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Original Research

Methylene Blue and Phenol Photocatalytic Degradation on Nanoparticles of Anatase TiO_2

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Abstract

A photocatalyst was obtained by treating the commercial amorphous anatase titanium dioxide with ammonia water. During the preparation of photocatalytic material the optimal conditions of the separation operation were found. The photocatalyst was characterized by UV/VIS-DR, FTIR-DR, and XRD techniques, and high-resolution transmission electron microscopy (HR-TEM). According to the XRD method, the mean crystalline size of TiO_2 was 12.7-13 nm. The particulates were characterized using a particle size analyzer (mean size 195.7 nm). TEM studies presented the morphology of the sample. The photocatalytic activity of the photocatalyst was determined on the basis of the decomposition rate of phenol and azo-dye (methylene blue) under UV irradiation. The pH effects on the photocatalytic degradation were investigated. The degree of the dye and phenol removal in the solutions was measured by UV/VIS spectroscopy and a TOC analyzer. The decomposition of methylene blue increased along with an increase of pH value, whereas the activity of the prepared photocatalyst toward phenol degradation was the highest at pH=6.5. TOC disappearance in solutions of both organic compounds during photocatalytic reaction corresponded to their decrease of concentration, but with a little delay.

Keywords: photocatalytic decomposition, titanium dioxide, methylene blue, phenol, pH

Introduction

Waste waters containing azo-dyes are some of the most recalcitrant classes of organic compounds to treat, due to their azo groups usually attached to radicals, of which at least one is an aromatic group [1, 2]. It is well known that some azo-dyes and their degradation products are highly carcinogenic. Colored waste waters in the ecosystem are a source of aesthetic pollution, of eutrophication, and of perturbations in aquatic life [3]. Among organic materials, phenolic compounds are also a serious group in aqueous solutions, which causes severe environmental problems [4]. Phenols and phenolic compounds are common pollutants of aquatic systems that also reveal toxicity. Moreover, chlorination of waters for disinfection produces chlorinated phenols [5].

Technologies involving physical or biological treatments [6, 7] do not achieve significant organic pollutant degradation. However, heterogenous photocatalysis is an advanced oxidation process (AOP) that can be successfully used to oxidize many organic pollutants present in aqueous systems [8, 9]. Among the semiconductors used, TiO_2 is considered particularly efficient [10, 11] owing to the formation of an electron-hole pair under illumination with near UV light [7]. Especially the TiO_2/UV system, due to its non-toxic, inexpensive, and high reactive nature, has been mainly used to oxidize wastewater-containing dyes [1, 12] and phenolic compounds [4, 5].

Many studies have shown the effects of operational parameters of the conducted photocatalytic processes on the quality and quickness of degradation of organic compounds using the TiO_2/UV system [13]. Lakshmi et al. [14] showed during their studies that the rate of photo-

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catalytic reaction increased with a rise of the amount of catalyst, and remained almost constant above a certain level. The influence of the initial concentration of methylene blue on decolorization time was observed. While conducting many photocatalytic processes, dependence indicating an increased rate of dye degradation along with an increase in the compound concentration to a certain level was found. But in case of phenol, Chiou et al. [4] indicated that photocatalytic oxidation is rather promising at low organic pollutant concentrations. Tang et al. [1] also raised strong dependence treatment efficiency upon wavelength, light intensity, and the molecular structure of compounds.

According to Wang et al. [15], one of the most important parameters having an effect on pollutant degradation is the pH value of a solution. They found that the decomposition of phenol in the TiO_2/UV process strongly indicated pH influence on such properties as semiconductor surface charge state, flat band potential, and dissociation of the solution [4]. Many dyes have negatively charged groups in their structures, and in acidic solutions strong adsorption of dyes onto photocatalyst surface improving decomposition of these pollutants does take place. This behavior in literature described elsewhere [16] is due to the amphoteric properties of TiO_2 particles. Since methylene blue is a cationic dye, its adsorption on TiO_2 surface and decomposition are favored at high pH values, which was put forward by Guillard et al. [17]. The present study also shows that there is a high probability that the degradation of substrates occurs on the surface of the photocatalyst.

The use of TiO_2 particles as a photocatalyst for the initiation of redox chemical reactions and finding their best condition are continuously an active area of investigations. In the present paper, we report photodegradation of methylene blue and phenol on prepared TiO_2 in tests under UV irradiation. In this work, we also carried out characterization of prepared TiO_2 and described the influence of pH of solutions on the degree of organic compounds decomposition.

Experimental

Materials

The commercial amorphous anatase titanium dioxide was used as a base material. The photocatalyst was supplied by the Police Chemical Factory in Poland.

Azo-dye (methylene blue), produced by the Boruta-Color Company (Poland) and phenol were used as model organic compounds for photocatalytic tests.

Preparation of the Photocatalyst

Crude commercial amorphous anatase titanium dioxide shows a strong acid reaction (1.3-2.0). Therefore, the investigated material was washed with ammonia water in order to neutralize acid reaction. Then it was washed off several times with distilled water in order to remove sulphate ions and an excess of ammonia. The following step was the separation of titanium dioxide particles from water solution. Subsequently, TiO_2 was dried at 80ºC for a few hours. Finally, the photocatalyst obtained was ground with a mortar.

H_2SO_4 was added into a little part of the photocatalyst obtained in this way in order to instantaneously neutralize alkali reaction caused by the excess of ammonia water. Two TiO_2 samples with and without the addition of H_2SO_4 were tested using the methods described below.

Characterization of the Photocatalyst

The photocatalyst sample has been characterized by UV-VIS/DR using a spectrophotometer (Jasco, Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra, where $BaSO_4$ was used as a reference. The spectra as well as band gap energy calculations were performed using Jasco procedure contained in the Jasco computer program.

The surface properties of the photocatalyst were recorded on the basis of FTIR/DRS spectra. The measurements were performed using an FTIR spectrometer (Jasco, Japan) equipped with a diffuse reflectance accessory from the Harrick Company (USA).

The photocatalyst sample has also been characterized by XRD technique using X'Pert PRO Philips diffractometer. The mean size of crystallites and the participation of TiO_2 phases was measured.

The particle size of the photocatalyst was measured with a Zetasizer Nano-ZS manufactured by the Malvern Company.

The morphology of the sample was also studied via an FEI Tecnai F30 high resolution transmission electron microscope.

Photocatalytic Decomposition

The photocatalytic activity of the prepared TiO_2 was analyzed by photocatalytic decomposition of phenol and methylene blue. The reactions were carried out in a glass batch photoreactor containing 500 cm^3 of a solution and 0.1 g of the photocatalyst. Aqueous solutions of phenol and methylene blue were used with concentrations of 50 mg/l and 10 mg/l, respectively. Aqueous suspensions of TiO_2 containing phenol or methylene blue (under constant magnetic stirring) were irradiated for different intervals of time. Irradiation of the solutions was performed under UV-Vis light (6 lamps with power of 20 W, Philips) with a radiation intensity of approximately 166.65 W/m^2 for Vis and 182.873 W/m^2 for UV. The concentration of the dye and phenol was monitored by measuring the absorbance of the samples using a UV-Vis spectrometer (Jasco, Japan). The concentrations in the solutions were calculated by a computer program based on the calibration curve. The program determines the absorbance of a solution at the maximum wavelengths of the investigated organic compounds. The progress of the reaction was followed by monitoring the disappearance of the methylene blue at 664 nm and the phenol at 270 nm. In order to evaluate the mineralization of chemical substances, the total organic carbon (TOC) of the samples was also analyzed with a multi N/C 2000 Analytic Jena analyzer.

The photocatalytic degradations of phenol and methylene blue were carried out at different pHs. The pH of the solutions was adjusted with a Seven Multi Mettler Toledo using NaOH or HCl.

Results and Discussion

The operation of separation was important to our study. After washing with ammonia water and several times with distilled water the photocatalyst should be separated from the water solution. Such TiO_2 has a negative pzc. An addition of an acid solution, i.e. H_2SO_4 in our case, to titania washed off with ammonia water, enabled us to find zeta potential of the prepared TiO_2 equal to zero. Zeta potential is a potential difference between the absorbing layer and diffuse layer [18]. When the zeta potential equals zero, TiO_2 particles do not have any interaction. The important feature is the fact that pH affects the zeta potential. In the present experiments it was shown that the zeta potential of the studied TiO_2 is equal to zero at pH=6.8. At this zero point of charge the sedimentation of the photocatalyst proceeded quickly and precisely.

The UV-VIS/DR spectra of a crude photocatalyst after treatment with NH_{3aq}, as well as the TiO_2 after an addition of H_2SO_4, are presented in Fig. 1. For both photocatalysts prepared for this study there is one absorption edge in the UV region (of λ=370 nm, E_g=3.351 eV for the catalyst after treatment with NH_{3aq} only and of λ=374 nm, E_g=3.315 eV for the catalyst after the addition of H_2SO_4). From the presence of the UV absorption edge it can be supposed that the catalyst should be active under UV light illumination only. The character of UV-VIS/DR spectra and the band-gap energy of both samples of the photocatalyst are nearly the same. An addition of H_2SO_4 during the preparation of the photocatalyst has no influence on UV-VIS-DR spectra or on any band-gap energy of the photocatalyst.

FTIR spectroscopy was used to analyze the prepared photocatalyst. FTIR patterns of both samples of the photocatalyst, TiO_2 after treatment with NH_{3aq}, and the same after the addition of H_2SO_4 are shown in Fig. 2. In the case of both samples, absorption bands appeared on the absorption spectra in the range of 3,300-3,500 cm^{-1}. The fact that these bands are to be found is due to the presence of adsorbed water and hydroxyl groups [19]. The bands can also be observed in both spectra of 1,630-1,640 cm^{-1}. It can be assigned to molecular water-banding mode [19, 20]. It is possible to observe insignificant bands in the range of 2,400 cm^{-1}. This fact is caused by the presence of CO_2 during the preparation of these samples. According to Ihara et al. [21] the exhibition bands at ca. 1,430-1,440 cm^{-1} could be attributed to bending vibrations of NH_4^+. It can be supposed that the spectra of TiO_2 treated with NH_{3aq} could exhibit some bands in this range. However, in both discussed samples bands in the spectra with a maximum at ca. 1,430-1,440 cm^{-1} were not observed. An absence of the mentioned bands could be explained by a properly conducted process of photocatalyst preparation and by precise washing of the excess of ammonia. In conclusion, NH_4^+ ion was not inbuilt into the surface of the photocatalyst. Hadjiivanov [22] observed a drastic absorbance increase below 1,000 cm^{-1} due to the self-adsorption of rutile. As shown below (X-ray powder diffraction), a small amount of a crystal phase of rutile was present in the investigated photocatalyst.

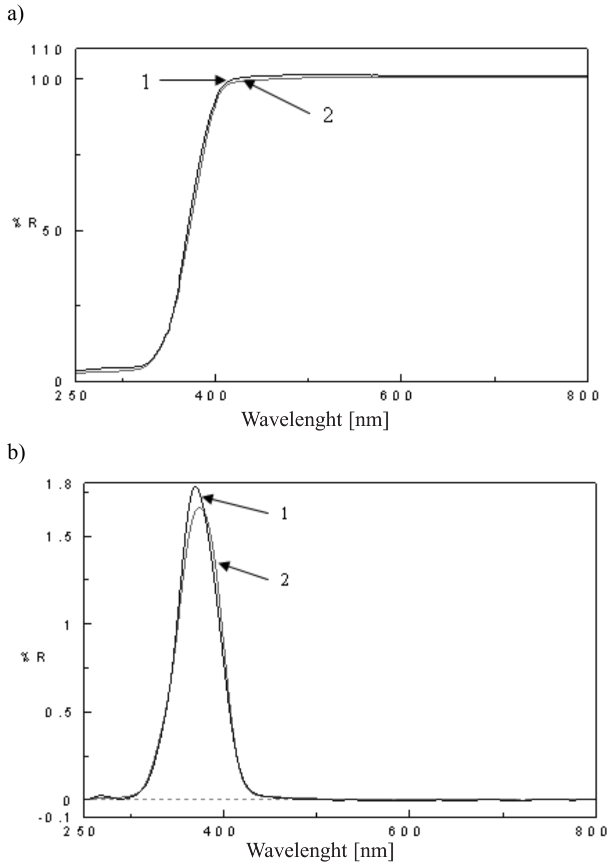

Fig. 1. (a) UV-Vis/DR reflection spectra of the photocatalysts: with NH_{3aq} only (1) and with H_2SO_4 in addition (2), respectively, (b) The first derivative of UV-Vis/DR absorption spectra of photocatalysts.

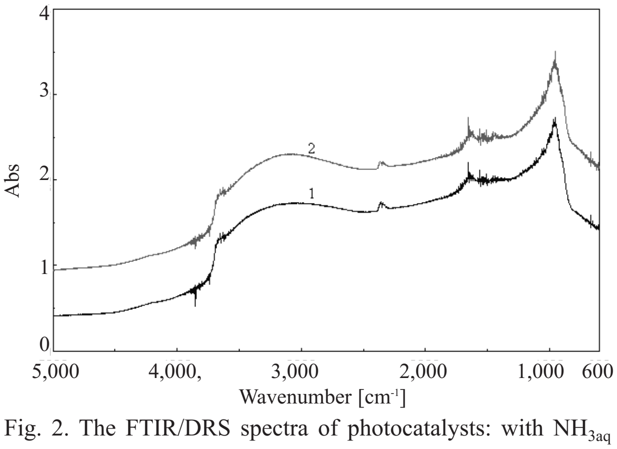

Fig. 2. The FTIR/DRS spectra of photocatalysts: with NH_{3aq} only (1) and with H_2SO_4 in addition (2), respectively.

Therefore, some bands with a high intensity in the low-frequency were detected. The spectra of both samples are nearly the same. This indicates that an addition of H_2SO_4 during preparation of the photocatalyst in order to improve the operation of sedimentation does not influence the surface properties of TiO_2 photocatalyst.

The powder X-ray diffraction patterns of TiO_2 after treatment with NH_{3aq} were taken using the diffractometer, where the X-ray source was CoK_α radiation. The pattern was collected in the range of 26-34º 2θ with a scan step of 0.02 in a continuous scan mode. The mean size of crystallites was calculated from the line broadening corresponding X-ray diffraction peaks, according to the Sherrer equation:

$$D = \lambda / \beta \cos\theta$$

...where D is the crystallite size, λ is the wavelength of X-ray radiation (CoK_α radiation, λ=0.17889 nm), β is line width at medium height, and θ is the diffraction peak angle. In order to find β, the full-width of the peak was calculated at half maxima of X-ray diffraction peaks. The results were obtained after the instrument was corrected. The mean crystallite size of the researched photocatalyst calculated from the discussed method increases to 12.7-13 nm.

Fig. 3 shows the diffractogram of the photocatalyst. It can be seen from the pattern that the prepared titanium dioxide exhibits diffraction lines of anatase phase. It was observed using XRD technique that the researched TiO_2 was not completely crystallized, but it consisted of crystalline (anatase and rutile) and amorphous fractions of titanium dioxide. Amounts of three forms of TiO_2 in the sample were calculated according to the following three equations:

$$R_A = \frac{I_A \cdot 100}{I_A + I_R \cdot 1.242}(\%)$$

$$R_R = \frac{1,242 \cdot I_R \cdot 100}{(I_A + I_R \cdot 1.424)}(\%)$$

$$R_{am}(\%) = 100 - [R_A(\%) + R_R(\%)]$$

...where R_A, R_R, R_{am} are contents of anatase, rutile, and amorphous phase, respectively. I_A and I_R are peak intensities of anatase and rutile.

The results obtained show that the values of the phases contained in the TiO_2 were equal to 35% of anatase, 3.5% of rutile, and 61.5% of amorphous phase.

Particle size distribution for the TiO_2 suspension is presented in Fig. 4a. The presented results were estimated on the basis of intensity according to the calculations contained in the computer program. The particles' size distribution can also tell about the stability of the suspension that is shown in Fig. 4b. The resulting mean particle size of the photocatalyst was 197.5 nm.

The transmission electron microscopy analysis of the prepared photocatalyst indicated the presence of a nanomaterial shown in Fig. 5. The sample is formed by the small crystalline phases embedded into the amorphous structure. The grains of the sample exhibit a regular round shape. These observations of the sample are in full agreement with the above-described XRD results.

The role of pH on the rate of photocatalytic degradation in solutions of phenol and methylene blue was studied. The effect of pH on the decomposition of these two organic compounds was summarized in Figs. 6 and 7, and pH was examined as one of the most important factors that can affect photo-oxidation processes. In order to check the degree of the photocatalytic degradation of phenol and methylene blue in solutions in different conditions, the percentage of decomposition during UV irradiation was analyzed. The best results in case of solutions of phenol were obtained at pH=6.5. After 6 h of illumination 35.18% of dye

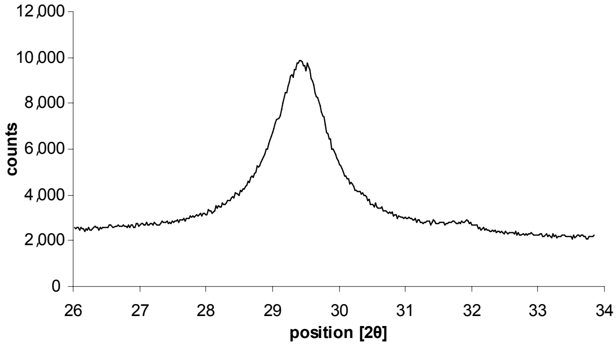

Fig. 3. The XRD pattern of photocatalyst washed off with ammonia water in the range 26-34º.

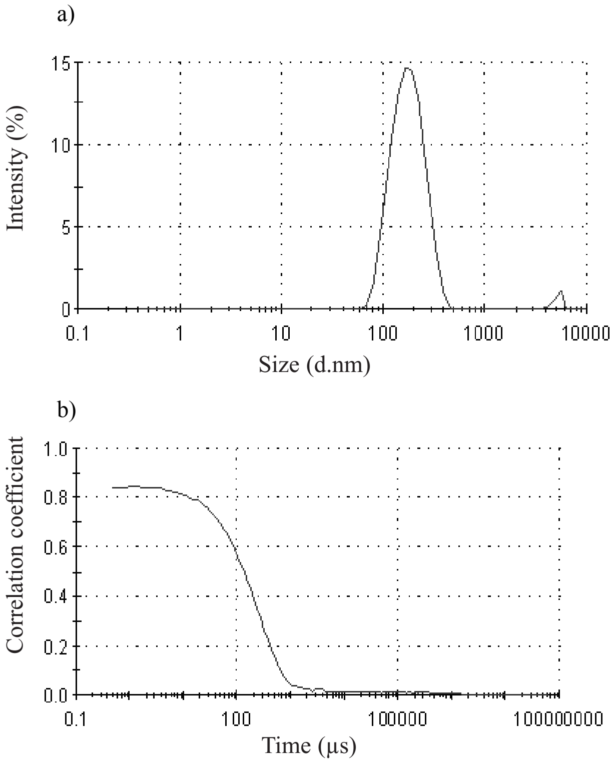

Fig. 4. (a) Size distribution by intensity of the TiO_2 in suspension, (b) raw correlation date.

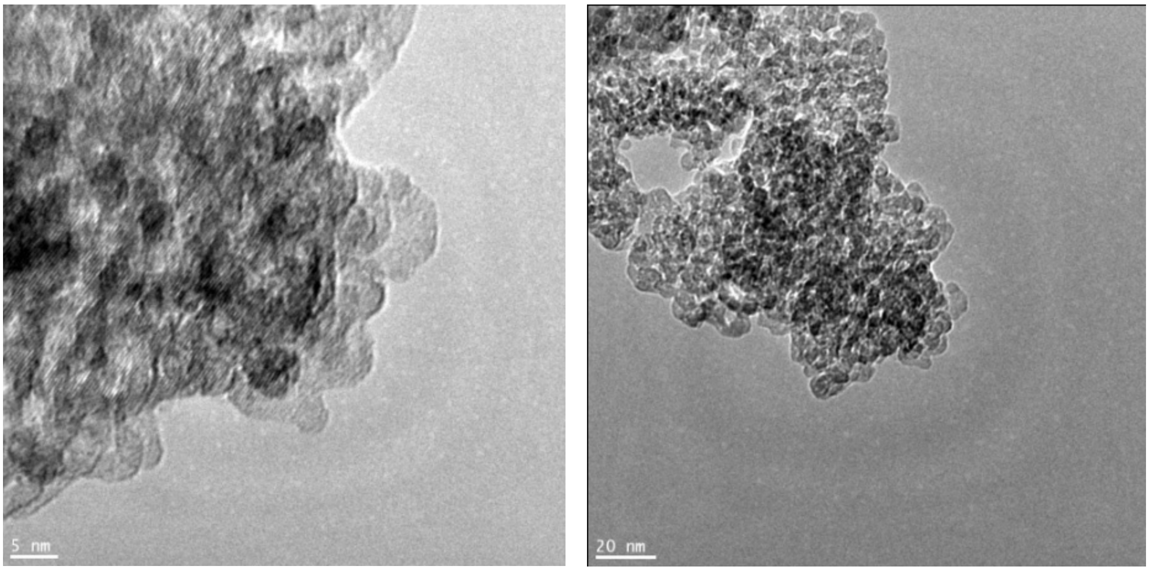

Fig. 5. TEM images of the prepared TiO_2 photocatalyst.

was removed. Nevertheless, after 14 h of irradiation this degree reached 60.55%. At the same time, others carried out experiments achieving 54.01%, 48.05%, and 39.95% of removal for solutions of phenol at pH=9, 3, and 7.2, respectively. A decrease of methylene blue concentration in the three conducted experiments at different conditions was observed. In the solutions of dye the influence of pH on the degree of dye decoloration in a decreasing order is as follows: pH=9 > pH=5.8 > pH=3. It is clear that the highest degree of photocatalytic degradation of methylene blue gave the basic solution (above 96% after 6 h of UV radiation). The difference of the degree of the decomposition in basic solutions in comparison with acidic solutions appeared to be significant. Removal of the described organic dye in the same period of time amounted to 50.05% for a solution at pH=5.8 and 48.56% for that at pH=3. After 10 h of illumination with UV light, the amount of dye that underwent decomposition reached 100%. These measurements demonstrate that methylene blue can be completely decolorized at basic pH during 10 h UV irradiation using the prepared TiO_2. The photocatalyst showed the stability of its activity during multiple experiments (date not presented here). In the presented study, an increase in the rate of the photocatalytic degradation with an increase in pH was observed.

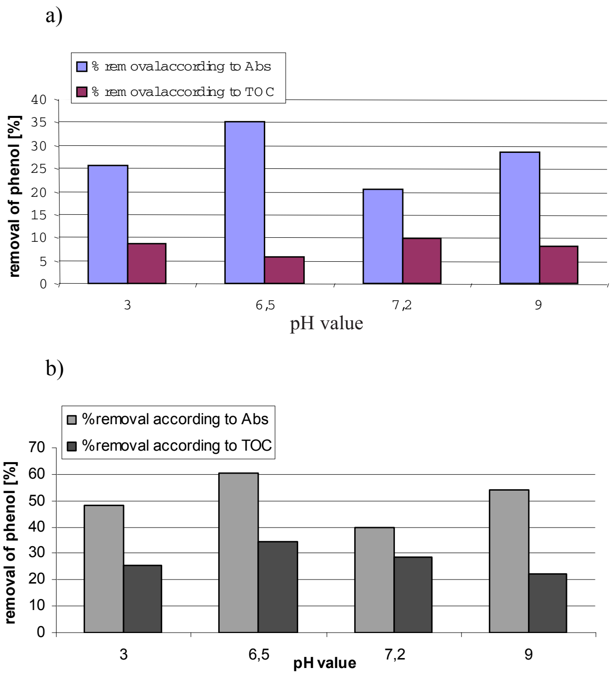

Fig. 6. Photocatalytic removal of phenol in the presence of TiO_2: (a) after 6 h UV radiation, (b) after 14 h UV radiation. Experimental conditions: initial phenol concentration 50 mg/dm^3, catalyst content 0.2 g/dm^3.

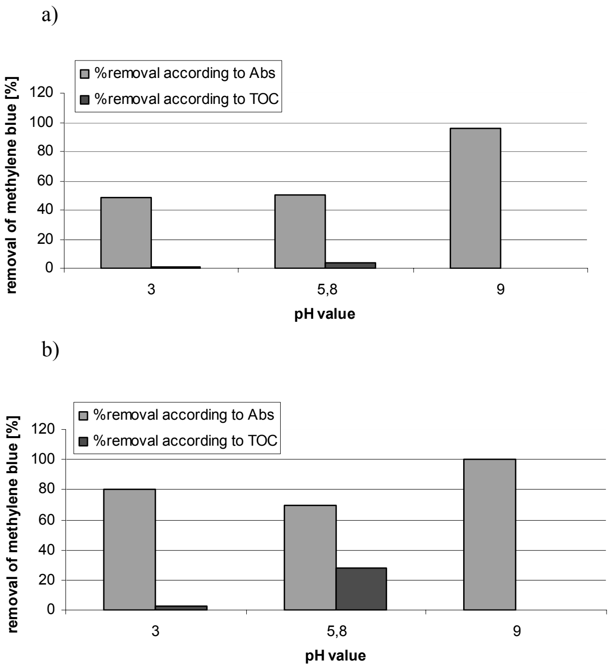

Fig. 7. Photocatalytic removal of methylene blue in the presence of TiO_2: (a) after 6 h UV radiation, (b) after 10 h UV radiation. Experimental conditions: initial dye concentration 10 mg/dm^3, catalyst content 0.2 g/dm^3.

Our results corresponded with an observation that has been made by other authors. According to Ling [23], basic pH electrostatic interactions between negative TiO^- and methylene blue cation leads to a strong adsorption with a corresponding high rate of degradation. Here it should be concluded that pH affects the adsorption properties of organic compounds and their dissociating state in a solution. The surface charge properties of TiO_2 also changed with the changes of pH value due to the amphoteric behaviour of semi conducting TiO_2 [7, 16, 17, 23, 24].

In Figs. 6 and 7 the removal of TOC in solutions of phenol and methylene blue at different pH during an illumination period was presented as well. In the case of phenol solution after 6 h of irradiation at pH=6.5, the percentage of photocatalytic decomposition of phenol in aqueous TiO_2 suspension was the highest, but the removal of TOC only reached 5.87%. It was the lowest result corresponding with solutions of phenol at other pH. TOC analysis shows degradation that leads to the conversion of organic compounds into harmless gaseous CO_2 and inorganic ions [25]. After 6 h of irradiation, mineralization was not enough. However, the removal of TOC after an extension for a 14-h irradiation period at the same value of pH was almost 25%. The mineralizations for solutions at pH=3, 7.2, and 9 achieved 25.19%, 28.87%, and 22.18%, respectively. The obtained results show that the mineralization of phenol does not immediately follow the degradation of the solution. At the beginning, intermediates were present, which underwent further photocatalytic oxidation. A decolorization of solutions of methylene blue also produced TOC disappearance. The photocatalytic degradation of the analyzed dye reached, for example, given the natural pH equal to 5.8 and after 6 h of irradiation the removal of TOC amounting to 3.99%. Then the solution was additionally illuminated for 4 hours. At this time the extent of degradation increased to 28.29%. The tendency to later total organic carbon decrease in comparison with concentration of the organic compound was observed here as well.

Conclusions

In the present investigations, an industrial hydrolyzed $TiOSO_4$ was used as the precursor for preparation of a photocatalyst after ammonia treatment. During studying characterization of the photocatalyst, the absence of nitrogen in TiO_2 structure was confirmed by FTIR/DRS spectra of the titania. The prepared TiO_2 had photocatalytic efficiency under UV light only because of the presence of one absorption edge in the UV region according to UV-Vis/DR measurements. The mean particle size of the studied material was found to be 197.5 nm, while the average size of crystallites increased to 12.7-13 nm. The nanostructured material of the sample and the presence of amorphous and crystalline phases in the photocatalyst were revealed by TEM analysis as well. It was found that the pH value of the solution strongly influences the photocatalysis degradation of organic compounds under UV radiation. The photocatalytic decomposition of phenol was most efficient at pH=6.5. However, in the case of applied methylene blue dye solution high photocatalytic activity was preferred by basic reaction. The mineralization of phenol and methylene blue measured by a level of TOC showed a similar tendency to remove organic compounds like UV-Vis spectrometry, which confirms photocatalytic mineralization reactions conducted using the prepared TiO_2.

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