

Photocatalytic properties of ceramics TiO₂ nanocomposites from waste resources

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Ceramics TiO₂ nanocomposites were prepared by using titanium oxide (TiO₂) nanoparticles, fly ash from the thermal power plant and the mixed waste glass powder. We applied a mechanical milling method and thermal reaction in this process. The photocatalytic activities were estimated for methyl orange (MO), acetaldehyde (ATA), 2,4-dichlorophenoxyacetic acid (2,4-D), and methylene blue (MB) as photodegradation targets. Crystallinity, morphological properties, and chemical compositions for prepared ceramics TiO₂ nanocomposites were also observed by X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), and energy dispersive X-ray spectrometer (EDS). In addition, density, compressive strength, bending strength and chemical durability were measured to characterize the physicochemical properties of TiO₂ nanoparticle contents (0-20 wt%). It was verified that addition of TiO₂ nanoparticles considerably improves the physicochemical properties of the prepared nanocomposites samples. With increased TiO₂ nanoparticle content, the photocatalytic activities of the ceramics TiO₂ nanocomposites for photodegradation target materials increased under UV light irradiation. The degree of photocatalytic degradation of MO, ATA, 2,4-D, and MB in the ceramics TiO₂ nanocomposites improved to about 0.264, 0.141, 0.302, and 0.368, respectively, after the UV irradiation for 240 min when 20 wt% TiO₂ nanoparticle was added. In addition, the photocatalytic degradation rate of photodegradation target materials was evaluated using the pseudo-first-order kinetics proposed by Lagergren.

Key words: Ceramics TiO₂ nanocomposites, Thermal reaction, Mechanical milling method, Photocatalytic degradation.

Introduction

Titanium oxide (TiO₂) is a photocatalyst most frequently used for decomposing harmful organic materials because it has high photocatalytic activity and chemical stability. It is not only nontoxic and abundantly available but also highly cost-effective. [1, 2]. TiO₂ photocatalyst has introduced practical uses in the environment areas such as deodorization, sterilization, air and water purification, and it is self-cleaning because of its strong oxidizing ability [3-5]. Moreover, nanocomposites can be made to have a variety of enhanced physical, thermal and other unique properties. Since they possess properties that are superior to conventional microscale composites, they can be synthesized using simple and inexpensive techniques. In many studies, nanocomposite have been prepared by using nano-clay, nano-SiO₂ or whiskers as nanofibrils, and their mechanical properties, thermal properties, and water resistance have been demonstrated [6-13].

In this work, ceramics TiO₂ nanocomposites were prepared by using TiO₂, waste glass powder, and fly ash from the thermal power plant. This paper focuses on TiO₂ nanoparticles as inorganic filler in composites matrix. We synthesized ceramics m oxide TiO₂

nanocomposites that possess enhanced physical, thermal and other distinctive photocatalytic properties. The properties that are advanced to conservative micro scale composites can be fabricated using simple and inexpensive techniques [14-20]. More significantly, the waste resources such as fly ash, waste glass are recycled, and many recycling difficulties such as chemical bonding by high heat-treatment temperature and high cost required by several thermal steps are resolved by the proposed mechanical processing of the disk type ball milling.

Crystallinity and morphological properties of the ceramics TiO₂ nanocomposites synthesized with TiO₂ nanoparticles contents were analyzed by X-ray diffractometer (XRD), field emission scanning electron microscopy (FE-SEM). Energy dispersive X-ray spectrometer (EDS) was used to observe and analyze their chemical composition. The mechanical properties (compressive strength, bending strength, and Vickers hardness) of the prepared ceramics TiO₂ nanocomposites were also investigated. Furthermore, we evaluated the degree of photocatalytic degradation of methyl orange (MO), acetaldehyde (ATA), 2,4-dichlorophenoxyacetic acid (2,4-D), and methylene blue (MB) as photodegradation targets using the ceramics TiO₂ nanocomposites under UV light irradiation.

Experimental

Materials

Commercial titanium oxide (TiO₂) (P-25, Degussa Corporation, Germany) having a specific surface area

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$50 \text{ m}^2\text{g}^{-1}$ and an average particle diameter 30 nm was dried at 100°C for 4 h in a vacuum oven before use. Fly ash from municipal waste incinerators (Yeocheon, South Korea) and waste glass cullet mixed with various types of waste glass (bottle, automobile window shield, plate, etc.) were used in this study as raw materials. Methyl orange (MO) and 2,4-dichlorophenoxyacetic acid (2,4-D) was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). Acetaldehyde (ATA) and methylene blue (MB) were obtained from Carlo Erba (Milan, Italy) and Junsei Chemical (Tokyo, Japan), respectively. Distilled deionized water (D.W.) was used in all experiments.

Preparation of ceramics TiO_2 nanocomposites

The chemical compositions of the raw materials, fly ash (dry bottom ash) and waste glass cullet are listed in Table 1. The chemical analysis showed that the fly ash (dry bottom ash) consists of oxides (in wt%); 44.32% SiO_2 , 28.91% CaO , 8.47% MgO , 13.65% Al_2O_3 , and 4.65% Fe_2O_3 . Fine scale powder (-150mesh) of the fly ash from the municipal waste incinerators was used in these experiments. Glass cullet was carefully washed in a water bath to remove the contaminants and dried in a dry oven at 80°C for 24 h. Glass powder was obtained by grinding the glass cullet in a disk type ball mill (Retsch GmbH & Co.KG, D-42781 HAAN, TYPE:RS1, Germany) for 20 minute (700 rpm). Ceramics TiO_2 nanocomposites were obtained by the mechanical processing of the milling method. First, the powder mixtures consist of waste glass powder (70 wt%) and fly ash (30 wt%). Two different powder mixtures, about 20 g of waste glass and fly ash, were mechanically ground in a disk type ball mill for 6 h (700 rpm). After the grinding, the particle size was determined by a particle size analyzer (PSA, Malvern Ins. Lab., MS 1002). Most of the particles fell in the range of $0.1\text{--}1 \mu\text{m}$. Then, TiO_2 nanoparticles (0, 5, 10, 15 and 20 wt%) were mixed directly together using a mixer for 20 min. The mixtures were pressed into cylindrical shape having a diameter of 10 mm and length of 30–50 mm without using a binder. The formed samples were fired to 900°C at a heating rate of $5^\circ\text{C}/\text{min}$ for 1 h in air (flow rate: $150\text{--}200 \text{ mL}/\text{min}$) and in a box-type SiC furnace, and then allowed to cool inside the furnace. After

firing, the sample was cleaned with ethyl alcohol in an ultrasonic bath and dried at 70°C for 10 h.

We measured the Crystalline phases in the ceramics TiO_2 nanocomposites by using a Bruker D8 Advance with DAVINCI X-ray diffractometer (XRD, Bruker AXS GmbH, Karlsruhe, Germany) with the $\text{Cu-K}\alpha$ radiation generated at 40 kV and 40 mA, in the $5 < 2\theta < 80$ range at a scanning rate of 0.2 sec. The morphology and surface composition of the ceramics nanocomposites were evaluated using field emission scanning electron microscopy (FE-SEM, S-4700, Hitachi Co., Japan) equipped with an energy dispersive X-ray spectrometer (EDS) that has a robinson type backscattered electron detector. The density, bending strength, and chemical durability were also examined. Density was measured using an Electronic Densimeter (ED-120T, MFD BY A&D CO., LTD, Japan). The compressive strength was investigated by the universal tester (Instron 4302, Instron Co., England), and the bending strength was determined from the 3-point bending strength test in the universal tester (Instron N8872, Instron Co., England). The Vickers hardness was estimated by using a Vickers' hardness tester (Shimadzu Co., HMV-2 series, Japan). The chemical durability was observed by the measurement of weight change. To investigate the chemical durability, the FA glass-ceramic specimens were immersed into 15 mL acidic solution (1 N H_2SO_4) at 60°C for 48 h. After immersing, the samples were washed with distilled water and dried at 80°C for 12 h. The photocatalytic degradation of MO, 2,4-D, ATA, and MB was performed using the method by Yun *et al* [21].

Results and Discussion

Fig. 1 presents the result of a FE-SEM morphological analysis of the TiO_2 nanoparticles showing spherically and irregularly round-shaped powder, typical particle morphology of TiO_2 .

Fig. 2 shows the XRD patterns of ceramics nanocomposites with/without added TiO_2 nanoparticles.

Table 1. Chemical composition (wt.%) of the raw materials.

Oxide	Waste glass	Fly ash
SiO_2	70.89	44.32
Na_2O	12.37	—
CaO	9.63	28.91
MgO	3.27	8.47
Al_2O_3	1.95	13.65
K_2O	1.89	—
Fe_2O_3	—	4.65

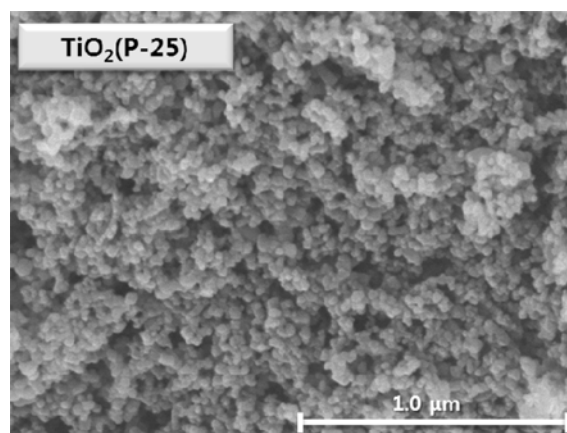


Fig. 1. FE-SEM image of TiO_2 nanoparticle used in this study.

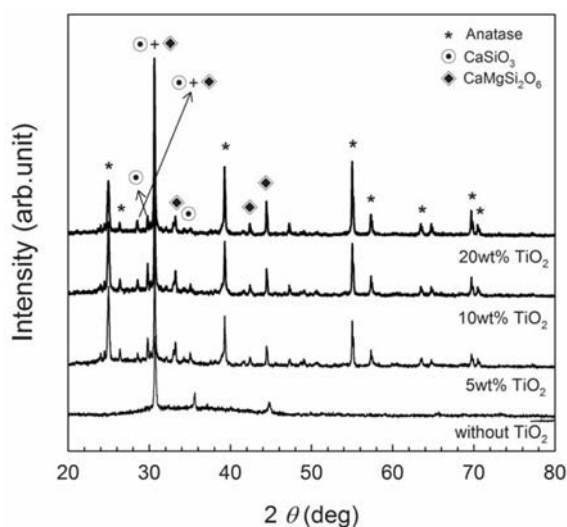


Fig. 2. X-ray diffraction patterns of ceramics nanocomposites with/without added TiO₂ nanoparticles.

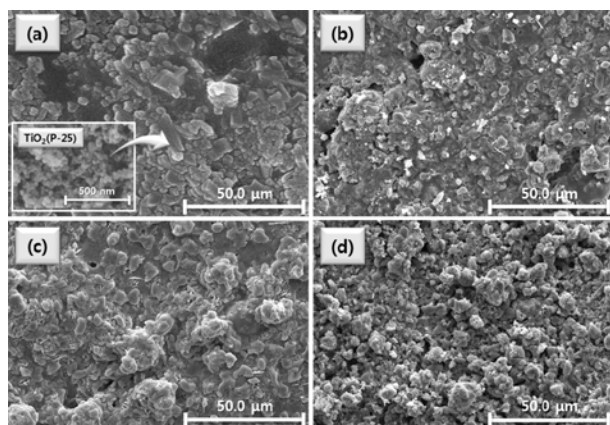


Fig. 3. Field-emission scanning electron microscopy images of ceramics nanocomposites added TiO₂ particles: (a) without TiO₂, (b) 5 wt%, (c) 10 wt%, and (d) 20 wt%.

The crystalline phases existent in the ceramics TiO₂ nanocomposites correspond to anatase TiO₂, CaSiO₃ (JCPDS File 76-0925) and CaMgSi₂O₆ (JCPDS File 78-1390). The TiO₂ diffraction patterns show the 2 theta significance main peaks of 25.31°, 27.45°, 37.92°, 54.34°, 55.18°, 62.94°, and 69.12° corresponding to anatase TiO₂. The intensity of TiO₂ distinctive peaks increased with increasing amount of TiO₂ loaded on ceramics nanocomposites. This means that TiO₂ is combined into the specimens because no clear changes were observed in the TiO₂ phase by the amalgamation of nanocomposites. This is advantageous for our purpose because the anatase phase TiO₂ is known to have a relatively higher photocatalytic activity. Peak intensities corresponding to the CaSiO₃ + CaMgSi₂O₆, CaSiO₃ and CaMgSi₂O₆ crystal were still identified in the specimens. It is also significant that these intensities are caused by the formation of wollastonite and diopside crystals, and that the heat-treatment temperature at 900 °C is accountable for the existence of the crystals.

Fig. 3 shows FE-SEM images of surface morphologies and microstructures of the manufactured ceramics nanocomposites added TiO₂ particles (0, 5, 10, and 20 wt%). As shown in Fig. 3(a), the morphological analysis of the specimen heat-treated at 900 °C (without TiO₂) by using FE-SEM. Fig. 3(a) shows many unsystematically disordered grains and the grain's surface condition of the erratic and inhomogeneous size in the matrix. As seen in Fig. 3 [(b): 5 wt % and (c): 10 wt %], due to the increase in the content of TiO₂ nanoparticle of the samples at 900 °C, the sample's surface is made up of the many round-shape grains unbalanced and disorganized.

Crystallization step of the specimen shown in Fig. 3 (b) and (c) is examined with a rough and intricate surface microstructure. It is an intermediate stage of the deposition process of the TiO₂ nanoparticle in which the inconsistent round shape changed into the grains of relatively stable surface. The FE-SEM morphological analysis of the specimen at 900 °C (20 wt% TiO₂) shows that TiO₂ nanoparticle of well-deposited orbicular type grains is generally amassed in matrix (Fig. 3(d)). Fig. 3(d) shows the microstructure of spherical grain, and the surface condition is homogeneous and regular compared with Fig. 3(b) and (c). As clearly shown in Fig. 3, the increases in the content of the TiO₂ nanoparticle cause variations in the grain forms and surface circumstance of samples. These outcomes led us to conclude that TiO₂ nanoparticle is a significant factor in the stable surface formation.

The photocatalytic activity of ceramics nanocomposite with/without the addition of TiO₂ nanoparticles was investigated by measuring the degree of decomposition of MO, ATA, 2,4-D, and MB as photodegradation targets under UV light. The prepared specimens were irradiated by UV light that has a broad emission spectrum of 315–400 nm. The maximum illumination yielded at 352 nm. The degree of photocatalyst degradability of photodegradation targets was calculated as the ratio of initial (C_0) and final concentration (C). Fig. 4 shows the degree of photocatalyst degradation of MO in the prepared ceramics nanocomposite with/without added TiO₂ as a function of the UV irradiation time. The initial concentration of MO was 10 ppm. Noticeable differences in the photocatalyst degradability of MO were observed with/without the addition of TiO₂ and with TiO₂ contents. Compared with ceramics nanocomposites and TiO₂, the photocatalyst decomposition of MO for TiO₂ was better than that of ceramics nanocomposites. However, the decomposition by UV irradiation was also good for the ceramics nanocomposites added TiO₂. As the TiO₂ nanoparticle content increased, the decomposition of MO also increased. The degree of photocatalyst decomposition of MO in ceramics nanocomposites added 20 wt% TiO₂ was about 0.264. Fig. 5 represents the degree of the decomposition (C/C_0) of ATA, 2,4-D, and MB in the ceramics nanocomposite added 20 wt% TiO₂ as a function of UV light irradiation time. It could be verified that the

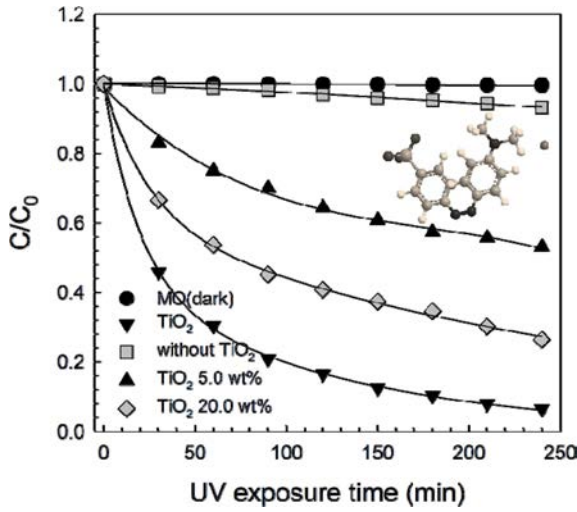


Fig. 4. The degree of photocatalytic decomposition and kinetic linear simulation of methyl orange (MO) for ceramics nanocomposite with/without added TiO₂ under UV irradiation.

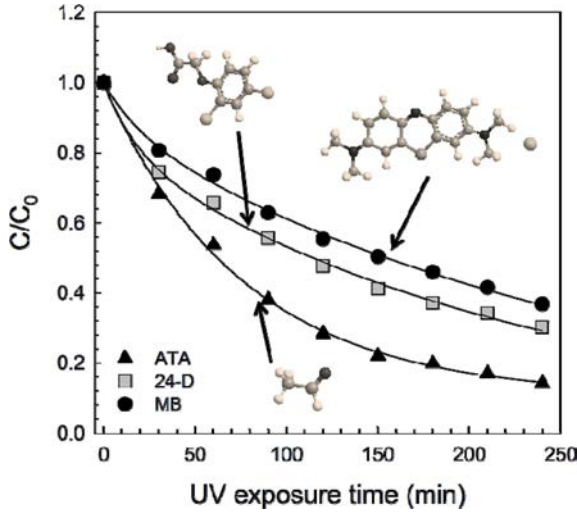


Fig. 5. The degree of photocatalytic decomposition of acetaldehyde (ATA), 2,4-dichlorophenoxyacetic acid (2,4-D), and methylene blue (MB) in the ceramics nanocomposite added 20 wt% TiO₂.

C/C_0 remarkably decreased with UV irradiation time. In addition, the kinetic rate of the decomposition for photodegradation targets was investigated using the kinetic constants. They are calculated using a pseudo-first-order equation [Eq. (1)] and a simplified version of the Lagergren equation [Eq. (2)]. Lagergren [22, 23] proposed a rate equation for the sorption of a solute, based on the adsorption capacity. The Lagergren equation is the most widely used rate equation in sorption and this kinetic model is expressed as:

$$\frac{dq_t}{dt} = k_t(q_e - q_t) \quad (1)$$

Integrating the above equation for the boundary conditions $t = 0$ to $t = t$ and $q_t = q_t$ gives:

$$\ln(q_e - q_t) = \ln(q_e - k_t t) \quad (2)$$

Table 2. The kinetic constants (k_t) and correlation coefficients (R^2) of the pseudo-first-order model for the liner plots of ceramics nanocomposite added TiO₂.

Photodegradation targets / Sample names		Kinetic constants (k_t)	Correlation coefficients (R^2)
MO	TiO ₂ 20 wt%	$1.26 \times 10^{-2} \text{ min}^{-1}$	0.980
ATA	TiO ₂ 20 wt%	$1.60 \times 10^{-2} \text{ min}^{-1}$	0.994
2,4-D	TiO ₂ 20 wt%	$1.32 \times 10^{-2} \text{ min}^{-1}$	0.987
MB	TiO ₂ 20 wt%	$1.17 \times 10^{-2} \text{ min}^{-1}$	0.978

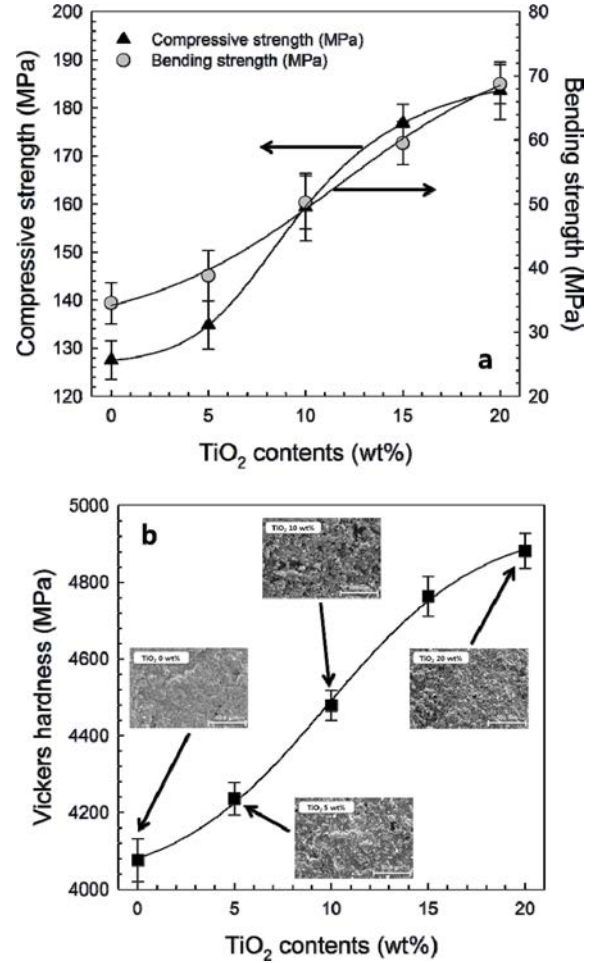


Fig. 6. Physical properties of ceramics nanocomposites with added TiO₂ nanoparticles contents (0, 5, 10, 15, and 20 wt% TiO₂ contents). (a) Compressive strength (MPa) and Bending strength (MPa) of the prepared ceramics nanocomposites. (b) Vickers hardness (MPa) of the prepared ceramics nanocomposites.

The kinetic constant (k_t) was determined by plotting $\ln(q_e - q_t)$ versus t or $\ln(q_e - q_t)/q_e$ versus t . The results indicate that the correlation coefficients (R^2) of the pseudo-first-order model for the linear plots of prepared ceramics TiO₂ nanocomposite are very close to 1. This indicates that the photocatalytic degradation kinetics can be successfully explained by this pseudo-first-order model. The k_t and R^2 of the ceramics TiO₂ nanocomposite added 20 wt% TiO₂ for MO, ATA, 2,4-D, and MB as photodegradation targets are shown in

Table 3. Density and weight change% of ceramics nanocomposites in terms of TiO₂ nanoparticles contents.

	Without TiO ₂	5 wt%	10 wt%	15 wt%	20 wt%
Density (g/cm ³)	2.428	2.573	2.497	2.601	2.587
Weight change% (1N H ₂ SO ₄)	0.139	0.157	0.142	0.140	0.144

Table 2.

The compressive strength and bending strength of the ceramics TiO₂ nanocomposites heat-treated at 800 °C (0, 5, 10, 15, and 20 wt% TiO₂ nanoparticle) were investigated. All the tests were performed 10 times/each samples, and the outcomes are shown in Fig. 6. With the increase in TiO₂ contents, the compressive strength increases from 127.5 to 183.5 MPa. The bending strength also improved from 34.52 to 68.72 MPa. Figs. 6(a) clearly indicates that the growth of the compressive and bending strength at 900 °C (20 wt% TiO₂) is caused by the increasing TiO₂ nanoparticle of the specimens. This suggests that the mechanical strength of our samples TiO₂ nanoparticle included in the ceramics nanocomposites is sufficiently strong, since specimens reinforced by the bonding TiO₂ nanoparticle mainly show a good mechanical strength. Fig. 6(b) shows the Vickers hardness measurements of the specimens heat-treated at 900 °C. It is clear from Fig. 6(b) that the hardness value increases as the content of TiO₂ nanoparticle increases from 0 to 20 wt%. Therefore, the TiO₂ nanoparticle at the highest content accounts for the increase in hardness value. As shown in Fig. 6(b), the sample heat-treated at 900 °C (20 wt% TiO₂) has the maximum hardness value of 4882 ± 45 MPa. In this work, the improvement of well-dispersed TiO₂ nanoparticle in the ceramics nanocomposites developed the compressive and bending strength at 900 °C (20 wt% TiO₂). These findings led us to conclude that the samples in all the TiO₂ nanoparticle content-ranges have appropriate mechanical strength suitable for practical usage. Table 3 shows the chemical durability (weight change%) of the TiO₂ (0, 5, 10, 15 and 20 wt%) added samples heat-treated at 900 °C. The weight change values were evaluated according to the following equation:

$$\text{Chemical durability (weight change\%)} = (m_1 - m_2) / m_1 \times 100$$

where m_1 and m_2 are the weights of the samples before and after immersing in acidic solution [24]. The weight change of the samples is not influenced by the increase in the content of TiO₂, and it is hard to suggest any relation between the weight changes and the differences in the content of TiO₂.

Conclusions

Ceramics TiO₂ nanocomposites were successfully prepared by using TiO₂ nanoparticles, fly ash and waste glass powder as an additive. The photocatalytic activity of the prepared ceramics TiO₂ nanocomposites was

evaluated using MO, ATA, 2,4-D, and MB as photodegradation targets under UV light irradiation. All the ceramics nanocomposites-added TiO₂ nanoparticles tested indicated the photocatalytic activity under UV light irradiation. The test results indicated that the degree of photocatalytic degradation (C/C_0) in the ceramics nanocomposites-added 20 wt% TiO₂ is about 0.264 (MO), 0.141 (ATA), 0.302 (2,4-D), and 0.368 (MB), respectively. The test results also showed that the physical properties of the ceramics nanocomposites are improved by the addition of TiO₂ nanoparticles. The physical properties, i.e., density, compressive strength, bending strength and chemical durability of the ceramics nanocomposites added TiO₂ were estimated. Compressive strength and bending strength increased 183.5 MPa and 68.72 MPa, respectively, when TiO₂ contents were increased from 0 to 20 wt%. The increased TiO₂ contents enhanced the physical properties of the ceramics nanocomposites because the specific matrix-reinforcement bonding is formed by the addition of TiO₂ between the components.

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