Introduction

Because of a big demand for colored chemical compounds, more than 0.7 million tons of organic synthetic dyes are manufactured each year. They are produced mainly for use in the textile, leather goods, industrial painting, food, plastics, cosmetics, and consumer electronics sectors [1]. However, the release of colored wastewaters is considered to be a dramatic source of non-aesthetic pollution, eutrophication, and perturbations in aquatic life. Therefore, new efficient methods of their removal need to be evaluated. Among advanced oxidation processes, heterogeneous photocatalysis seems to be the most efficient. Therefore, it is commonly used in the removal of undesired substances. Dyes are also used as model compounds in studies concerning synthesis and/or preparation of new photocatalysts [7, 8]. Photocatalysis was also used for the degradation of other compounds. They include insecticides – imidacloprid [9]; pharmaceuticals – olanzapine [10], bezafibrate [11], sulfamethazine [3], chloramphenicol [12], anilinium [13], tetramethylammonium [4], benzoate [4], β-naphthol [14], toluene [15], pentachlorophenol [16], p-toluenesulfonic acid [17], dichloroacetate [4], propanol [18], and acetaldehyde [8], as well as bacteria, e.g. Escherichia coli [19]. Photodegradation also has been applied in a decontamination of complex mixtures like petroleum refinery wastewater [20].

Among other semiconductors titanium dioxide (TiO2) seems to be the most commonly used photocatalyst. However, as TiO2 possesses a 3.2 eV energy band-gap its excitation requires ultraviolet light, which lowers the effi-
ciency of the catalytic photodegradation process. What is more, there is a need to eliminate the possibility of the electron-hole pair (e\textsuperscript{−}-h\textsuperscript{+}) recombination. Therefore, different steps already have been taken toward enhancing photocatalytic activity of inorganic semiconductors. They include: dipping photocatalyst in acid solutions [21], surface chemical modification through preparation of dye-modified photocatalysts [4, 22], or by attaching other organic compounds like sulfanilic acid [23], porphyrin [24], hypocrellin B [25], metal [19], and nonmetal [26-28] doping of inorganic semiconductors and co-catalysts preparation [29].

Carbon nanostructures – TiO\textsubscript{2} composites constitute another group of potential photocatalysts. Different types of carbonaceous materials [30] such as carbon black [31, 32], graphite [33, 34], and graphitized materials [35, 36], have already been applied. A significant potential lies in carbonaceous nanostructures in conjunction with TiO\textsubscript{2} since photocatalytic activity can be attributed to the TiO\textsubscript{2} while the absorptivity to the fullerene. The carbonaceous-titania composites are usually obtained by sol-gel [37, 38] or evaporation-drying methods [30, 39].

The aim of our presented studies was to prepare the TiO\textsubscript{2}-C\textsubscript{60} nanocomposites and examine their photocatalytic activity. The applied evaporation-drying procedure allowed us to obtain in a short time a series of materials with varying mass ratios of C\textsubscript{60} to TiO\textsubscript{2}. Photocatalytic activity of the obtained nanocomposites was examined by investigating the methylene blue degradation in water. UV-VIS spectrophotometry was applied to monitor the bleaching of a dye. A series of techniques, including SEM and TEM microscopies, Raman and UV-VIS diffuse-reflectance spectroscopies along with DSC and TGA analysis, was used to characterize the prepared material.

Materials and Methods

Materials

TiO\textsubscript{2} (anatase) and methylene blue from Park Scientific Limited. HPLC-grade acetonitrile was purchased from J. T. Baker. All solutions were prepared using deionized water, which was obtained by Polwater apparatus.

C\textsubscript{60}-fullerene, sublimed 99.9%, was purchased from Sigma-Aldrich, Poland

Photocatalyst Preparation

C\textsubscript{60}/TiO\textsubscript{2} nanocomposites were prepared by evaporation-drying method as others described [39]. 2 mg of C\textsubscript{60} were dispersed in deionized water and sonicated for 15 min. After that time TiO\textsubscript{2} powder was added and an additional 15 min of sonication were applied. The obtained suspension was heated to 80\textdegree C in the water bath and constantly sonicated. After water evaporated, the obtained composite was dried overnight in an oven at 100\textdegree C. C\textsubscript{60}/TiO\textsubscript{2} nanocomposites were prepared at 1:100, 1:20, 1:10, and 1:1 mass ratios of C\textsubscript{60} to TiO\textsubscript{2}.

Characterization of the Composite

A Renishaw Raman InVia Microscope equipped with a high sensitivity ultra-low noise CCD detector was employed. The radiation from an argon ion laser (514 nm) at an incident power of 1.15 mW was used as the excitation source. Raman spectra were acquired with 3 accumulations of 10 s each, 2400 l/mm grating and using 20x objective.

Scanning electron microscopy was applied to investigate the morphology of the C\textsubscript{60}/TiO\textsubscript{2} nanocomposites. They were imaged by secondary electron SEM with the use of an INSPECT S50 scanning electron microscope from FEL. The accelerating voltage of the electron beam was 30 keV and the working distance was 10 mm.

Differential scanning calorimetric (DSC) and thermogravimetric (TGA) analyses were performed by a Thermal Analyzer TGA/DSC 1 (METTLER TOLEDO) with a heating rate of 15\textdegree C/min under nitrogen environment with flow rate = 20 ml/min. All runs were carried out from 25\textdegree C to 1500\textdegree C. The measurements were made in alumina crucibles with lids.

Photolytic as well as photocatalytic degradation experiments were carried out by irradiation with a solar simulator apparatus, namely SUNTEST CPS+ (ATLAS, USA) having energy density of 250 W/m\textsuperscript{2}.

Photocatalytic Degradation Experiment

Photocatalytic degradation experiments were performed in a 50 mL glass cell. The reaction mixture consisted of 20 mL of methylene blue (MB) sample (6x10\textsuperscript{5} mol/L) and a photocatalyst (1.6 mg/mL). Prior to irradiation the dye-catalyst suspension was kept in the dark with stirring for 1 hour to ensure an adsorption-desorption equilibrium. To determine MB degradation, the samples were collected at regular intervals (10 min during 1\textdegree hour and 15 min during 2\textdegree hour) and centrifuged to remove photocatalyst.

Spectrophotometric Analysis

UV spectrophotometry was used to monitor the current concentration of MB. All spectrophotometric determinations were done using a U-2800A Hitachi spectrophotometer. The following working conditions of the apparatus were applied: scan speed 1,200 nm/min and spectral bandwidth (1.5 nm). UV studies were done using 1 cm quartz cell. Absorbance was recorded in the range of 190-700 nm, and the maximum absorption wavelength experimentally registered at \(\lambda=610\) nm was used for the calibration curve and further concentration measurements.

HPLC Analysis of MB Intermediates

The chromatographic system (Thermo Separation) consisted of a 2D UV 3000 Spectra System, a P2000 low-gradient pump, a vacuum membrane degasser SCM Thermo Separation, and a Rheodyne loop injector (20 µL) were used. ChromQuest Chromatography Data system software
for Windows NT was applied for acquisition and storage of data. Waters Spherisorb ODS-2 150 mm × 4.6 mm analytical column packed with 5 μm particle size was used. Separation was achieved using an isocratic method. The mobile phase consisted of acetonitrile:water (60:40 v/v). The flow rate of the mobile phase was 1 mL/min and the injection volume was 100 μL. The column was maintained at room temperature. The DAD detector was set at 245 nm. The detected retention time of methylene blue was 2.07 min.

Results and Discussion

Characterization of C\textsubscript{60}/TiO\textsubscript{2} Composites

The homogeneity of the obtained materials was examined. Fig. 1 shows the scanning electron micrographs of the C\textsubscript{60} (Fig. 1a), TiO\textsubscript{2} (Fig. 1f), and C\textsubscript{60}/TiO\textsubscript{2} composites (Figs. 1b-e). The larger flakes with a smooth surface correspond to the C\textsubscript{60} while the smaller particles to the TiO\textsubscript{2}. The proportions of smooth flakes to the smaller particles in the pre-

Fig. 1. SEM micrographs of C\textsubscript{60} (a), C\textsubscript{60}/TiO\textsubscript{2} (with mass ratios of 1:1 (b), 1:10 (c), 1:20 (d), 1:100 (e)) and TiO\textsubscript{2} (f).
sented pictures is in agreement with the mass ratios of C_{60} to TiO_2 in the prepared composites. It can be seen that the greater amount of TiO_2 that was introduced, the smaller smooth surface that is present in the image. This can be attributed to the coverage of C_{60} surface by TiO_2 particles.

Transmission electron microscopy (TEM) images of C_{60}/TiO_2 (1:20) composite are presented in Fig. 2. Two sets of well-resolved lattice fringes are visible from a magnified image of Fig. 2a. The spacing of 0.35 and 0.81 nm measured for these two sets of fringes (Figs. 2b and c) coincides with the d-spacing of (011) type planes in anatase form of titania and face-center-cubic (fcc) C_{60} crystal, respectively.

The Raman spectra of the C_{60}/TiO_2 composites are illustrated in Fig. 3. In each spectrum the same number of peaks at the same Raman shifts are present. Five of them, at 142, 198, 396, 514, and 639 cm^{-1} (Fig. 2a), correspond to the anatase phase of TiO_2. They are designated as E_g(1), E_g(2), B_1g(1), A_1g+B_1g(2d), and E_g(3) modes [27, 28], respectively. Those characteristic peaks of the anatase phase confirm that the TiO_2 crystal phase remained unchanged in the prepared composites. The last peak at 1,468 cm^{-1} corresponds to the pentagonal pinch mode A_g(2) of C_{60} [29]. Above-mentioned spectra indicate the presence of both components of the C_{60}/TiO_2 nanocomposite.

Thermal profile of prepared composites was obtained by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis. TGA curves of C_{60}/TiO_2 (1:100, 1:20, 1:10, 1:1) (Fig. 4A) show mass loss at around 740, 790, 800, and 910°C, respectively. It was attributed to the C_{60} decomposition on the basis of the increased mass loss with the increasing mass ratios of C_{60} to TiO_2. In those temperature ranges DSC endothermic peaks appeared too (Fig. 4B). The higher amount of fullerene was applied in C_{60}/TiO_2 composites, the greater heat flow was released. Therefore, both TGA and DSC curves confirm the appropriate mass ratios of C_{60} to TiO_2 as they were introduced during synthesis. Besides, the small endothermic peaks at 730, 800, 820, and the curve bend at 920°C on the curves of C_{60}/TiO_2 (1:100, 1:20, 1:10, 1:1, respectively) can be attributed to the polymorphic anatase-rutile transformation [40].

Fig. 5 shows the UV-VIS diffuse-reflectance spectra of TiO_2 and prepared C_{60}/TiO_2 composites. It was found that TiO_2 exhibits only one absorption band edge, while C_{60}/TiO_2 displayed two absorption band edges. The band gap energies of the samples were estimated using the following equation: E_g = 1240/\lambda, where E_g is the band gap energy (eV) and \lambda is the absorption wavelength (nm). The first E_g for TiO_2 and C_{60}/TiO_2 (1:100; 1:20; 1:10; 1:1) was determined to be 3.14 eV, 3.06 eV, 2.99 eV, 2.95 eV and 2.25 eV, respectively. The emergence of the second band edge for all C_{60}/TiO_2 composites indicates that C_{60} doping had occurred. The results suggest that C_{60}/TiO_2 composites have the possibility of higher photocatalytic activity under solar light irradiation.

**Photocatalytic Activity Studies**

The photodegradation of methylene blue (MB) was measured in order to probe how coupling C_{60} to TiO_2 affects photocatalysis. Fig. 6 shows the MB absorption spectra during the photodegradation reaction. A steady decrease of the absorbance of the methylene blue solution was
observed in the experimental time. The disappearing peaks at 244, 290, 610, and 662 nm in the UV-VIS-spectra indicate a degradation of the MB molecules. However, above 230 nm, where the isosbestic point has occurred, a small increase in absorbance values was observed. These observations suggest that the photochemical reduction of MB has taken place. According to previously published reports [41, 42], the observed photobleaching and the increase of the peak at 230 nm corresponds to the generation of leuco-methylene blue, which main absorption peak is at this wavelength. The presented conclusion was confirmed by chromatographic analysis. The obtained results proved that phodegradation of MB is a more complex process and at least four intermediates were detected after a 30-minute reaction. The recorded chromatograms showed five peaks at retention times 2.01, 3.38, 5.14, 6.49, and 9.33 min, which correspond to MB and its photoproducts, respectively. The same number of peaks at the same retention times were present in all chromatograms, no matter the mass ratio of C₆₀ to the TiO₂ in the applied photocatalysts. Those observations indicate that the mechanism of the MB degradation is the same in the case of the application of all composites. The only difference concerns the speed rate of the MB decomposition. It was observed that some generated photoproducts are light-sensitive and disappeared during irradiation [41, 42]. These results suggest that the presence of C₆₀ on TiO₂ surface enhances photocatalytic activity of TiO₂ by its sensitization. C₆₀ fullerene is easily transformed by UV/VIS radiation into a single excited state that is rapidly converted into the much longer-lived triplet excited state [43]. C₆₀ exhibits the ability to accept up to six electrons [44].

The energy levels of the C₆₀ LUMO orbital and TiO₂ conduction band are equal to -4.1 eV [45] and -4.26 eV [46], respectively. The difference in these values causes an electron transfer from C₆₀ to titania conduction band. The electron injected to the TiO₂ leads to the creation of radicals, which are responsible for degradation of organic matter [35]. The obtained results showed that anchoring fullerene on TiO₂ surface by evaporation-drying method improves its photocatalytic property.

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**Fig. 4.** Thermal analysis profile of C₆₀/TiO₂ composites with mass ratios of 1:100 (a), 1:20 (b), 1:10 (c), and 1:1 (d): TGA (A), DSC (B).

**Fig. 5.** UV-VIS diffuse-reflectance spectra of TiO₂ (a) and prepared C₆₀/TiO₂ in mass ratios of 1:100 (b), 1:20 (c), 1:10 (d) and 1:1 (e).

**Fig. 6.** Normalized UV-VIS spectra of MB with the increasing irradiation time during application of C₆₀/TiO₂ (1:20) as a photocatalyst.
Results of kinetic studies are presented in Table 1. The plot of ln(C₀/Cₜ) versus t (Fig. 7) was used for the estimation of the pseudo first-order rate constant, kapp, and the half-life, t₁/₂, of the MB photocatalytic degradation. The photocatalysis using the composite of 1:1 mass ratio of C₆₀ to TiO₂ was found not to suit pseudo first-order kinetics in the experiment time range. Nevertheless, when a shorter time (20 min) is considered, pseudo first-order kinetics can be observed. The rate of MB degradation in the case of its application was extremely high at the beginning of the process (0-20 min). However, further progress was insignificant. When other composites were introduced as photocatalysts, pseudo first-order kinetics were fulfilled during the whole irradiation process (120 min). The highest t₁/₂ value was obtained when bare TiO₂ was applied, while the lowest in the case of C₆₀/TiO₂ (1:20). It was found that the greater amount of C₆₀ was applied the lower kapp and higher t₁/₂ values were observed. This relationship worked until 1:10 mass ratio of C₆₀ to TiO₂ was reached, because this composite was found to be less photocatalytically active. The highest photocatalytic activity was revealed by C₆₀/TiO₂ (1:20) composite with kapp of 0.0117 mol/L and t₁/₂ of 59 min.

Higher photocatalytic activity of prepared nanocomposites can be undoubtedly attributed to the C₆₀ presence. We believe that that enhancement results from the absorptivity of C₆₀ and the sensitization of the TiO₂. Therefore, when solar energy is applied not only ultraviolet, but also a part of the visible spectrum can be used to observe photocatalytic activity of examined photocatalysts.

### Conclusions

Conducted experiments confirmed the photocatalytic ability of C₆₀/TiO₂ nanocomposites. Composites in all prepared mass ratios showed higher catalytic activity than sole TiO₂. However, the best photoactivity was reached in the case of the application of C₆₀/TiO₂ (1:20). We believe that huge potential lies in composites that are based on carbonaceous nanomaterials and TiO₂ as new efficient photocatalysts. As heterogeneous catalysis has been recently applied as a new route for the destruction of undesired compounds present in the environment, prepared nanocomposites could potentially be used during decontamination of organic pollutants. Dyes, to which MB belongs, represent a group of undesired compounds. Investigations concerning the degradation of other representatives of hazardous materials with the usage of described photocatalysts will be shown in a forthcoming paper.

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### References


