Research Article

Photocatalytic Performance of Carbon Monolith/TiO$_2$ Composite

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The new and simple approach for deposition of catalytically active TiO$_2$ coating on carbon monolith (CM) carrier was presented. CM photocatalysts were impregnated with TiO$_2$ using titanium solution and thermal treatment, and their photocatalytic activity was investigated in the process of methylene blue (MB) photodegradation. For the purpose of comparison, CM composite photocatalysts were prepared by dip-coating method, which implies binder usage. The presence of TiO$_2$ on CM carrier was confirmed by Raman spectroscopy and scanning electron microscopy. The sorption characteristics of CM and the role of adsorption in the overall process of MB removal were evaluated through amount of surface oxygen groups obtained by temperature-programmed desorption and specific surface area determined by BET method. CM has shown good adsorption properties toward MB due to high amount of surface oxygen groups and relatively high specific surface area. It was concluded that photocatalytic activity increases with CM disc thickness due to increase of MB adsorption and amount of deposited TiO$_2$. Good photocatalytic activity achieved for samples obtained by thermal treatment is the result of better accessibility of MB solution to the TiO$_2$ particles induced by binder absence.

1. Introduction

Nowadays, the mobilization of pollutants in the environment becomes a serious concern due to the increased industrial activities and effluents discharge into environment. Most of these effluents contain toxic substances, especially organic pollutants such as drugs, pesticides, and organic dyes. The presence of these pollutants in the environment is of a major concern because of their toxicity, threat to humans and other form of life. Therefore, it is essential to find the optimal method for removing the organic pollutants from the environment, especially from water. Several methods, such as combined photo-Fenton and biological oxidation, advanced oxidation processes, aerobic degradation, biodegradation, coagulation, nanofiltration, ozonation, adsorption, and heterogeneous photocatalysis [1–4], have been developed for the removal of organic pollutants from water and liquid waste. Recently, more attention is paid to photocatalytic degradation as an effective method for removal of these pollutants. Much work on the TiO$_2$-mediated heterogeneous photocatalysis as a successful and convenient alternative to the conventional methods for the treatment of wastewater containing organic pollutants has been reported so far [1]. Titanium dioxide (TiO$_2$) has advantages over other photocatalysts, such as good stability, high activity, little harmfulness to humans, easy availability, and low cost [5, 6]. Therefore, titanium dioxide is photocatalysts of choice for degradation of drugs, pesticides, organics dyes, and air pollutants [7–9]. For photocatalytic applications and water treatment, catalyst is usually dispersed in aqueous solution and used in slurry reactors. But this type of reactors has a major drawback: the catalyst particles must be separated from the liquid phase which involves a time and energy consuming process. To avoid the filtration/separation and catalyst recovery steps, the active phase is anchored on a suitable support and used in fixed or fluidized bed reactors [10, 11]. Different materials can

be used as catalytic carrier for TiO_2 in the photocatalytic degradation process. Recently, TiO_2 has been combined with different carbon materials in simple mixtures or as composite materials in order to create more highly reactive photocatalysts [12–16]. A number of methods can be used for loading the TiO_2 particles on carbon material carrier. According to the literature [17], one of the most frequently used methods for loading the TiO_2 particles on carbon material carrier is a sol-gel method. Although catalysts obtained in this way show good photocatalytic activity, sol-gel method represents a time consuming process, which is its main disadvantage. Another group of methods for loading the TiO_2 particles on carbon material carrier implies TiO_2 deposition from gas phase. Atomic layer deposition (ALD) and metal organic chemical vapor deposition (MOCVD) are extensively used surface coating technologies for preparation of the TiO_2 photocatalyst [18, 19]. These methods allow the obtaining of a desired TiO_2 loading by controlling the number of ALD cycles or deposition time in MOCVD method. The necessity of controlling a large number of experimental parameters makes these methods very complicated. Unlike the already mentioned complicated methods TiO_2 particles could be loaded to the carbon material surface by cheap and simple dip-coating method [6]. This method implies the use of binder in order to ensure firmly loading of TiO_2 particles on the surface on carbon materials.

In this work, the attempt was made to develop a simple and cheap method for obtaining firmly attached photocatalytically active TiO_2 coating on carbon material without using a binder. The baseline was that binder may cover a substantial amount of TiO_2, making it photocatalytically inactive. Carbon monolith (CM) was used as a catalyst carrier for TiO_2. In our previous work we have shown that cylindrical CM with its porous structure and surface oxygen groups represents a good carrier for silver deposition and it was successfully used for disinfection of drinking water [20]. In the present work, carbon monolith photocatalysts were prepared by deposition of titanium dioxide on CM surface, by adsorption from the fresh Ti solution, followed by evaporation of solvent and oxidation of $TiCl_4$ to TiO_2. Unlike dip-coating method, this method, tentatively called thermal treatment, does not require the usage of binder. Photocatalytic activity of obtained CM photocatalysts was compared with the activity of composite photocatalysts obtained by dip-coating method, for revealing the influence of the binder mass fraction on photocatalytic activity. Photocatalytic activity of obtained samples was examined by photodegradation of methylene blue in the flow system.

2. Experimental

2.1. Carbon Monolith as a Catalyst Carrier. Carbon monolith, made in the form of tubes of circular cross section and variable length, was purchased from Fractal Carbon (London, UK). The main feature of carbon monolith microstructure is the presence of 8600 capillary columns, with 80 μm in diameter each. This is a composite material, consisting of the glassy carbon bed and activated carbon on the inner capillary walls [21]. In our experiments CM discs of different thickness were used.

2.2. Surface Properties of Catalyst Carrier

2.2.1. Surface Oxygen Groups. Temperature-programmed desorption (TPD) in combination with mass spectrometry was used to investigate the nature and the thermal stability of CM surface oxygen groups. The TPD profiles were obtained using a custom-built setup, consisting of a quartz tube placed inside an electrical furnace. CM samples were outgassed in the quartz tube and subjected to TPD at a constant heating rate of 10°C/min to 900°C under high vacuum. The amounts of CO and CO_2 released from the carbon monolith sample (0.1 g) were monitored using an Extorr 300 quadrupole mass spectrometer (Extorr Inc., USA).

2.2.2. Specific Surface Area. Specific surface area of carbon monolith, S_{BET}, was determined by nitrogen adsorption at the temperature of liquid nitrogen using Automatic Surface Area Analyzer, model 4200 (Leeds & Northrup Instruments, USA).

2.3. Preparation of Photocatalysts. CM photocatalysts were obtained by thermal treatment. Titanium was dissolved in hydrochloric acid water solution ($HCl : H_2O = 1 : 1$). Using 10 mL of fresh $TiCl_4$ solution (3 g/dm³), CM discs were impregnated with $TiCl_4$ in the batch system and then heated at 300°C for 2 h. During the heating treatment, deposited $TiCl_4$ was oxidized, and CM impregnated with TiO_2 (CM/TiO_2) were obtained (Table 1).

The composite photocatalysts were obtained by dip-coating method [6], using mixture of TiO_2 powder and the binder for impregnation of CM surface. This kind of mixture was used in order to avoid attrition of TiO_2 from the CM surface. For this method, 10 mL of TiO_2 (anatase) water suspension (3 g/dm³) was mixed with sodium carboxymethyl cellulose and Teflon, as a binders, to achieve different mass fraction of binder (Table 1). The suspension obtained in this way was used for impregnation of CM with TiO_2 in the batch system. Impregnated samples were dried at 105°C for 2 h. In this way six different samples were obtained. Obtained samples were indicated with different labels given in Table 1. General mark of the used samples is $CM_A/TiO_2/Bx_{\%}$, where A is the thickness of the CM disc and B denotes a binder, while x is a type of binder used and % refers to the mass fraction of binder. All chemicals used were purchased from Aldrich Chemistry, USA.

2.4. Characterization of Photocatalysts. For determining the presence of titanium dioxide on the surface of the CM, Raman spectroscopy (Advantage 532 Raman spectrometer (DeltaNu Inc.)) was used. Additional structure analysis of obtained CM photocatalysts was performed by Phillips PW1710 diffractometer, using CuKα1,2 radiation.

Surface structure and morphology as well as morphology of TiO_2 deposited at the CM surface were studied by scanning electron microscopy (SEM JEOL JSM 5800 operated at 20 keV, Jeol, Ltd., Japan).

TABLE 1: CM photocatalysts obtained by dip-coating method and thermal treatment.

Sample	CM disc thickness, mm	Binder (B_x)	Mass fraction of the binder, %
$CM_{1.5}/TiO_2$	1.5		
CM_2/TiO_2	2	—	—
CM_3/TiO_2	3		
CM_5/TiO_2	5		
$CM/TiO_2/Bc_{0.2}$	2		0.2
$CM/TiO_2/Bc_{0.25}$	2	Sodium carboxymethyl cellulose (Bc)	0.25
$CM/TiO_2/Bc_{0.3}$	2		0.3
$CM/TiO_2/Bt_{0.2}$	2		0.2
$CM/TiO_2/Bt_{0.25}$	2	Teflon (Bt)	0.25
$CM/TiO_2/Bt_{0.3}$	2		0.3

2.5. Methylene Blue Adsorption Test. CM is composite carbon material containing activated carbon on the inner capillary walls, which is good sorbent for methylene blue (MB) [22]. Therefore, the disappearance of MB in the solution can be attributed to adsorption by CM and/or photodegradation by TiO_2 when CM with TiO_2 deposit is used. In order to examine the role of methylene blue adsorption on CM surface in the overall process of MB removal from aqueous solution, adsorption test in the flow system was performed without UV irradiation. Aqueous solution of MB, with initial concentration of $1 \, mg/dm^3$ and pH 4.7, was passed through the different samples of CM with TiO_2 deposit (CM_3/TiO_2, CM_5/TiO_2, $CM/TiO_2/Bc_{0.25}$, $CM/TiO_2/Bt_{0.25}$), until reaching equilibrium adsorption. Concentration of MB during the adsorption process was measured using visible spectrophotometer (Specol, Carl-Zeiss, Jena), by measuring absorbance at 675 nm. Methylene blue was purchased from Ciba, Aktiengesellschaft, Basel.

2.6. Photocatalytic Activity. The photocatalytic efficiency of CM coated with TiO_2 was assessed by photodegradation of aqueous solution of methylene blue. Experiment was carried out in the flow system with the flow rate of 2.4 mL/min. MB is a heterocyclic aromatic organic compound often used as target molecule for the evaluation of photocatalytic activity of TiO_2 [8]. After reaching the equilibrium adsorption in the dark, for 45 minutes, the UV light was turned on. At this time the concentration of MB in solution was denoted as $C_{0,MB}$. The decolorization of methylene blue, as a consequence of photocatalytic degradation, was carried out by irradiating methylene blue aqueous solutions entering the CM disc with a 125 W high-pressure mercury lamp (Philips, HPLN, emission bands in the UV region at 304, 314, 335, and 366 nm, with maximum emission at 366 nm). Position of the lamp is adjusted in a way that the front of the CM disc is illuminated with UV rays. The actual concentration of methylene blue during the decolorization experiments was followed by spectrophotometric measurements. The photocatalytic degradation efficiency is calculated as $(C_{MB}/C_{0,MB}) \times 100\%$, where C_{MB} is the concentration of MB during photocatalytic degradation.

The influence of the binder mass fraction in the composite photocatalysts on their photocatalytic activity was tested.
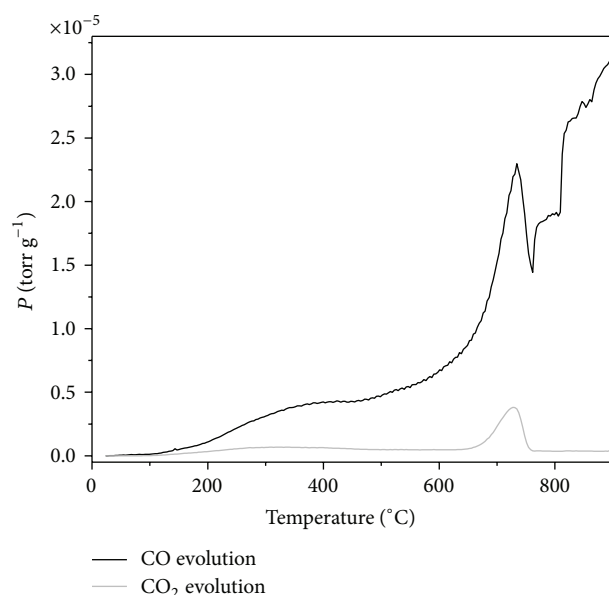

FIGURE 1: TPD spectra of carbon monolith.

Additionally, in order to increase the photocatalytic activity and find the optimal parameters of examined system, CM photocatalysts with different disc thickness were tested.

3. Results and Discussion

3.1. Surface Properties of Catalyst Carrier. During the TPD analysis, oxygen groups present on the surface of carbon material decompose by releasing CO and CO_2. According to the literature [23–26], TPD peaks can be assigned to specific surface groups. The CO_2 profile results from carboxylic acids at low temperatures and lactones at higher temperatures; carboxylic anhydrides are the origin of both CO and CO_2 peaks; phenols, ethers, and carbonyls are the origin of the CO peak.

TPD profiles of CO and CO_2 evolution, for tested carbon monolith, are shown in Figure 1. The TPD desorption profile of CO_2 shows one intensive peak at relatively high temperature (around 735°C). Additionally, the CO desorption profile

TABLE 2: CM surface properties—S_{BET} and amounts of CO (Q_{CO}) and CO_2 (Q_{CO_2}) evolving surface oxygen groups.

Sample	S_{BET} (m²/g)	Q_{CO} (mmol/g)	Q_{CO_2} (mmol/g)	$Q_{CO} + Q_{CO_2}$ (mmol/g)
CM	344	2.256	0.442	2.698

(a)

(b)
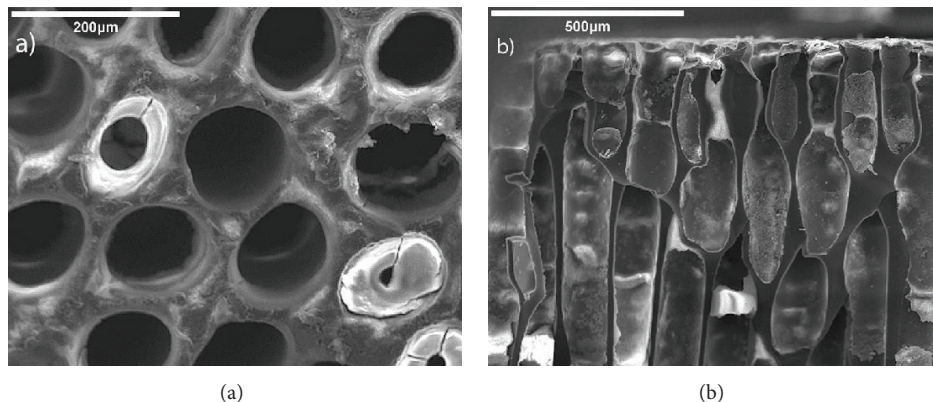
FIGURE 2: SEM photographs of the front (a) and cross section (b) of samples $CM_2/TiO_2/Bt_{0.2}$.

(a)

(b)
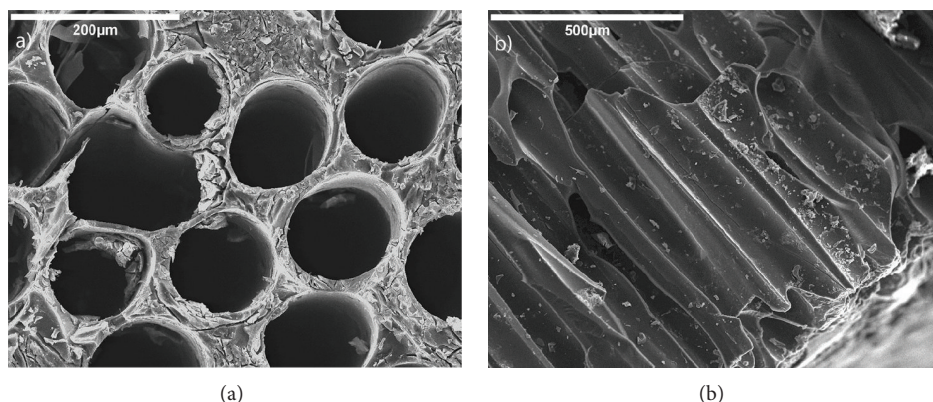
FIGURE 3: SEM photographs of the front (a) and cross section (b) of samples CM_3/TiO_2.

has a maximum at the temperature which coincides with the maximum in CO_2 desorption profile, which indicates the existence of anhydride groups [23]. The CO desorption profile has also broad maximum around 400°C. This is a very low temperature for CO evolution, and according to the literature [25] it may be due to thermal decomposition of carbonyl groups in α-substituted ketones and aldehydes. The CO evolution at the temperatures higher than 800°C may be attributed to phenols, ethers, carbonyls, or quinones.

The amounts of CO and CO_2 released from the surface of CM samples were obtained by integration of corresponding TPD curves. Specific surface area calculated by BET equation (S_{BET}) and the amounts of CO (Q_{CO}) and CO_2 (Q_{CO_2}) are given in Table 2.

Due to the fact that CM is composite material consisting of glassy carbon bed, which generally has very low specific surface area [27] and activated carbon on the inner capillary walls, obtained specific surface area value is expected.

3.2. Characterization of Photocatalysts.
Microstructure of the CM coated with TiO_2 obtained by using dip-coating method and thermal treatment is shown in Figures 2 and 3.

SEM photographs show visible differences in the TiO_2 coatings. The usage of binder in dip-coating method leads to clogging of the CM capillary columns and forming of heterogeneous TiO_2 coating (Figures 2(a) and 2(b)). On the other hand, thermal treatment gives more homogeneous coating without channel blocking (Figures 3(a) and 3(b)). Microstructured CM has microporous surface with relatively high specific surface area and amount of surface oxygen groups [21]. These surface characteristics are crucial for fine and uniform adsorption of titanium ions. Consequently, the obtained oxidized TiO_2 coating is more homogenous.

The presence of TiO_2 on the tested samples was confirmed by Raman spectroscopy (Figure 4). The main features of all obtained spectra are the two broad peaks referred to as the D band at 1340 cm^{-1} and G band at 1590 cm^{-1}. The G
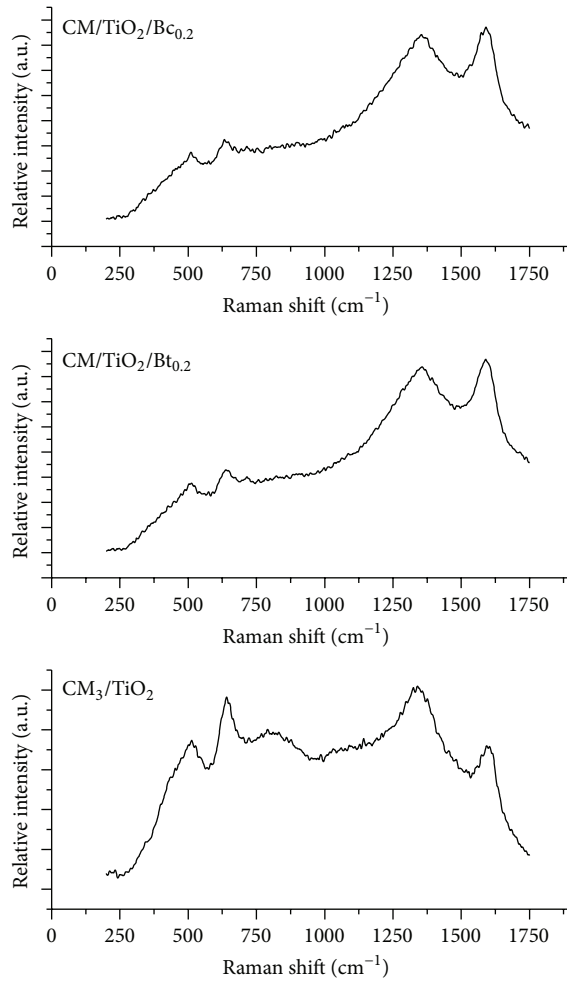
FIGURE 4: Raman spectra of CM/TiO$_2$/Bc$_{0.2}$, CM/TiO$_2$/Bt$_{0.2}$, and CM$_3$/TiO$_2$.

FIGURE 5: XRD patterns of CM/TiO$_2$/Bc$_{0.2}$, CM/TiO$_2$/Bt$_{0.2}$, and CM$_3$/TiO$_2$.
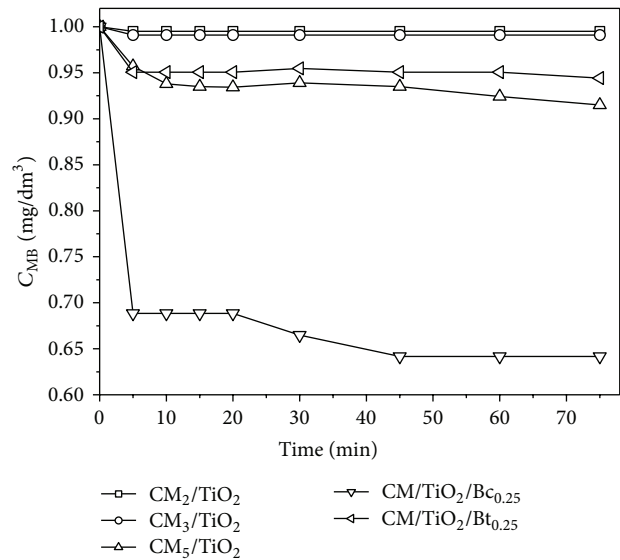
FIGURE 6: Adsorption of methylene blue on CM surface.

and D bands are characteristic of graphitic and disordered sp^2-bonded carbon. The G peak is due to a bond stretching vibration of all pair of sp^2 sites in both chain and rings, representing graphite like sp^2, while the D peak is due to the breathing vibration of sp^2 atoms in the rings and represents disordered sp^2 hybridized carbon [28]. For all tested samples TiO$_2$ peaks appear in the spectra near 510 cm^{-1} and 639 cm^{-1} originating from anatase, while CM$_3$/TiO$_2$ spectrum has additional weak peak at 837 cm^{-1} which may originate from rutile structure [29]. For sample CM$_3$/TiO$_2$ peaks originating from anatase are of much higher intensity compared to the peaks obtained for composite photocatalysts. The difference in anatase peak intensity is most likely the consequence of TiO$_2$ particles coverage with a binder.

The composition and crystallinity of TiO$_2$ deposits were additionally examined by X-ray diffraction (Figure 5). XRD patterns for all examined samples exhibited characteristic diffraction peaks at 2Θ of approximately 25.35°, assigned to (101) lattice planes of TiO$_2$, which is attributed to the signal of anatase phase [30]. However, XRD results have not confirmed the presence of rutile phase for sample CM$_3$/TiO$_2$, suggested by Raman spectroscopy.
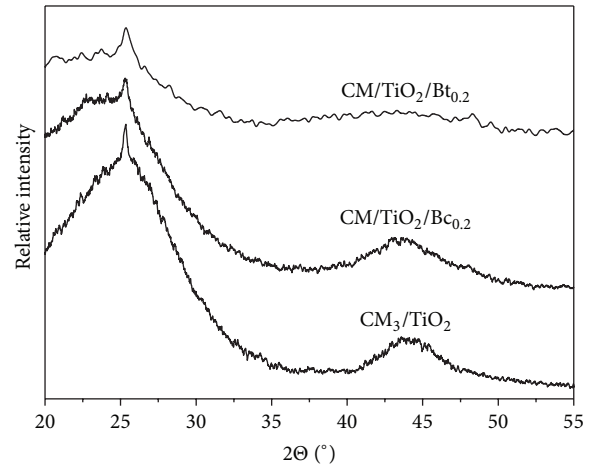
3.3. Methylene Blue Adsorption Test. The decrease of MB concentration in the solution as a consequence of adsorption on CM, carried out in the dark, is shown in Figure 6. Results obtained for CM photocatalysts prepared by thermal treatment (CM$_2$/TiO$_2$, CM$_3$/TiO$_2$, and CM$_5$/TiO$_2$) indicate that thicker disks induce better adsorption of MB. The level of MB adsorption is determined by CM specific surface area and the amount of surface oxygen groups, which function as centers of MB condensation in the physical adsorption process. In the flow system, thicker disc provides longer contact between MB solution and activated carbon on the CM inner capillary walls. Since activated carbon layer determines adsorption characteristics of CM, thicker discs provide better MB adsorption. Nevertheless, for samples CM$_2$/TiO$_2$,
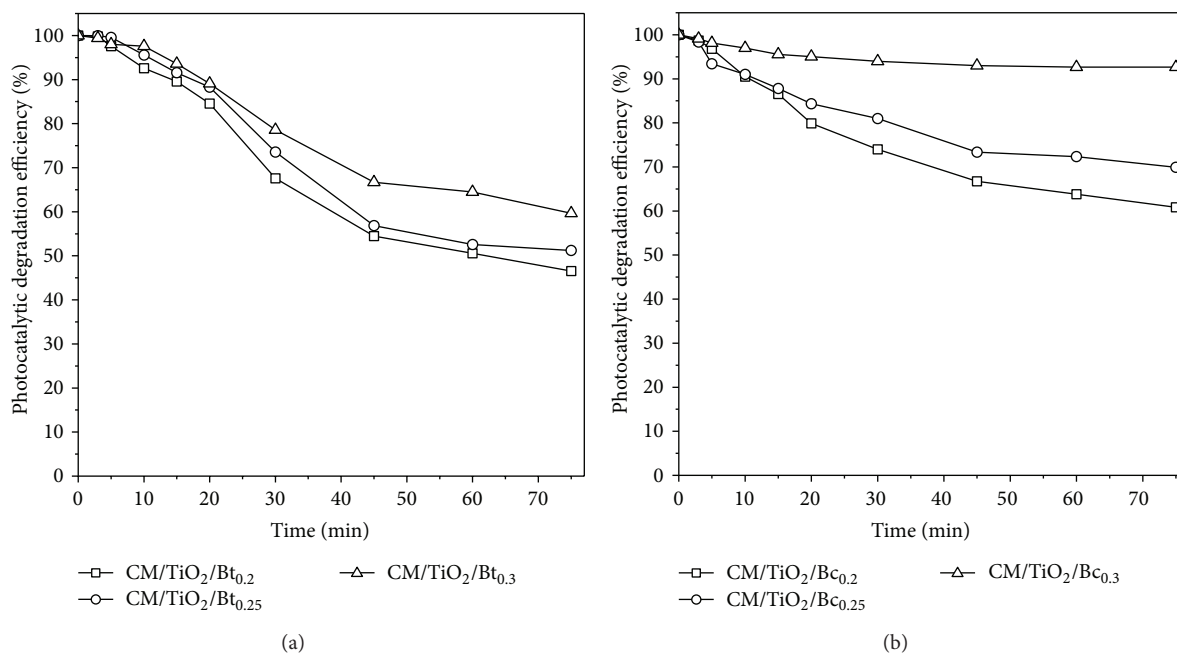
(a)

(b)

FIGURE 7: Degradation of MB in the presence of CM composite photocatalysts obtained by using Teflon (a) and sodium carboxymethyl cellulose (b) as a binder.

CM_3/TiO_2, CM_5/TiO_2, and $CM/TiO_2/Bt_{0.25}$ adsorption equilibrium was reached after 20 minutes and MB concentration was decreased up to 10%. However, in the presence of sample $CM/TiO_2/Bc_{0.25}$ equilibrium was reached after 45 minutes and concentration of MB was decreased for approximately 31%. Since sodium carboxymethyl cellulose can act as an ion-exchanger [31], decrease in the MB concentration may be the consequence of two simultaneous processes occurring on the $CM/TiO_2/Bc_{0.25}$ surface: adsorption onto CM surface and ion exchange reaction between MB and sodium carboxymethyl cellulose. Taking into account the decrease of the MB concentration induced by adsorption onto CM surface (up to 10%), relatively high concentration decrease and slower equilibrium reach in the case of sample $CM/TiO_2/Bc_{0.25}$ primarily originate from ion exchange reaction between sodium carboxymethyl cellulose and MB.

3.4. Photocatalytic Activity. After reaching the adsorption saturation on CM in the dark, the UV lamp was turned on and the photocatalytic degradation of methylene blue on carbon monolith photocatalysts was monitored. The photocatalytic activity and the influence of the binder mass fraction of composite photocatalysts are presented in Figures 7(a) and 7(b). Figure 7(a) shows the degradation of MB in the presence of TiO_2 mixed with different ratio of Teflon. It can be noted that photocatalytic activity decreases with increasing mass fraction of binder. The sample $CM/TiO_2/Bt_{0.2}$ shows the highest level of methylene blue degradation (Figure 7(a)).

The similar trend of photocatalytic activity is obtained for samples prepared with sodium carboxymethyl cellulose as a binder. As it is shown in the Figure 7(b), the highest

level of MB photocatalytic degradation was obtained in the presence of the sample with the lowest mass fraction of sodium carboxymethyl cellulose.

Additionally, samples obtained by using Teflon as a binder showed higher photocatalytic activity compared to the sodium carboxymethyl cellulose composites. At this point we can only assume that this higher photocatalytic activity is a consequence of binder nature which provides lower coverage of TiO_2 particles.

Photocatalytic activity of all tested composite photocatalysts is influenced by mass fraction of the binder. The reason of decreased photocatalytic activity lies in the possibility of masking titanium dioxide located on the surface of carbon monolith, as well as within the pores, with a binder. In order to assess the influence of the binder presence, photocatalytic activity of the composite catalysts, obtained by dip-coating method, was compared to the CM catalysts obtained by thermal treatment. As it is shown in the Figure 8, the sample without a binder, obtained by thermal treatment, has noticeably better photocatalytic activity than composite photocatalysts. The absence of binder allows more homogenous coverage of CM surface with TiO_2 particles (Figure 3). Furthermore, porous structure as well as oxygen groups on CM surface are more available for MB adsorption. As it was reported [5], high level of MB adsorption on the carbon carrier surface elevates the photocatalytic activity of TiO_2. Turning on the UV lamp leads to the photocatalytic degradation of more accessible, adsorbed, MB on CM/TiO_2 surface. After that, surface oxygen groups as well as porous structure are again available for adsorption which elevates the photocatalytic activity of sample CM/TiO_2 and therefore improves its efficiency in organic pollutants removal.
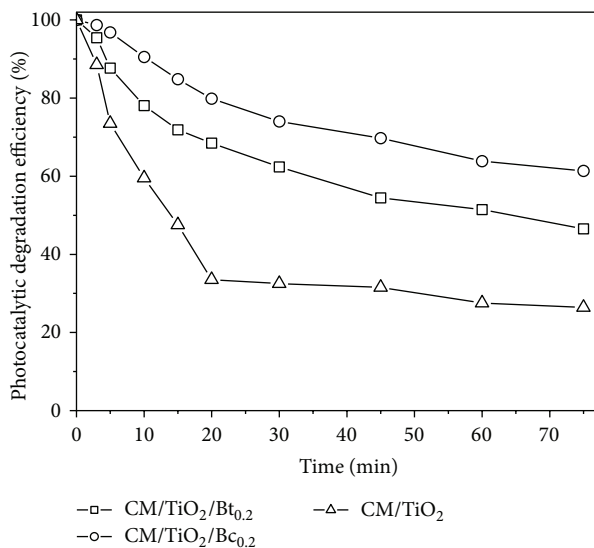
FIGURE 8: Degradation of MB in the presence of CM/TiO_2 with and without the binder (CM disk thickness of all samples is 2 mm).
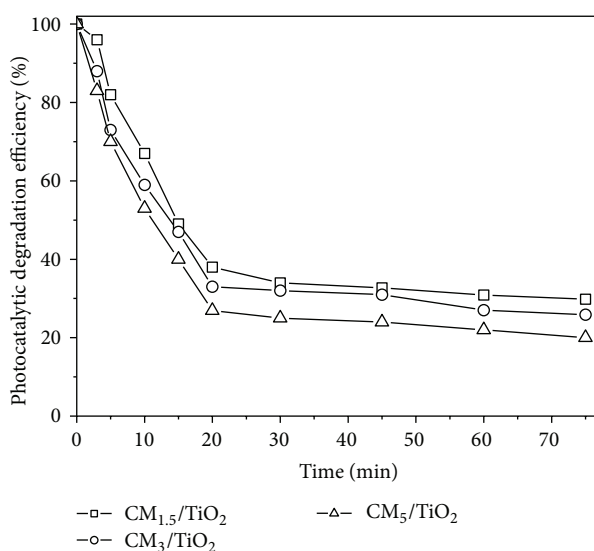

FIGURE 9: Degradation of MB in the presence of CM/TiO_2 for different discs thickness.

The influence of disk thickness on photocatalytic activity was tested using CM catalysts, obtained by thermal treatment, with different discs thickness. The photocatalytic activities of used samples were evaluated by measuring the decoloration rate of MB under UV irradiation, after adsorption saturation of used CM photocatalysts in the dark. The degradation curves are given in Figure 9.

The obtained results showed that decomposition rate of MB on examined samples follows the order, CM_5/TiO_2 > CM_3/TiO_2 > $CM_{1.5}/TiO_2$, and that photocatalytic activity increases for approximately 10% with increase of CM disc thickness from 1.5 to 5 mm. Thicker disk enables longer contact between MB solution and activated carbon on the CM inner capillary walls, which is responsible for adsorption.

For all samples, the MB concentration decreases rapidly in the first 20 minutes and then slows down until it reaches the equilibrium. Rapid decomposition of MB in the beginning is reasonable which is supposed to be due to the higher concentration gradient which causes faster diffusion and quicker photocatalytic degradation. As the time progressed, photocatalytic degradation starts to slow down due to the low solute concentration in the solution.

Comparing to the literature [5, 6, 30], all tested samples have good photocatalytic activity. Therefore, the sample CM_5/TiO_2 showed the best photocatalytic activity, since it decreases the MB concentration for nearly 80%.

4. Conclusion

Carbon monolith photocatalysts obtained by new thermal treatment showed much better photocatalytic activity toward methylene blue degradation than composite photocatalysts obtained by dip-coating method. The absence of binder in thermal treatment excluded the TiO_2 coverage and enables better accessibility of catalysts particles to the methylene blue solution. Carbon monolith carrier contains a considerable amount of surface oxygen groups, which, along with relatively high specific surface area, induced its good adsorption properties. It was found that high level of methylene blue adsorption on carbon monolith carrier elevates the photocatalytic activity of TiO_2. Photocatalytic activity increases with carbon monolith disc thickness due to increase in both level of methylene blue adsorption and amount of deposited TiO_2.

Due to its specific shape and good surface characteristics carbon monolith represents good carrier for TiO_2. Utilization of new thermal treatment as a method of TiO_2 deposition and carbon monolith as catalysts carrier represent cheap and simple way for obtaining photocatalysts for methylene blue removal from water solution.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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