PREPARATION, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF TiO₂/REDUCED GRAPHENE OXIDE NANOCOMPOSITE

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Abstract

In this paper, graphene oxide was synthesized from graphite by means of Hummer's method. The appropriate amounts of reagents (titanium tetraisopropoxide, i-propanol, acetylacetone, and nitric acid) were used to prepare a stable TiO₂ colloidal solution (sol). To order to improve the photocatalytic performance of TiO₂, TiO₂/rGO nanocomposite with 10 wt.% of rGO was prepared by a direct sol-gel method, followed by the hydrothermal method, and calcination treatment. The synthesized pure TiO₂ and TiO₂/10 wt. % rGO nanocomposite photocatalysts were characterized by Raman spectroscopy, Scanning electron microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy (SEM/EDXS), Fourier transform infrared spectroscopy (FT-IR/ATR), and powder X-ray diffraction (P-XRD). The photocatalytic activity was investigated by the methylene blue (MB) dye degradation under ultraviolet (UV) and simulated solar light irradiations. The effect of different amounts of the photocatalysts on the MB dye aqueous solution degradation under both irradiation sources was investigated. The obtained results show that prepared TiO₂/10 wt. % rGO photocatalyst is promising candidate for photodegradation of organic pollutants from water/wastewater under sunlight irradiation.

Keywords: Heterogeneous photocatalysis; TiO₂/rGO nanocomposite; simulated solar light; Water treatment

1. Introduction

Faster industrial development increases the production of specific byproducts which commonly end up in the environment. Such increasingly growing pollutants are dyes. They are extensively used in different fields, such as cosmetic, pharmaceutical, food, leather, paper, plastic, rubber, and textile industries. Especially, wastewater contains residuals and also their metabolites which can be even more toxic and harmful to living organisms. The chemical composition of each individual dye is very complex and it is difficult to degrade them into harmless compounds such as H₂O, CO₂, and mineral acid. To decompose these harmful organic compounds present in wastewater, researchers are globally looking for an effective approach such as photocatalysis [1], [2], [3]. Different techniques for the treatment of dye-containing wastewater have been developed including oxidative degradation, chemical precipitation, biochemical degradation, photocatalytic degradation, electrocoagulation, electrochemical degradation, and adsorption.

Nowadays, the Advanced Oxidation Processes (AOPs) based on the hydroxyl radicals ($\cdot\text{OH}$), among them especially heterogeneous photocatalysis, has gotten much attention for the wastewater treatment due to its efficient and environmentally friendly impact effect [4], [5]. In the last couple of decades, photocatalysis has been one of the most investigated processes for the degradation of organic compounds. CdS, WO_3 , ZnO, and TiO_2 are materials routinely utilized for photocatalytic applications, such as hydrogen production and dye degradation. There have been many reports on TiO_2 -based photocatalysts, which have received much attention due to their chemical and biological stability, unique structure, non-toxicity, low cost, and simple synthesis procedures.

TiO_2 crystallizes in three polymorphic forms: anatase, rutile, and brookite. The most stable and photoactive phase of TiO_2 is anatase. The major drawback, using heterogeneous TiO_2 -based semiconductor photocatalysis, is its high band gap energy (3.2 eV in the anatase and 3.0 eV in the rutile form) and a quick recombination of the photogenerated electron-hole pairs. When using photocatalytic degradation of organic pollutants in the environment, these limitations are the biggest challenge, because such broad band limits the photon absorption in the visible region [6], [7]. TiO_2 is the most effective under the irradiation with wavelengths shorter than 387 nm (UV-A), which is only about 5% of the total solar spectrum, and still a major limitation for effective use in other outdoor application [4]. To improve the photocatalytic efficiency of TiO_2 and to eliminate its disadvantages TiO_2 is commonly doped with noble metals (Ag, Pt, Au) or nonmetal (C, N, S) ions, and it is also coupled with mesoporous materials, zeolites, carbon-based materials, or semiconductors (ZnO , CdS, WO_3 , Bi_2WO_6) [8].

Nowadays, novel carbon- TiO_2 nanocomposites have received a lot of attention as an effective photocatalyst. Graphene, a carbon-based material can be used in many potential applications due to its unique chemical structure, graphene gives excellent optical, electrical, and mechanical properties, large surface area, and the excellent mobility of charge carriers [7], [9]. These excellent properties can have a positive influence, when graphene is incorporated in the titanium dioxide, resulting in better properties of the produced nanocomposites. Among them, nanocomposites could exhibit an increase in the adsorption of dyes and better degradation during the reaction [10], [11].

Within this study, the degradation of aqueous solution of MB dye under UV and simulated solar irradiations using different amounts of synthesized pure TiO_2 and $\text{TiO}_2/10$ wt. % rGO nanocomposite photocatalysts was investigated.

2. Materials and methods

2.1. Chemicals and Reagents

Commercially available natural graphite flakes (particle size ≤ 50 μm) and titanium (IV) isopropoxide ($\text{Ti}(\text{C}_3\text{H}_5\text{O}_2)_4$, TTIP, 97%) were purchased from Sigma-Aldrich. Concentrated sulfuric acid (H_2SO_4 , 95-97%), and concentrated nitric acid (HNO_3 , $\geq 65\%$) were ordered at Fluka and Lab Expert, respectively. Concentrated hydrochloric acid (HCl, 37%), potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), hydrogen peroxide (H_2O_2 , 30% w/v), *i*-propanol ($\text{C}_3\text{H}_7\text{OH}$), acetylacetone ($\text{CH}_3(\text{CO})\text{CH}_2(\text{CO})\text{CH}_3$) were supplied from Gram mol. The solutions with stated chemicals were prepared using ultrapure water (Millipore) obtained with a Direct-Q Millipore system.

2.2. Synthesis of graphene oxide (GO) and preparation of TiO_2 sol (colloidal solution)

GO was synthesized by Hummer's method. Firstly, flake-like graphite powder (3 g) was dispersed in a mixture of H_2SO_4 (69 mL) and NaNO_3 (1.5 g) by magnetic stirring (30 min) at low temperature (0-5 $^\circ\text{C}$). Then KMnO_4 (9.0 g) was slowly added, to keep the reaction temperature lower than 20 $^\circ\text{C}$. Subsequently, the mixture was heated to 35 $^\circ\text{C}$ and stirred for 30 min, at which time water (138 mL) was slowly added. The process initiated an exothermic reaction, which resulted in spontaneous heating up to 98 $^\circ\text{C}$. Additional heating was subsequently introduced to maintain the temperature at 98 $^\circ\text{C}$ for the next 15 min, after which the reaction vessel was cooled down in a water bath. Additional water (420 mL) this time with H_2O_2 (3 mL) were added one more time, resulting in another exothermic reaction. When the reaction mixture was cooled down to room temperature, the resulting suspension was centrifugated at 3000 rpm for 10 minutes to remove remaining impurities and to isolate the GO. GO was first washed with dilute HCl (10%) and then with deionized water several times to produce a slurry of GO with a neutral pH.

TiO_2 sol was prepared using titanium (IV) isopropoxide (TTIP) as a precursor, *i*-propanol (PrOH) as a solvent, acetylacetone (AcAc) as a chelating agent and nitric acid (HNO_3) as a catalyst. The molar ratio of the reactants was: TTIP:PrOH:AcAc:HN = 1:35:0.63:0.015.

2.3. Synthesis of TiO_2 nanoparticles and $\text{TiO}_2/10$ wt.% rGO nanocomposite

$\text{TiO}_2/10$ wt. % rGO nanocomposite was synthesized by the *in situ* procedure, using the TiO_2 colloidal sol prepared by the sol-gel route, which was hydrothermally treated in the presence of the GO substrates. The prepared slurry of GO was added into a colloidal solution of TiO_2 sol and stirred for 1 h until the liquid became a black-brown suspension. After that, the liquid was further homogenized for 10 min in an ultrasonic bath. Subsequently, the suspension was transferred into a Teflon-lined autoclave and kept at 180 $^\circ\text{C}$ during the next 6 hours. The containers were removed from the oven and cooled to ambient temperature.

The synthesized nanocomposite was washed to neutral pH value with *i*-propanol and deionized water and dried in a dryer at 60 °C for 1 h. Finally, the synthesized powders were calcinated at 300°C. The obtained nanocomposite contains 10 wt.% of rGO and it was labelled TiO₂/10 wt. % rGO. TiO₂ nanoparticles were synthesized following the same procedure, only without the addition of the GO suspension.

2.4. Characterization of the obtained materials

The crystal structure of the samples was examined by powder X-ray diffraction (P-XRD) using PANalytical X'Pert High-Resolution PRO diffractometer (PANalytical B.V., Netherlands) with an Alpha1 configuration in the 2 θ range 10–80°, with a step of 0.034°/100s using a fully opened 100 channel X'Celeator detector and Cu-K α radiation (1.5406 Å). The XRD patterns were compared to diffractograms from the JCPDS database (ICDD; International Centre for Diffraction Data, PA, USA) to identify the phase compositions. The microstructural characteristics of samples were investigated using Scanning Electron Microscope with Energy-Dispersive X-ray Spectroscopy (SEM/EDXS). Measurements were made with Jeol JSM-7600F equipment. The crystalline phases of the synthesized materials were analysed by Raman microscope (NT-MDT Spectra II) using the Raman excitation energy at 633 nm. Fourier transform infrared (FT-IR/ATR, Bruker Vertex 70) spectroscopy were performed to analyze the functional groups in the structure of the synthesized materials. Spectra were collected in frequency range between 4000–400 cm⁻¹ with 42 scans and spectral resolution 2 cm⁻¹.

2.5. Photocatalytic test

To test the photocatalytic activity of the prepared nanocomposites, 1 and 5 mg of the synthesized photocatalyst were dispersed in 10 mL of Methylene blue dye solution (with concentration of 10 mg/mL) and irradiated with simulated solar light (lamp: ULTRA-VITALUX, 230 V, 300 W, Osram) and UV-A light (lamp: Supratec 18W/73, Osram) for 120 minutes. The degradation process was monitored by UV-Vis spectroscopy, taking aliquots at regular intervals. Each aliquot was centrifuged with small centrifuge (10 minutes, 13.4 rpm) to remove the photocatalyst and the resulting clear liquid was analyzed. The absorbance was recorded by a UV-Vis spectrophotometer (Lambda 950 Spectrophotometer, PerkinElmer) in the range from 550 to 850 nm using quartz cells with a path length of 10 mm. Before the photocatalytic test, the prepared suspensions were kept in the dark for 60 minutes to achieve the adsorption-desorption equilibrium. The adsorption process in the dark was also monitored by UV-Vis spectroscopy.

3. Results and Discussions

3.1. Characterization of photocatalysts structure

Several characterization techniques were used to verify the quality of synthesized materials, to determine information about their chemical structure and surface morphology.

Fig. 1. X-ray diffractogram of A) GO and B) rGO, TiO₂ and TiO₂/10 wt. % rGO nanocomposite

The XRD patterns of GO, rGO, TiO₂, and TiO₂/10 wt. % rGO nanocomposite are presented in Fig.1. The diffractogram of GO in Fig. 1A shows the peak at 10.68°, the pattern was modified by oxidation of GO. A strong sharp peak at 10.68° (001) is a result of a huge number of oxygen-containing functional groups (epoxide, carbonyl, and hydroxyl) on the surface of the GO sheets [12], [13].

After hydrothermal reduction of the GO nanosheets, the X-ray diffraction spectrum of rGO shows two characteristic peaks. One broad peak appears at 23.98° and corresponds to the (002) lattice planes, signifying the formation of sp^2 bonds in the structure of carbon. This result is related to the reduction process of GO during the hydrothermal treatment, consequence of the water removal, and oxygen-containing functional groups formation. The peak at 42.94° is attributed to the band of disordered carbon materials [14]. All peaks of pure TiO_2 and $TiO_2/10$ wt. % rGO nanocomposite could be indexed to the anatase phase, which match the JCPDS Card No. 21-1272. In addition, diffractograms of the synthesized materials do not show any peaks related to rutile and brookite, Fig. 1B, which indicates that TiO_2 is free of the rutile and brookite phase [15]. No peak corresponding to rGO was observed in the diffractogram spectrum of $TiO_2/10$ wt. % rGO nanocomposite, likely because the typical peak of anatase phase centered at 25.32° overlaps the typical peak of rGO at 23.98° [13].

Fig. 2. Raman spectra of A) GO and rGO and B) pure TiO_2 and $TiO_2/10$ wt. % rGO nanocomposite

Samples	D-band, cm^{-1}	G-band, cm^{-1}	I_D/I_G	L_a , nm
GO	1336.59	1595.02	1.09	35.4
rGO	1324.80	1590.54	1.27	30.3

Table 1. Parameters obtained from Raman spectra of GO and rGO

Raman spectroscopy was further used to analyze and confirm structural and also some electronic properties of carbon materials, and the crystal structure of TiO_2 . In the spectra of graphene materials, two major peaks appear. The D band, at ~ 1354 cm^{-1} , is attributed to the presence of a disorder or sp^3 defects in carbon materials. The G band, at ~ 1575 cm^{-1} , corresponds to a perfect graphite structure, where carbon atoms are bonded with sp^2 hybridization. Figure 2A presents the Raman spectra of GO and rGO, and the obtained characteristic parameters of their analysis are collected in Table 1. After the oxidation process followed Hummer's method, in the Raman spectrum of GO, bands at 1336.59 cm^{-1} (D) and 1595.02 cm^{-1} (G) were observed. The D and G bands were observed at 1324.80 cm^{-1} and 1590.54 cm^{-1} for the rGO sample. The vibrations of the D and G peaks in rGO materials were significantly shifted compared to GO material. The reason for shifting is in the structure of graphene materials. The shifting of the vibration of D and G bands and change in their intensity corresponds to the partial elimination of oxygenated groups. These results indicate that the reduction process was effective and that oxygenated groups were not totally removed in the rGO sample [12], [16]. The ratio of intensities between D and G bands gives the proportion of sp^3 defects with sp^2 hybridization to graphitic carbon and amorphous ones. The I_D/I_G ratio is 1.09 for GO and 1.27 for rGO. The ratio of rGO is higher than for GO. The removal of oxygenated groups with hydrothermal treatment indicates a reduction in the mean size of sp^2 domains. The reduction of GO causes novel graphitic domains and enormous amounts of edges that behave as defects, resulting in increased intensity of the D bands [12], [17].

The ratio of intensities between D and G bands is utilized to determine the crystal size parallel to basal planes (L_a), using the equation of Tuinstra and Koenig, where the coefficient 38.5 is for measurements at 633 nm [18]:

$$L_a(nm) = \frac{38.5}{I_D/I_G} \quad (1)$$

The L_a values are 35.4 nm for GO and 30.3 nm for rGO as shown in Table 1. A lower L_a value demonstrates decrease in sp^2 domains in the rGO sample. Figure 2B represents Raman spectra of synthesized pure TiO_2 and its composite with rGO and parameters obtained from their analysis are collected in Table 2. The pure TiO_2 particles show bands at frequencies between 100-700 cm^{-1} . The typical peaks of the anatase phase are detected as can be seen in Table 2. The presence of the anatase phase is also confirmed in the composite material. The brookite and rutile phases were not observed, which is consistent with the results of XRD analysis.

Samples	E_g , cm^{-1}	B_{1g} , cm^{-1}	$A_{1g}+B_{1g}$, cm^{-1}	E_g , cm^{-1}	D-band, cm^{-1}	G-band, cm^{-1}	I_D/I_G	L_a , nm
TiO_2	151.16	399.53	521.86	645.64	-	-	-	-
TiO_2/rGO_{10}	159.73	394.78	516.02	635.31	1323.72	1594.55	1.31	29.41

Table 2. Parameters obtained from Raman spectra of TiO_2 and its composite with rGO

The peaks which appear at 151.16 cm^{-1} and 645.64 cm^{-1} are assigned to the symmetric valence vibrations (E_g) of the O-Ti band. The symmetric bending vibration (B_{1g}) O-Ti-O appears with the signal at 399.53 cm^{-1} and the asymmetric vibration (A_{1g}) of the O-Ti bond is observed at 521.86 cm^{-1} . In the synthesized composite, the E_g band appears at 159.73 cm^{-1} . The band shifts to a higher wavelength as it is in the pure TiO_2 particles. This phenomenon could be ascribed to the assembling of the Ti-O-C structure in the composite [12].

FT-IR spectroscopy is a powerful method to confirm a chemical composition and its structures by the presence of different functional groups. Figure 3A depicts the FT-IR spectra of GO and rGO samples. The successful oxidation of graphite, used as starting material, was recorded by FT-IR analysis. The spectrum of GO has several peaks of functional groups. The absorption peaks of GO appeared at 3183 cm^{-1} (O-H stretching vibrations), 1719 cm^{-1} (C=O stretching vibration of carbonyl/carboxyl groups), 1617 cm^{-1} (C=C skeletal vibrations), 1365 cm^{-1} (O-H deformation vibration), 1221 cm^{-1} (C-O-C of epoxy groups), and at 1054 cm^{-1} (C-O stretch of the alkoxy group) [19], [20].

The spectrum of rGO exhibits two characteristic absorption peaks at 1670 and 1013 cm^{-1} . As seen in Figure 3A, all the absorption peaks corresponding to the oxygen-containing functional groups of rGO were decreased compared to the absorbance of GO peaks and even more some of them disappeared. These results confirm the successful reduction of graphene oxide by hydrothermal treatment.

Figure 3B depicts the FT-IR spectra of TiO_2 and $TiO_2/10$ wt. % rGO samples. The FT-IR spectrum of pure TiO_2 particles shows a wide band at 3342 cm^{-1} and the band at 1637 cm^{-1} which is assigned to the presence of O-H vibrations on the surface of titania. Moreover, the band appeared at 444 cm^{-1} correspond to Ti-O vibrations. In the composite, the oxygen functional vibrations are still present. In addition, bands appeared at 1544 cm^{-1} (C=C skeletal vibrations) and at 555 cm^{-1} which could be attributed to Ti-O-C [6].

Fig. 3. FT-IR spectra of A) GO and rGO, and B) pure TiO_2 particles and $TiO_2/10$ wt. % rGO nanocomposite

The morphologies of rGO, pure TiO_2 particles, and $TiO_2/10$ wt. % rGO nanocomposite were recorded by scanning electron microscopy (SEM) as is showed in Figure 4. In Figure 4A the characteristic rGO structure with the rich wrinkled and ultrathin morphology of the graphene sheets, confirming the successful reduction treatment, can be seen. Impurities were not found on the surface of rGO material [8].

The SEM image of TiO_2 particles is shown in Figure 4B. The image shows that TiO_2 particles agglomerate in a unit of different sizes. The SEM image (Figure 4C) of $TiO_2/10$ wt. % rGO nanocomposite, which was synthesized by the hydrothermal and calcination method, presents that TiO_2 particles were embedded in the structure of rGO [21]. Further, EDX analysis confirmed the presence of TiO_2 nanoparticles in the nanocomposite, as shown in Figure 4D.

Fig. 4. SEM images of A) rGO, B) pure TiO₂ particles, and C) TiO₂/10 wt. % rGO nanocomposite; D) EDX analysis of nanocomposite

3.2. Photocatalytic decomposition of MB

The performance of the synthesized materials was evaluated on the basis of the degradation of aqueous solutions of MB dye as an organic pollutant model. The degradation of MB was monitored through the change of its characteristic peak at 663 nm. Firstly, the adsorption in the dark was observed for 60 minutes and subsequently, photocatalytic degradation of MB under UV and simulated solar irradiation was measured, up to 120 minutes. After reaching the adsorption-desorption equilibrium (60 minutes), the irradiation source was turned on and the MB concentration in the observed suspensions started to decrease, as seen in Fig. 5A and 7A.

Firstly, the photoactivity study of the synthesized powders TiO₂ and TiO₂/10 wt. % rGO nanocomposite was performed under UV irradiation, using different amounts of photocatalysts (1 mg and 5 mg). It was found that MB was not exposed to degradation without the catalyst in the UV light irradiation. Regarding the decomposition of MB, over a period irradiated with UV light (0-120 minutes), the TiO₂/10 wt. % rGO nanocomposite shows a faster photoactivity performance than pure TiO₂ nanoparticles. The amount of photocatalyst added to the pollutant model plays an important role. The highest photoactivity was achieved using 5 mg of TiO₂/10 wt. % rGO nanocomposite, however, the decomposition efficiency of MB after 120 minutes was still low, only 28%. The photodegradation efficiencies achieved by the synthesized photocatalysts, shown in Fig. 5B and 7B were calculated by the equation:

$$\eta = \frac{A_0 - A_t}{A_0} \cdot 100\% \quad (2)$$

where, η is photodegradation efficiencies of the MB dye, A_0 is the absorbance of the initial MB concentration (before irradiation) and A_t is the concentration of MB at time t expressed as absorbance after irradiation at the selected time t (min), during the photocatalytic process.

Fig. 5. A) The dark adsorption and photocatalytic degradation of MB dye under UV light irradiation; B) photodegradation efficiencies of MB as a function of time

The change in the maximum absorption peak for MB versus the irradiation time under the simulated solar irradiation is shown in Fig. 6A-B. The maximum of the peak at 633 nm decreases with longer irradiation time. The same trend can be observed for both measurements (TiO_2 nanoparticles and $\text{TiO}_2/10 \text{ wt. \% rGO}$ nanocomposite), when 5 mg of the photocatalyst was used.

Fig. 6. The absorption spectra during the photodegradation of MB and under simulated solar irradiation in the presence of catalyst :A) TiO_2 , 5 mg and B) $\text{TiO}_2/10 \text{ wt. \% rGO}$, 5mg

In addition to UV irradiation, the investigation of photoactivity for synthesized TiO_2 and $\text{TiO}_2/10 \text{ wt. \% rGO}$ nanocomposite was also performed under simulated solar irradiation, Figure 7. Similarly, different amounts of photocatalysts (1 mg and 5 mg) were tested. The adsorption-desorption equilibrium and photocatalytic performance tests were recorded after 60 minutes in the dark and 120 minutes under irradiation with simulated solar light, Figure 7A. By exposing the material in the dark the adsorption ability of the photocatalyst was eliminated. This can be seen because the concentration of MB did not drop during the dark period of the test, Fig 7A.-From Fig. 7C, it was found that the efficiency of MB degradation increases with an increasing amount of photocatalysts in the model solution of organic pollutants. MB degradation efficiency increases from 42%, 52%, 57% to 92% for TiO_2 , 1mg, $\text{TiO}_2/10 \text{ wt. \% rGO}$, 1mg, TiO_2 , 5mg, and $\text{TiO}_2/10 \text{ wt. \% rGO}$, 5mg, respectively, after 120 min under simulated solar irradiation, Fig. 7B.

Fig. 7. A) The dark adsorption and photocatalytic degradation of MB dye under simulated solar light irradiation; B) time evolution of relative MB concentration using synthesized materials; C) photocatalytic degradation of MB in percentage at different time; D) first-order kinetic curves of the MB degradation

The first-order rate constant is calculated by the slope of the straight line obtained from plotting linear regression of $-\ln(A/A_0)$ versus irradiation time, t , as shown in Fig. 7D, and it was calculated with the following equation:

$$A_t = A_0 \cdot e^{-k \cdot t} \quad (3)$$

where, k (min^{-1}) is the degradation rate constant, A_t is the absorption of MB solution at the chosen time of the photocatalytic process and A_0 is its absorption at the beginning of the experiment.

The half-life ($t_{1/2}$) was calculated by the following equation:

$$t_{1/2} = \frac{\ln 2}{k} \quad (4)$$

In Table 3 the coefficient of determination (R^2), the reaction rate constant ($k \times 10^{-3}$), and half-life photo-degradation rate ($t_{1/2}$) are collected. The reaction rate constant ($k \times 10^{-3}$) and half-life degradation rate ($t_{1/2}$) were determined assuming that the photo-degradation process follow the first-order kinetics model. The coefficient of determination (R^2) is very high, proving the first-order kinetics for the photocatalytic degradations.

The reaction rate constant and the half-life degradation rate of the photocatalysts with a lower amount of the photocatalysts (1 mg) shows slower removal of MB dye than in the case when a higher amount of photocatalysts were added (5 mg).

Sample	R^2	$k \times 10^{-3}, \text{min}^{-1}$	$t_{1/2}, \text{min}$
TiO ₂ , 1mg	0.9962	4.56	152.00
TiO ₂ , 5mg	0.9987	7.12	97.35
TiO ₂ /10 wt. % rGO, 1mg	0.9988	6.22	111.44
TiO ₂ /10 wt. % rGO, 5mg	0.9568	19.5	35.55

Table 3. Photodegradation kinetics of MB under simulated solar light irradiation

After all photocatalytic tests under different parameters, TiO₂/10 wt. % rGO nanocomposite presents a higher efficiency of photoactivity than pure TiO₂ nanoparticles. Moreover, increased amount of photocatalyst plays significant role in the removal of MB dye from its aqueous solution.

4. Conclusions

The purpose of this study was to investigate the photocatalytic decomposition of MB in aqueous solution under the under UV and simulated solar light irradiations. In order to demonstrate that photocatalytic oxidation using TiO₂/10 wt. % rGO nanocomposite as photocatalyst is a highly-efficient and “green” method for wastewater treatment when the surface of pollutants is exposed to sunlight irradiation.

Pure TiO₂ nanoparticles and TiO₂/10 wt. % rGO nanocomposite, photocatalysts were used for the photocatalytic experiments. Powders were synthesized using a direct sol-gel route followed by the simple and low-cost hydrothermal method with subsequent calcination treatment.

The presented research, on the basis of the obtained results, can be summarized as follows:

- The GO suspension was successfully prepared by Hummer's method using graphite flakes.
- Pure TiO₂ nanoparticles and TiO₂/10 wt. % rGO composite were successfully prepared by the hydrothermal method, photocatalysts were analyzed in detail (morphology, structure) using different characterization methods.
- Higher photocatalytic degradation efficiency of MB was achieved with the TiO₂/10 wt. % rGO nanocomposite as a catalyst using simulated solar light irradiation in comparison with pure TiO₂.
- It was found that photocatalytic rates of MB dye degradation increase with an increasing the amount of both investigated photocatalysts.

Further work of the study is to investigate the photocatalytic performance of synthesized catalysts on the degradation of pharmaceuticals, and to determination of degradation products and their toxicity. Also, mechanisms of photodegradation will be explain.

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