. Eng., 2017, 1.
- [14] SHARMA A., KARN R.K., PANDIYAN S.K., *Synthesis of TiO₂ nanoparticles by sol-gel method and their characterisation*, J. Basic Appl. Eng. Res., 2014, 1, 1.
- [15] DIN 38 404, *German methods for the examination of water, wastewater and sludge, physical and physical-chemical parameters (group C). Determination of color*, Deutsches Inst. für Normung, Berlin 1991, 1.
- [16] SONI H., KUMAR J.I.N., PATEL K., KUMAR R.N., *Photocatalytic decoloration of three commercial dyes in aqueous phase and industrial effluents using TiO₂ nanoparticles*, Desalin. Water Treat., 2016, 57, 6355.
- [17] KOLI V.B., DHODAMANI A.G., DELEKAR S.D., PAWAR S.H., *In situ sol-gel synthesis of anatase TiO₂-MWCNTs nanocomposites and their photocatalytic applications*, J. Photochem. Photobiol., A, Chem., 2017, 333, 40.
- [18] MAMBA G., MBIANDA X.Y., MISHRA A.K., *Enhanced visible light photocatalytic degradation of Erichrome Black T and Eosin Blue shade in water using tridoped titania decorated on SWCNTs and MWCNTs. Effects of the type of carbon nanotube incorporated*, Mater. Chem. Phys., 2015, 149–150, 734.
- [19] MAMBA G., MBIANDA X.Y., MISHRA A.K., *Gadolinium oxide decorated multiwalled carbon nanotube/tridoped titania nanocomposites or improved dye degradation under simulated solar light irradiation*, Mater. Res. Bull., 2016, 75, 59.
- [20] FLORES U.C., ROMERO J.L., MEDINA J.Z., BATISTA M.J.M., ACUNA R.H., MUNOZ E.M.R., CORTES J.R., *Enhanced photocatalytic activity of MWCNT/TiO₂ heterojunction photocatalysts obtained by microwave assisted synthesis*, Catal. Today, 2016, 266, 102.
- [21] LI X., WANG T., QU G., LIANG D., HU S., *Enhanced degradation of azo dye in wastewater by pulsed discharge plasma coupled with MWCNTs-TiO₂/γ-Al₂O₃ composite photocatalyst*, J. Environ. Manage., 2016, 172, 186.

- [22] GIWA A., NKEONYE P.O., BELLO K.A., KOLAWOLE E.G., *Solar photocatalytic degradation of Reactive Yellow 81 and reactive violet 1 in aqueous solution containing semiconductor oxides*, Int. J. Appl. Sci. Technol., 2012, 2 (4), 90.
- [23] ALAHIANE S., QOURZAL S., OUARDI M.E., ABAAMRANE A., ASSABBANE A., *Factors influencing the photocatalytic degradation of Reactive Yellow 145 by TiO₂-coated non-woven fibers*, Am. J. Anal. Chem., 2014, 5, 445.
- [24] VIJAYAN B.K., DIMITRIJEVIC N.M., SHAPIRO D.F., WU J., GRAY K.A., *Coupling titania nanotubes and carbon nanotubes to create photocatalytic nanocomposites*, ACS Catal., 2012, 2, 223.
- [25] WANG W., SERP P., KALCK P., FARIA J.L., *Visible light photodegradation of phenol on MWNT-TiO₂ composite catalysts prepared by a modified sol-gel method*, J. Mol. Catal. A, Chem., 2005, 235, 194.
- [26] KAUR N., KAUR S., SINGHA V., *Preparation, characterization and photocatalytic degradation kinetics of Reactive Red dye 198 using N, Fe codoped TiO₂ nanoparticles under visible light*, Desalin. Water Treat., 2015, 1.
- [27] LEI Z., ZEDA M., CHUN O.W., *Fabrication and characterisation of tailored TiO₂ and WO₃/MWCNT composites for methylene blue decomposition*, Chinese J. Catal., 2011, 32, 926.
- [28] ZOUZELKA R., KUSUMAWATI Y., REMZOVA M., RATHOUSKY J., *Photocatalytic activity of porous multiwalled carbon nanotube-TiO₂ composite layers for pollutant degradation*, J. Hazard. Mater., 2016, 3117, 52.
- [29] MAHMOODI N.M., *Photocatalytic degradation of dyes using carbon nanotube and titania nanoparticle*, Water, Air, Soil Poll., 2013, 224, 1612.
- [30] KHAN W.Z., NAJEEB I., ISHTIAQUE S., *Photocatalytic degradation of a real textile wastewater using titanium dioxide, zinc oxide and hydrogen peroxide*, Int. J. Eng. Sci., 2016, 5, 7, 61.