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Photocatalytic activity of polyvinyl borate/titanium dioxide composites for UV light degradation of organic pollutants

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ABSTRACT

In this study, it is aimed to prepare polyvinyl borate (PVB)/titanium dioxide (TiO_2) composites through the condensation reaction of polyvinyl alcohol and boric acid in the presence of TiO_2 nanoparticles. The scope of this study contains the photocatalytic activity of the prepared composites with varying TiO_2 content from 0 to 35 wt.% for the degradation of methylene blue in aqueous medium under UV light irradiation. The structure and morphological properties of the prepared composites were studied with FTIR, TGA, EDX, SEM and TEM analyses. The photocatalytic activity of the prepared samples was analyzed by UV-Vis spectrophotometer measurements. In parallel with TiO_2 content up to 30 wt.%, the photocatalytic activity of PVB/TiO_2 composites was enhanced and the composites exhibited higher discoloration rate of the model dye, methylene blue.

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photocatalytic activity; titanium dioxide; polyvinyl borate; polymer composite; UV irradiation

1. Introduction

In recent times, water shortages get increasing problem because of uncontrolled groundwater use, global warming and rapid industrial growth, which gives rise to depleted water resources and environmental pollution.[1] Textile and dye industry-like industries consume a substantial amount of water in its manufacturing processes and discharge large amounts of highly colored wastewater. The increased demand for the use of dyes in the specified industries contributed to colored wastewater becoming one of the major sources of environmental pollution problems.[2,3] Due to the environmental protection laws for the receiving waters, the wastewater needs to be treated prior to discharge through removing dye color from the waste. Among wastewater treatment processes, biological treatment methods, efficient for suspended solids removal and biochemical oxygen demand, are mostly ineffective for removing dye color. Physico-chemical treatment processes, containing chemical precipitation, adsorption and photocatalytic oxidation, have been shown to be an effective alternative to biological treatment for the removal of dye color in the treatment of wastewater.[3]

Wastewater treatment through the photocatalytic oxidation process is based on solar energy in the band gap of the photocatalyst and the following photo-generated electron transfer. There are few effective photocatalysts and titanium dioxide is the most common used among them due to the following reasons. TiO_2 is chemically stable in aqueous, acidic and alkaline solutions, and it is biocompatible, inexpensive and recyclable[1,4]. In addition, TiO_2 photocatalyst possesses superior optical and electrical properties.[5] The photocatalytic oxidation process with titanium dioxide photocatalyst is gaining importance as an effective wastewater treatment method. This process can be applied to the wastewater treatment including different type of dyes as well as organic contaminants since TiO_2 as photocatalyst can achieve complete removal of dyes and complete mineralization of the organic contaminants from the waste at ambient conditions.[4] The band gap of TiO_2 photocatalyst ranges from 3 to 3.2 eV. In other words, the wavelength of UV light irradiation, exposing to the TiO_2 photocatalyst, needs to be less than 400 nm to initiate the photocatalytic oxidation reactions. When TiO_2 photocatalyst is irradiated with UV light below the specified wavelength value, organic compounds like colored dyes are decomposed completely into carbon dioxide and water molecules through the formation of photoinduced charge carriers and the following active (superoxide and hydroxyl) radicals on TiO_2 surface.[1]

One of the major drawbacks of photocatalytic oxidation processes using TiO_2 photocatalyst is the limitation in mass processing systems. In detail, the photocatalytic system composed of pure TiO_2 nanoparticles requires an additional recovery and separation step from the waste following the photocatalytic oxidation reaction.[1] In addition, there are limitations for the commercial use of TiO_2-like nanoparticles alone in drinking water and irrigation water because of their impact on ecosystems and human health. Immobilization of photocatalyst nanoparticles in polymer matrix overcomes the specified problem by eliminating the necessity of the recovery and separation steps from the waste and reducing the ecotoxicity problems.[6] The significance of immobilization of TiO_2 photocatalyst in polymer matrix for the removal of dye color in the treatment of wastewater is highlighted by the recent studies. In literature, low density polyethylene/TiO_2 and high

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density polyethylene/TiO_2[5], poly(methyl methacrylate)/TiO_2[6], polytetrahydrofuran-urethane dimethacrylate/TiO_2,[7] polypyrrole/TiO_2, [8] poly(3-hexylthiophene)/TiO_2,[9] polyhydroxybutyrate/TiO_2[10] composite systems were studied and the photocatalytic activity of TiO_2 photocatalyst within the mentioned polymer matrices was determined from degradation of a model dye in aqueous medium under UV light irradiation. Photocatalytic degradation that is the photocatalytic oxidation process of the model dye indicates the effectiveness and sufficiency of TiO_2 containing composites in decolorization of colored wastewater.

There is another drawback to the use of TiO_2 as photocatalyst for the removal of dye color in the treatment of wastewater. The recombination of the photoinduced charge carriers, which are electrons and holes, reduces the photocatalytic reaction efficiency. In detail, the photoinduced electron moves from its conduction band state into the empty valance band state known as the hole, which prevents the photoinduced charge carriers forming active radicals necessary for the photocatalytic degradation.[11] Combining TiO_2 with various organic and inorganic materials has the potential to enhance the photocatalytic activity through suppressing the charge carriers recombination.[1] As an organic material, graphene oxide was combined with TiO_2 within the composite structure, which creates a channel for fast transfer of photoinduced electrons before being recombined.[12] In addition, TiO_2 photocatalyst was deposited on activated carbon fiber to enhance both the light adsorption ability and the quantum efficiency of TiO_2 by hindering the recombination of charge carriers.[13] As an alternative to organic materials, TiO_2 was combined with MoS_2,[14] BiO_3,[15] WO_3,[16] Bi_2S_3[17] and ZnO[18] to improve the photocatalytic activity by reducing the recombination rate of the photoinduced charge carriers. Additionally, boron oxide (B_2O_3) was deposited on TiO_2 to enhance the photocatalytic activity of the photocatalyst.[19]

Polyvinyl borate (PVB) is a crosslinked polymer containing boron oxide (B_2O_3) functional groups along its chains.[20] Crosslinking polyvinyl alcohol (PVA), which is an environmentally friendly and inexpensive polymer, with boric acid is an approach to improve the mechanical and thermal properties and moisture resistance of PVA.[21] PVB might be a good polymer support for the photocatalyst since it is thermally and mechanically stable for long term operations[11,21]. Besides being a support material, the contact of B_2O_3 with TiO_2 improved the photocatalytic activity of the photocatalyst.[19] There is no study in the literature on the photocatalytic activity of PVB/TiO_2 composites. TiO_2 nanoparticles were immobilized within PVB matrix through synthesizing the polymer in the presence of TiO_2 nanoparticles. The photocatalytic activity of the prepared composites was evaluated by investigating the photocatalytic decomposition of a model dye under ultraviolet light irradiation.

2. Experimental

2.1. Preparation of PVB/TiO_2 composites

Polyvinyl alcohol (PVA) and boric acid (H_3BO_3), obtained from Sigma-Aldrich, were used to synthesize polyvinyl borate (PVB). The molecular weight of PVA changes in the range from 89000–98000 g/mol and its degree of hydrolysis is greater than 99 mol.%. TiO_2 nanoparticles (anatase, <25 nm, 99.7 trace metal basis), from Sigma-Aldrich, were used as photocatalyst within PVB composite systems. Methylene blue (Sigma-Aldrich) was used as the model dye for the photocatalytic activity experiments. Pure PVB was prepared through the condensation reaction of PVA and boric acid in a B–OH: PVA–OH molar ratio of 1.4:1. For this purpose, 2.0 g of PVA was dissolved in 50 ml of distilled water by heating at 80°C under stirring. Meanwhile, the same amount of boric acid was dissolved in 50 ml of distilled water with constant stirring at room temperature. Then, the boric acid solution was added into polyvinyl alcohol solution and kept under stirring for half an hour, which gave rise to PVB film after drying in an oven at 120°C.[20] PVB/TiO_2 composites, containing 5, 10, 15, 20, 25, 30 and 35 wt.% photocatalyst nanoparticles, were prepared with the same procedure followed to prepare pure PVB film. The only difference was that TiO_2 nanoparticles were added in PVA solution and kept under stirring before mixing with the boric acid solution.

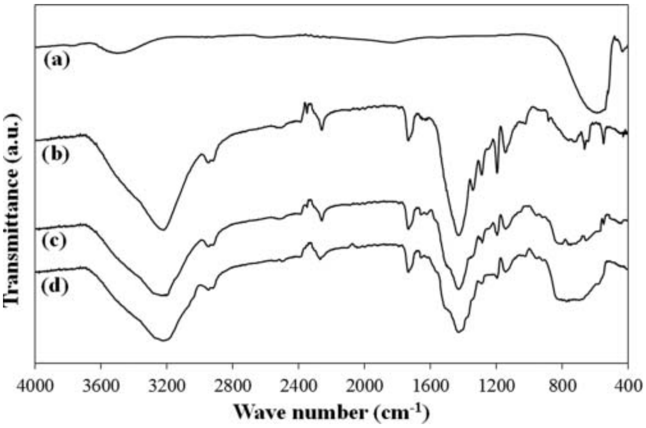

Figure 1. FTIR spectra of (a) TiO_2, (b) PVB, (c) PVB/TiO_2 (15 wt.%) and (d) PVB/TiO_2 (30 wt.%).

2.2. Methods of characterization

Fourier transform infrared (FTIR) spectra of TiO_2 nanoparticles, pure PVB and PVB/TiO_2 composites (15 wt.% and

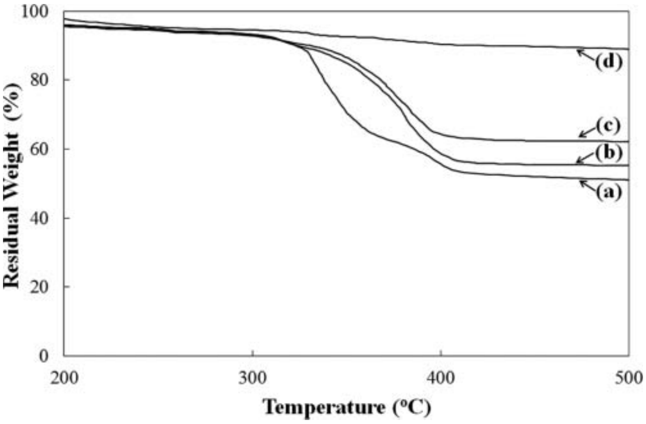

Figure 2. TGA curves of (a) pure PVB, (b) PVB/TiO_2 (15 wt.%), (c) PVB/TiO_2 (30 wt.%) and (d) TiO_2.

30 wt.%) were recorded with a Nicolet 380 (Thermo Scientific) spectrometer at a resolution of 2 cm^{-1} between 4000 and 400 cm^{-1}. The thermogravimetric analyses (TGA) of TiO_2, pure PVB and PVB/TiO_2 composites (15 wt.% and 30 wt.%) were carried out with a thermogravimetric analyzer (Setaram Labsys TGA/DTA) operating at a heating rate of 5°C/min. up to 500°C under nitrogen atmosphere. The surface structure of PVB/TiO_2 composites (15, 30 and 35 wt.%) were examined by QUANTA 400F model field emission scanning electron microscope (FE-SEM) equipped with JXA-8230 EDX Microanalysis Instrument. EDX analyses were carried out to exhibit the elemental compositions PVB/TiO_2 composites, containing 15, 30 and 35 wt.% TiO_2, respectively. Prior to SEM analyses, the samples were coated with Au-Pd against charging effects of the insulating polymer under electron beam irradiation. FEI-Tecnai G^2 Spirit Biotwin model conventional transmission electron microscope (CTEM) was used for the morphological investigation of the composites, containing 15 and 30 wt.% TiO_2, respectively. For this purpose, the samples in powder form were attached on carbon coated copper grids.

The photocatalytic activity of pure PVB, pure TiO_2 and PVB/TiO_2 composites was assessed through degradation of the model dye, methylene blue, in aqueous solution under UV light irradiation. In detail, 1.0 g of the prepared samples was immersed into 50 ml methylene blue solution (10 mg/L) and it was held in the dark for half an hour for an adsorption-desorption equilibrium. Then, the sample within methylene blue solutions was irradiated with UV light supplied by a 30 W UV lamp at 254 nm wavelength. The distance between the UV lamp and the sample was 10 cm. At specific time intervals, 3 ml sample of methylene blue solution was withdrawn and was subjected to UV–visible spectroscopy (Thermo Scientific, Genesys 10S UV-VIS Spectrophotometer) at 665 nm to determine the dye concentration. Then, the sample solution was refilled into

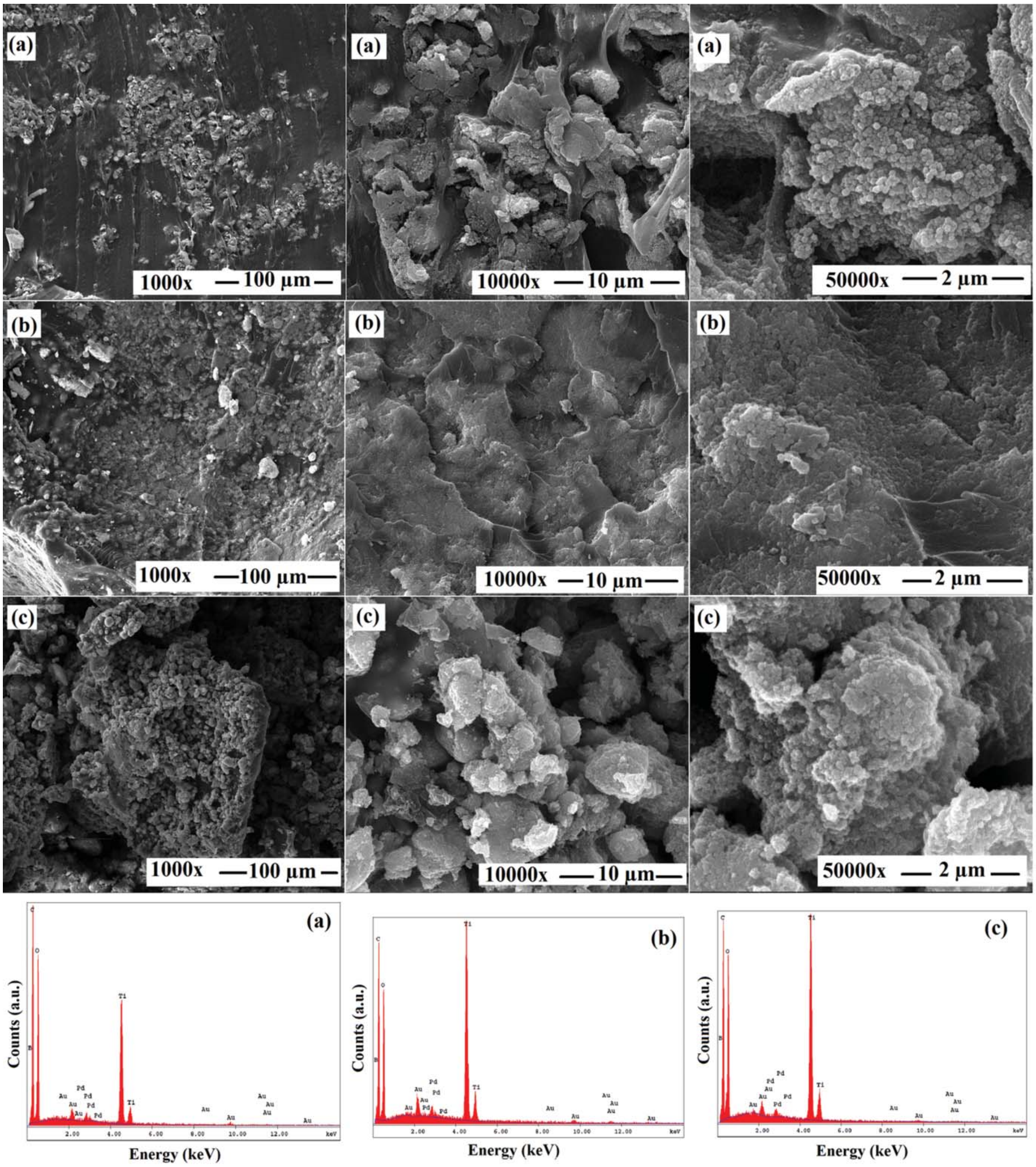

Figure 3. SEM images of the composite containing (a) 15 wt.% TiO_2, (b) 30 wt.% TiO_2 and (c) 35 wt.% TiO_2.

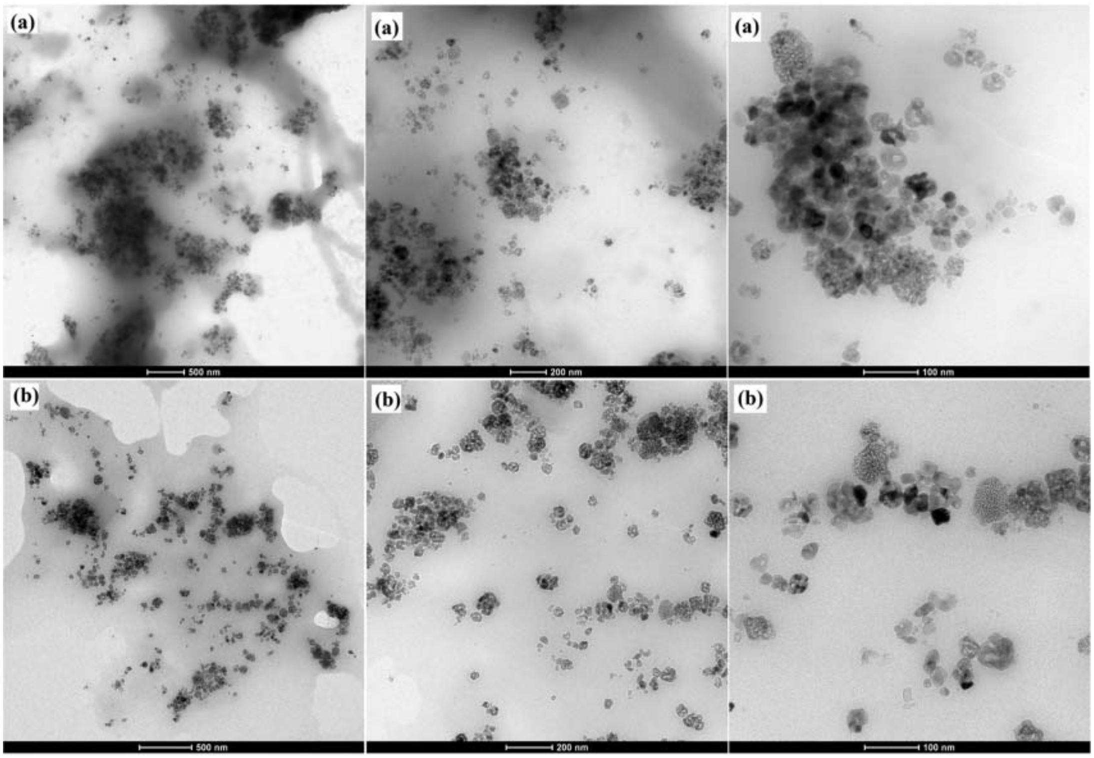

Figure 4. TEM images of the composite containing (a) 15 wt.% TiO_2 and (b) 30 wt.% TiO_2.

the reaction medium again and UV light irradiation was continued. The degradation of the model dye was evaluated using the relation of C_t/C_0, where C_0 is the initial concentration of methylene blue and C_t is the concentration of the model dye after irradiation.[22] All the degradation experiments were repeated three times and their results were given with standard deviations.

3. Results and discussion

3.1. FTIR analysis

FTIR spectra of TiO_2, pure PVB and PVB/TiO_2 composites are shown in Figure 1. The spectrum of TiO_2 is composed two broad transmission bands between 450–850 cm^{-1} and 3300–3600 cm-^{1}, corresponding to the stretching vibration of Ti-O-Ti, and corresponding to the O-H vibrations due to presence of adsorbed water on the photocatalyst, respectively[7,23,24] (Figure 1a). The broad band from 3000 to 3600 cm^{-1} is attributed to OH group of polyvinyl alcohol, formed complexes with boron-containing oxyanions.[25] The peak at 1423 cm^{-1} is assigned to B-O stretching vibration. Transmission peaks at 1286 cm^{-1} and 1139 cm^{-1} are related to stretching vibrations of B-O-C bonds, confirming the condensation reaction of polyvinyl alcohol and boric acid to form polyvinyl borate. In addition, transmission peaks seen at 2925 cm^{-1}, 1731 cm^{-1} and 1340 cm^{-1} correspond to C=O, C-H and C-O bonds, respectively (Figure 1b).[20,25,26] The spectra of the composites, containing 15 and 30 wt.% TiO_2, respectively, are similar to the spectrum of pure PVB. The peaks at 1139 cm^{-1}, 1286 cm^{-1} and 1423 cm^{-1} are also present on the spectra of the composites, which indicate the formation of PVB chains. In addition, the characteristic feature from 450 cm^{-1} to 850 cm^{-1} belonging to Ti-O-Ti also appears on the spectra of PVB/TiO_2 systems, confirming the presence of the photocatalyst. An increase in TiO_2 content of the composite gives rise to the following increase in the intensity of the specified broad band related to Ti-O-Ti (Figure 1c and 1d).

Table 1. Elemental ratios (wt.%) of C, O, B, Ti in PVB/TiO_2 composites.

System	Carbon	Oxygen	Boron	Titanium
PVB/TiO_2 (15 wt.%)	49.67	21.99	15.00	9.20
PVB/TiO_2 (30 wt.%)	43.04	19.95	14.30	15.93
PVB/TiO_2 (35 wt.%)	44.17	20.99	17.20	15.20

3.2. Thermal analysis

TGA curve of pure PVB does not show major weight loss up to about 300°C and the boron containing polymer is stable up the specified temperature.[27] TGA curve contains two main degradation steps between 300–375°C and 375–400°C, corresponding to deacetylation and chain scission reactions, respectively.[21] A mass loss of 37% appeared between 300°C and 400°C (Figure 2a). The thermal property of PVB was influenced by TiO_2 nanoparticles. When compared with pure PVB, the composites exhibit higher stability, especially after 320°C. The composites, containing 15 and 30 wt.% TiO_2, exhibit mass losses of 34% and 29%, respectively, between 300°C and 400°C (Figure 2b and 2c). Because of the thermal stability of TiO_2, no significant weight loss was observed with the photocatalyst from 200°C to 500°C. A total weight loss of 8% occurred between 200°C and 500°C, relating to evaporation of physisorbed water and water resulted by condensation of surface hydroxyl groups of TiO_2 (Figure 2d).[28-31]

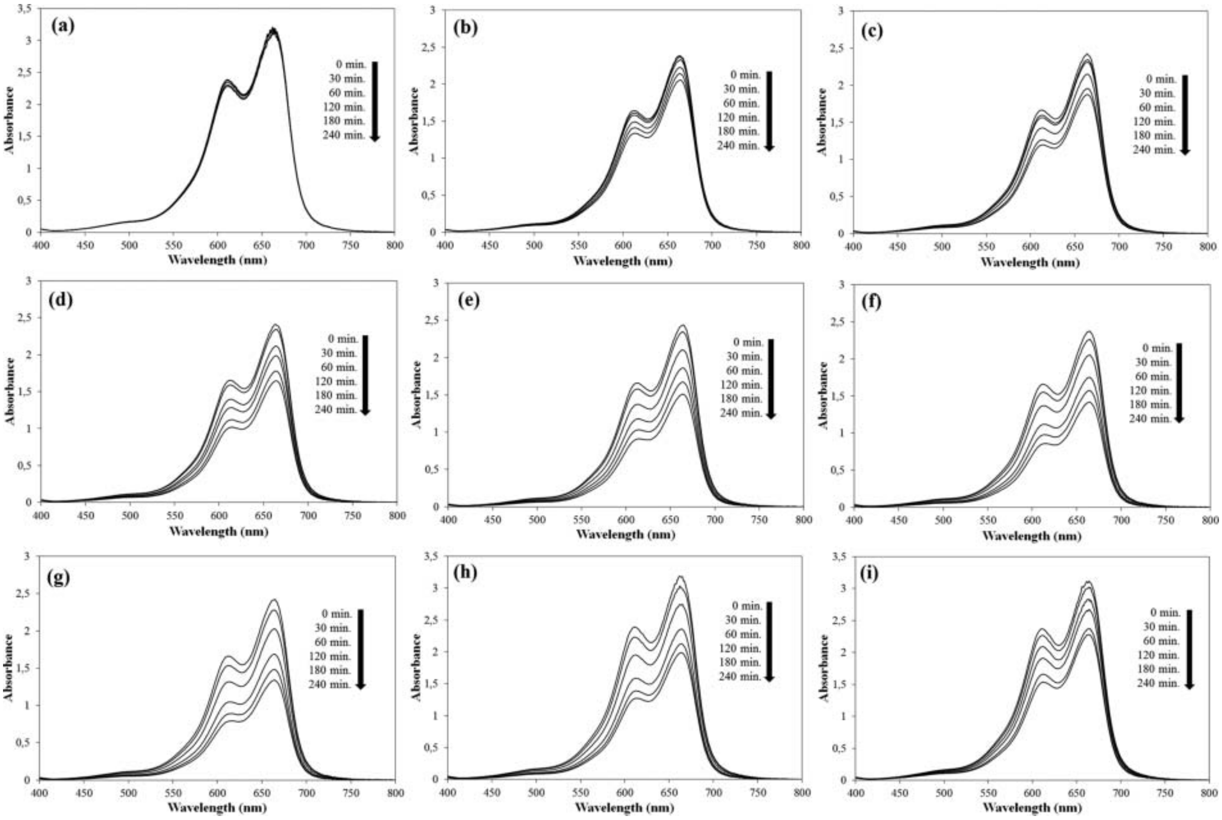

Figure 5. The variation in the UV–visible spectrum of methylene blue solution containing (a) pure PVB, (b) PVB/TiO_2 (5 wt.%), (c) PVB/TiO_2 (10 wt.%), (d) PVB/TiO_2 (15 wt.%), (e) PVB/TiO_2 (20 wt.%), (f) PVB/TiO_2 (25 wt.%), (g) PVB/TiO_2 (30 wt.%), (h) PVB/TiO_2 (35 wt.%) and (i) pure TiO_2.

3.3. Morphological analyses

The surface of PVB/TiO_2 composites is not very smooth due to some TiO_2 aggregations distributed homogeneously in PVB matrix (Figure 3). Aggregated TiO_2 structures, composed of dozens of nanospheres, can be observed on composite surfaces regardless of the photocatalyst content, which reveals the agglomeration tendency of TiO_2 nanoparticles. As PVB/TiO_2 composites were prepared, the boric acid solution was poured into the polyvinyl alcohol-TiO_2 solution with constant stirring and an insoluble gel structure was obtained in a short time, which prevented agglomeration and sedimentation of the nanoparticles to a certain extent. TiO_2 aggregates with a diameter ranging from 50 nm to 500 nm can be observed on TEM images of the composites (Figure 4). PVB matrix holds the photocatalyst nanoparticles in intimate contact form and provides homogeneous TiO_2 dispersion within itself, which exhibit the interfacial interaction between the composite constituents. A good contact is essential in terms of the synergistic effect of PVB and TiO_2 on the photocatalytic activity.

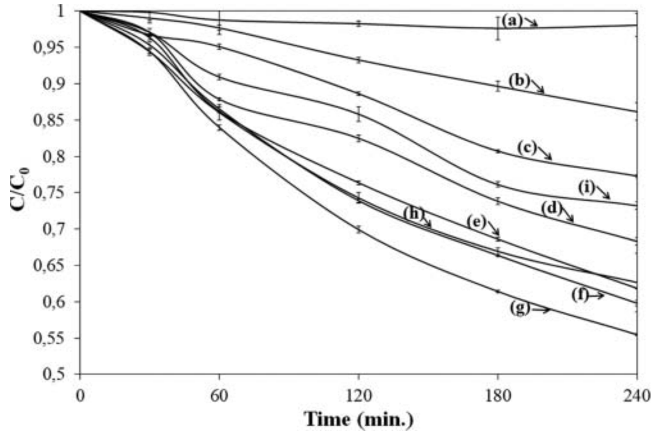

Figure 6. Photocatalytic degradation of methylene blue in aqueous solution containing (a) pure PVB, (b) PVB/TiO_2 (5 wt.%), (c) PVB/TiO_2 (10 wt.%), (d) PVB/TiO_2 (15 wt.%), (e) PVB/TiO_2 (20 wt.%), (f) PVB/TiO_2 (25 wt.%), (g) PVB/TiO_2 (30 wt.%), (h) PVB/TiO_2 (35 wt.%) and (i) pure TiO_2.

EDX spectra of PVB/TiO_2 composites reveal the presence of the following elements, boron (B) and titanium (Ti) (Figure 3). According to the EDX analyses, it is possible to say that PVB was formed through the condensation reaction of PVA and boric acid, and the photocatalyst nanoparticles entered into the composite structure. During PVB synthesis, PVA and boric acid were dissolved in distilled water. TiO_2 nanoparticles were dispersed within PVA solution. Following the condensation reaction, insoluble PVB and PVB/TiO_2 composites were obtained and the soluble part of the reaction medium, containing unreacted components, was separated from the insoluble phase. Hence, the boron and the titanium observed in the EDX analyses are thought to be the element of the PVB chain structure and the composite constituents, respectively. Parallel to the increase in the composite content, the weight percentage of the Ti detected on EDX spectra also increased (Table 1).

3.4. Photocatalytic activity

Figure 5 illustrates the variation in the UV–visible spectrum of methylene blue solution containing the prepared samples. Figure 6

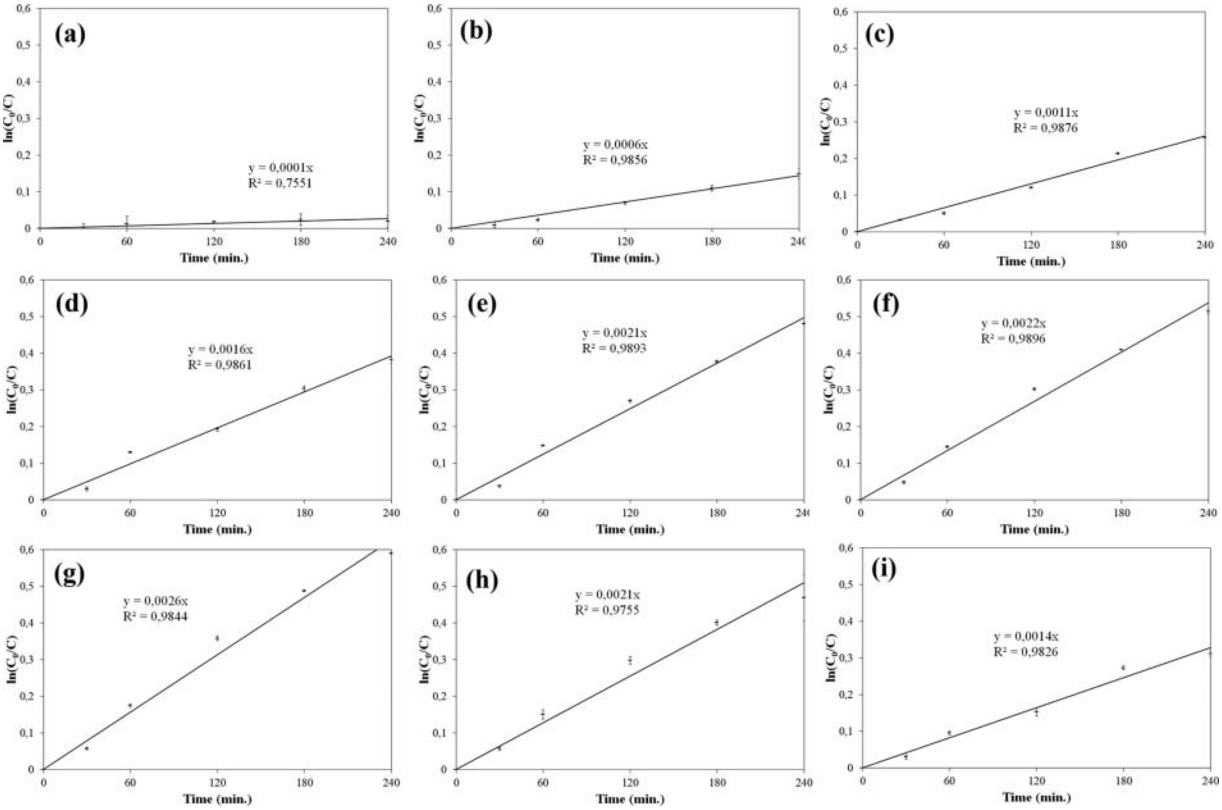

Figure 7. Photocatalytic degradation kinetics of methylene blue in aqueous solution containing (a) pure PVB, (b) PVB/TiO_2 (5 wt.%), (c) PVB/TiO_2 (10 wt.%), (d) PVB/TiO_2 (15 wt.%), (e) PVB/TiO_2 (20 wt.%), (f) PVB/TiO_2 (25 wt.%), (g) PVB/TiO_2 (30 wt.%), (h) PVB/TiO_2 (35 wt.%) and (i) pure TiO_2.

shows methylene blue degradation curves of pure PVB, pure TiO_2 and PVB/TiO_2 composites as a function of irradiation times. As expected, pure PVB resulted in insignificant degradation of the model dye. After 240 minutes under UV light irradation, almost 2% dye removal was obtained, which can be ascribed to low light harvesting efficiency of pure polymer.[8] Pure TiO_2 can hardly degrade methylene blue owing to the limitation of wide band gap of the photocatalyst.[9] Approximately 27% dye removal was achieved in the presence of pure TiO_2. For the composites with 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%, 30 wt.% and 35 wt.% of TiO_2 nanoparticles, the dye removal values are 14%, 23%, 32%, 38%, 40%, 45% and 38%, respectively. For PVB/TiO_2 composites, boron oxide (B_2O_3) functional groups along the chains of PVB may serve as an electron acceptor of the photoinduced electrons of TiO_2, enhancing the photocatalytic activity of the photocatalyst by suppressing the charge carriers recombination.[32] Thus more photoinduced charge carriers remain to form active radicals necessary for the photocatalytic degradation of the model dye. The synergic contribution of boron oxide on PVB chains and TiO_2 nanoparticles enhanced the photocatalytic activity of the composites compared to the pure polymer and pure TiO_2. Especially, PVB/TiO_2 composites with 15 wt.%, 20 wt.%, 25 wt.%, 30 wt.% and 35 wt.% of TiO_2 nanoparticles illustrated more effective photocatalytic activity.

From the model dye degradation results (Figure 6), it can be claimed that increasing the photocatalyst content of PVB/TiO_2 systems over 30 wt.% does not enhance the photocatalytic activity of the composites. This result may be due to a limitation of the amount of the photocatalyst nanoparticles on the composite surface.[6] As an alternative to this claim, the synergic contribution of PVB and the photocatalyst after the composition of 30 wt.% may have begun to lose its effect on the photocatalytic activity. The weight percentage of titanium within the composites, including 30 wt.% and 35 wt.% TiO_2, should be around 18% and 21%, respectively. According to the EDX analysis of the mentioned composites, the weight percentages of the Ti detected on PVB/TiO_2 surfaces are 15.93% and 15.20% respectively (Table 1). When compared with the composite containing 30 wt.% TiO_2, there should be more titanium on the surface of the sample with TiO_2 at 35 wt.%, which supports the first mentioned claim.

The photodegradation data of the model dye with pure PVB, pure TiO_2 and PVB/TiO_2 composites were evaluated using the pseudo-first order kinetics equation, given below[22,33].

$$\ln(C_0/C_t) = kt \tag{1}$$

where t is the time and k is the rate constant, obtained from the slope of the straight fitting line of the plot $\ln(C_0/C_t)$ vs. t (Figure 7). Besides, C_0 is the initial concentration of methylene blue and C_t is the concentration of the model dye after irradiation at time t. According to Figure 7, the photodegradation reaction of methylene blue in the presence of pure PVB, pure TiO_2 and PVB/TiO_2 composites presents approximately first order kinetics. The discoloration rate of the model dye for pure PVB, pure TiO_2 and PVB/TiO_2 composites is given on Table 2. When compared with pure PVB and pure TiO_2, the composites, containing 15 wt.%, 20 wt.%, 25 wt.%, 30 wt.% and 35 wt.% of TiO_2 nanoparticles, exhibited higher photocatalytic activity and the highest discoloration rate of the model dye was obtained with the composite, containing 30 wt.% TiO_2.

Table 2. The discoloration rate of the model dye for pure PVB, pure TiO_2 and PVB/TiO_2 composites

Sample	k (min^{-1})	R^2
Pure PVB	0.0001	0.7551
Pure TiO_2	0.0014	0.9826
PVB/TiO_2 (5 wt.%)	0.0006	0.9856
PVB/TiO_2 (10 wt.%)	0.0011	0.9876
PVB/TiO_2 (15 wt.%)	0.0016	0.9861
PVB/TiO_2 (20 wt.%)	0.0021	0.9893
PVB/TiO_2 (25 wt.%)	0.0022	0.9896
PVB/TiO_2 (30 wt.%)	0.0026	0.9844
PVB/TiO_2 (35 wt.%)	0.0021	0.9755

4. Conclusions

PVB/TiO_2 composites were prepared through the condensation reaction of polyvinyl alcohol and boric acid in the presence of the photocatalyst nanoparticles. FTIR, TGA, EDX, SEM, TEM and UV–visible spectroscopy were performed to characterize prepared samples. FTIR and TGA results confirmed the formation of the boron containing polymer, polyvinyl borate. In addition, the mentioned analyses and EDX analysis revealed the presence of TiO_2 within PVB matrix. Both SEM and TEM images of the composites illustrate good dispersion of the photocatalyst nanoparticles in the polymer matrix. The loading of the photocatalyst nanoparticles in PVB improved the photocatalytic decomposition of the model dye in aqueous medium under UV light irradiation.

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