

# Fabrication of TiO<sub>2</sub>/Carbon Photocatalyst using Submerged DC Arc Discharged in Ethanol/Acetic Acid Medium

T E Saraswati, A O Nandika, I F Andhika, Patiha, C Purnawan, S Wahyuningsih and S B Rahardjo

Department of Chemistry, Mathematic and Natural Sciences Faculty, Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan, Surakarta 57126 Indonesia

Email: teguh@mipa.uns.ac.id

**Abstract.** This study aimed to fabricate a modified photocatalyst of TiO<sub>2</sub>/C to enhance its performance. The fabrication was achieved using the submerged direct current (DC) arc-discharge method employing two graphite electrodes, one of which was filled with a mixture of carbon powder, TiO<sub>2</sub>, and binder, in ethanol with acetic acid added in various concentrations. The arc-discharge method was conducted by flowing a current of 10–20 A (~20 V). X-ray diffraction (XRD) patterns showed significant placements of the main peak characteristics of TiO<sub>2</sub>, C graphite, and titanium carbide. The surface analysis using Fourier transform infrared spectroscopy (FTIR) revealed that fabricated TiO<sub>2</sub>/C nanoparticles had stretching vibrations of Ti–O, C–H, C=O, C–O, O–H and C=C in the regions of 450–550 cm<sup>-1</sup>, 2900–2880 cm<sup>-1</sup>, 1690–1760 cm<sup>-1</sup>, 1050–1300 cm<sup>-1</sup>, 3400–3700 cm<sup>-1</sup> and ~1600 cm<sup>-1</sup>, respectively. In addition, the study investigated the photocatalysts of unmodified and modified TiO<sub>2</sub>/C for photodegradation of methylene blue (MB) dye solution under mercury lamp irradiation. The effectiveness of the degradation was defined by the decrease in 60-minute absorbance under a UV-Vis spectrophotometer. Modified TiO<sub>2</sub>/C proved to be significantly more efficient in reducing dye concentrations, reaching ~70%. It indicated that the oxygen-containing functional groups have been successfully attached to the surface of the nanoparticles and played a role in enhancing photocatalytic activity.

## 1. Introduction

Titanium dioxide is an excellent photocatalyst because of the high oxidizing power of photogenerated holes and its chemical inertness and non-toxicity [1]. However, due to its low adsorption, titanium dioxide must be modified by carbon to increase its photocatalytic activity. It is known that carbon-based nanoparticles can be produced using the arc-discharge method. Sano et al. (2002) fabricated carbon onions using the arc-discharge method in water [2]. It has been reported that nanoparticles produced via arc-discharge in a liquid medium have been of higher purity, larger quantity, and lower cost than those produced by other methods.

Several fabrication routes for carbon-modified TiO<sub>2</sub> have been reported, including oxidative annealing, hydrolysis followed by carbonization [3,4], solvothermism [5], electrospinning [6,7], chemical vapor deposition (CVD) [8], hydrothermism [9] and sol-gel [10]. To prevent carbon from being deposited directly into bulk TiO<sub>2</sub>, an appropriate technique is needed to allow the co-assembly of carbon and TiO<sub>2</sub> into carbon-modified TiO<sub>2</sub>, which has a nanoarchitecture structure. Torimoto et



al. (1996) reported another simple method of synthesizing a composite of TiO<sub>2</sub>/carbon: sonication of the raw materials of TiO<sub>2</sub> and activated carbon [11]. The material produced using this approach had enhanced adsorption and photodegradation abilities. Saraswati *et al.* confirmed that arc discharge could produce TiO<sub>2</sub> which is encapsulated within graphite layers in liquid media, including titanium dioxide suspension in ethanol [12]. However, problems remained, including the dispersion of nanoparticles in water. The commonly used carbon product was hydrophobic, so the interaction of the nanoparticle surfaces with a water-based environment could not optimally be achieved.

Oxygen-containing functional groups, including hydroxyl (-OH), play major roles in degrading and mineralizing colored dyes. Surface modification using oxygen-containing functional groups can be performed by plasma [13, 14], chemical [15, 16] and electrochemical [17] routes. Introducing an oxidation agent containing functional groups into the liquid medium used in the submerged arc-discharge method has been considered a useful way to modify the condensed carbon material formed during the arc discharge. Supplying suitable oxidizing agents to the pores of the carbon matrix has been believed to be the key to successfully introduce oxygen-containing functional groups to the surface of the carbon material [18]. A successful surface modification enhances the photodegradation activity of titanium dioxide.

The present study investigated the synthesis of carbon modified TiO<sub>2</sub> (TiO<sub>2</sub>/C) functionalized by oxygen-containing functional groups using an arc-discharge method performed in an ethanol/acetic acid liquid medium. To the best of our knowledge, this has not previously been reported. The fabrication process was followed by photocatalytic experiments using methylene blue (MB) dye. The activity of the TiO<sub>2</sub>/C photocatalyst was observed by measuring the efficiency of photocatalytic degradation of aqueous MB in 60 minutes under mercury lamp irradiation in batch mode.

## 2. Experimental Method

### 2.1. Fabrication of TiO<sub>2</sub>/Carbon

Nanoparticles were fabricated using an arc-discharge method in an ethanol/acetic acid medium employing graphite taken from a dry-cell battery for the electrodes. The anode was filled with carbon powder, titanium dioxide, and silica glue as a binder at a ratio of 3:1:1 w/w and was formed precisely to facilitate the electrical breakdown. Ethanol (35.7%) and acetic acid (5.0%, 12.6%, 25.3%, 37.9% and 50%) formed the liquid medium.

The anode and cathode electrodes were submerged in the liquid medium with a 1–2-mm gap between them. The discharge current was ~10–20 A. When the arc-discharge process began, there was a bright area between the two electrodes, indicating the arc-plasma region. This arc caused the carbon graphite in the cathode to evaporate. Furthermore, the interaction between carbon graphite and TiO<sub>2</sub> produced the TiO<sub>2</sub>/C nanoparticles. This fabrication included two types of powder: floating and sedimentary. The floating material had a hydrophobic surface, and the sedimentary material had a hydrophilic one. Therefore, the sediment was analyzed further using several instruments.

### 2.2. Photodegradation of methylene blue (MB)

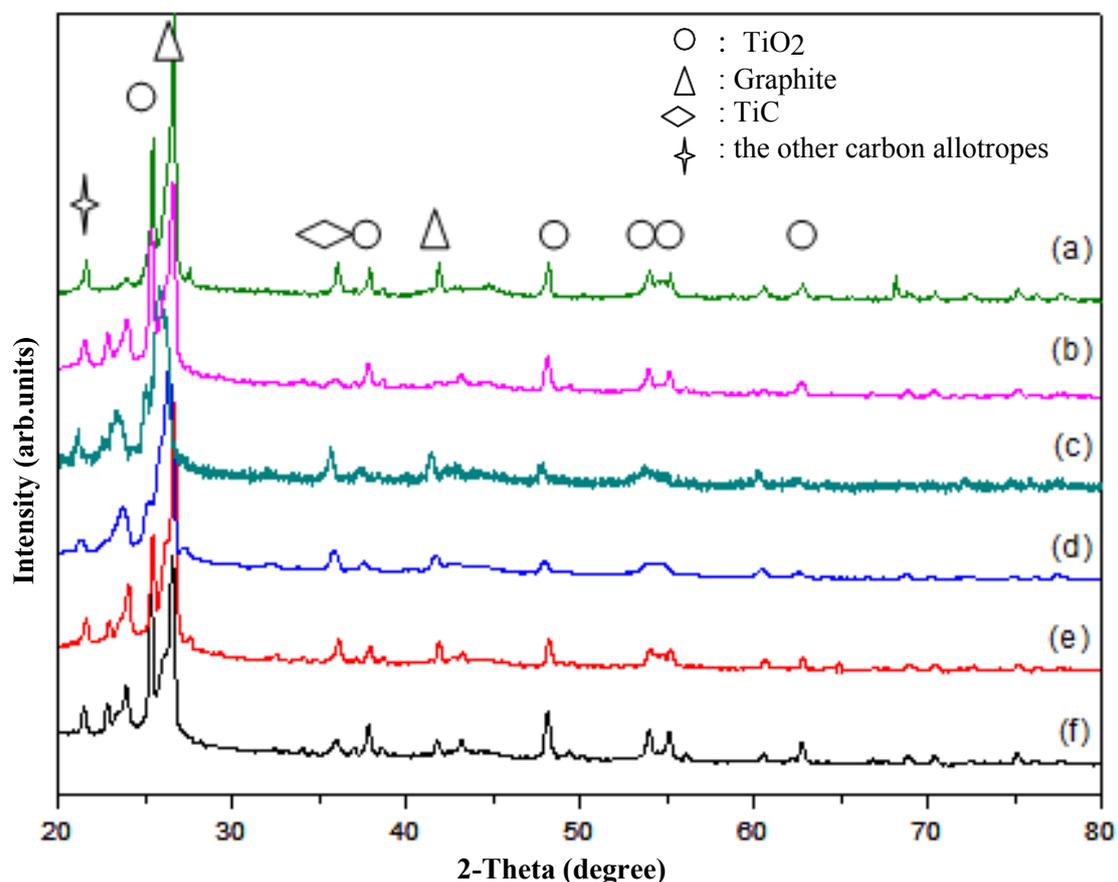
A photocatalyst nanoparticle of TiO<sub>2</sub>/C (0.01 g) was added into dye sample in a vial containing 3-ppm MB solution. The sample was sonicated for ~30 min in a dark room and then irradiated under a 125-W mercury lamp for ~60 min. The solution was centrifuged to separate the nanoparticle from the MB solution. The absorbance of the MB was measured every 15 min. Each sample was tested to identify its photodegradation efficiency.

## 3. Results and Discussion

The arc-discharge method used two electrodes, i.e. anode, and cathode, which were momentarily brought into contact, striking an arc. Then, the distance between the two electrodes was reduced and a constant gap maintained between them by adjusting the position of the anode. The high temperature sublimated the carbon in the anode during this process. During cooling in the cool zone, the sublimated carbon became carbon nanomaterials, including carbon onions, fullerenes and other

carbon allotropes with  $sp^2$  hybridization carbon structures. In addition, the fabrication process produced  $TiO_2/C$  resulted from the interaction between the carbon graphite and  $TiO_2$  were found as floating and sedimentary nanoparticles. The floating nanoparticles were typically hydrophobic while the sedimentary nanoparticle was hydrophilic, meaning that the latter had better dispersion in the liquid medium. The sedimentary powder from the surface of the liquid medium was characterized using several instruments.

Figure 1 shows the X-ray diffraction (XRD) patterns of the original materials,  $TiO_2$  anatase, and carbon graphite. The patterns showed high crystallinity of  $TiO_2$  at some peaks, including hkl (101)  $2\theta = 25.33^\circ$ ; hkl (200)  $2\theta = 48.06^\circ$  and hkl (105)  $2\theta = 53.95^\circ$ , compared to the standard for  $TiO_2$  anatase (JCPDS No. 86-1157) in hkl planes: (101)  $2\theta = 25.32^\circ$ ; hkl (200)  $2\theta = 48.06^\circ$  and hkl (105)  $2\theta = 53.98^\circ$ . The XRD pattern of the graphite showed peaks at hkl (002)  $2\theta = 26.60^\circ$ , which matched the standard for graphite (JCPDS No. 41-1487) at hkl (002)  $2\theta = 26.62^\circ$ . Furthermore, the peak at  $2\theta = 20$  to  $25^\circ$  was indicated to  $C_{60}$  (fullerene), carbon onions and other carbon allotropes with  $sp^2$  hybridization carbon structures.

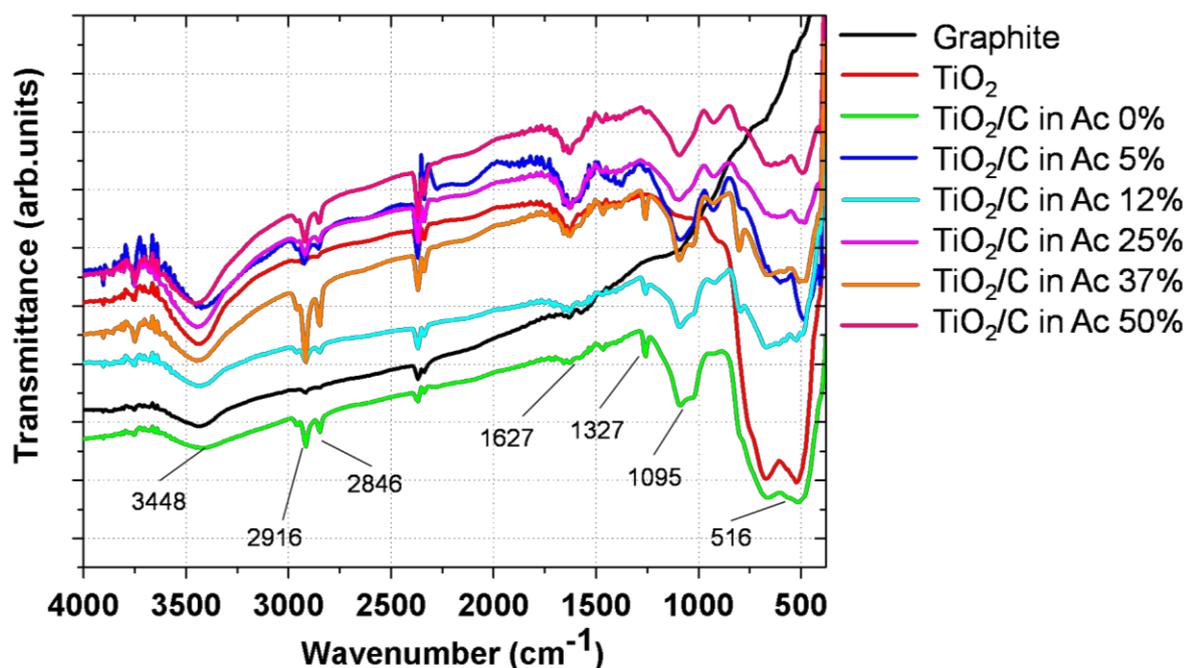


**Figure 1.** XRD patterns of the nanoparticles of (a)  $TiO_2/C$  0, (b)  $TiO_2/C$  5, (c)  $TiO_2/C$  12, (d)  $TiO_2/C$  25, (e)  $TiO_2/C$  37 and (f)  $TiO_2/C$  50.

Figure 1 also reveals the XRD patterns of the  $TiO_2/C$  nanoparticles, which had peaks similar to those of the original materials. However, Figure 1 also shows new peaks at hkl (202)  $2\theta = 36.02^\circ$  (JCPDS TiC No. 72-2496) and hkl (222)  $2\theta = 20.75^\circ$  (JCPDS  $C_{60}$  No. 47-0787) that refer to TiC and  $C_{60}$ . It indicated that the nanoparticles were composites in which the main peak characteristic of the original material still appeared, along with newly generated peaks. The formation of titanium carbide has been shown in the reaction of  $TiO_{2(s)} + 3C_{(s)} \rightarrow 2CO_{(g)} + TiC_{(s)}$  [19].

Fourier transform infrared spectroscopy (FTIR) was used to characterize the functional groups on

the surface of the carbon graphite by comparing transmittance of the peak lines. The FTIR technique was mainly used qualitatively to assess the surface character of the carbon layer. The original material, graphite carbon, absorbed almost all radiation in the visible spectra, and the peaks obtained were usually a sum of the interaction of the various types generated by the functional groups.



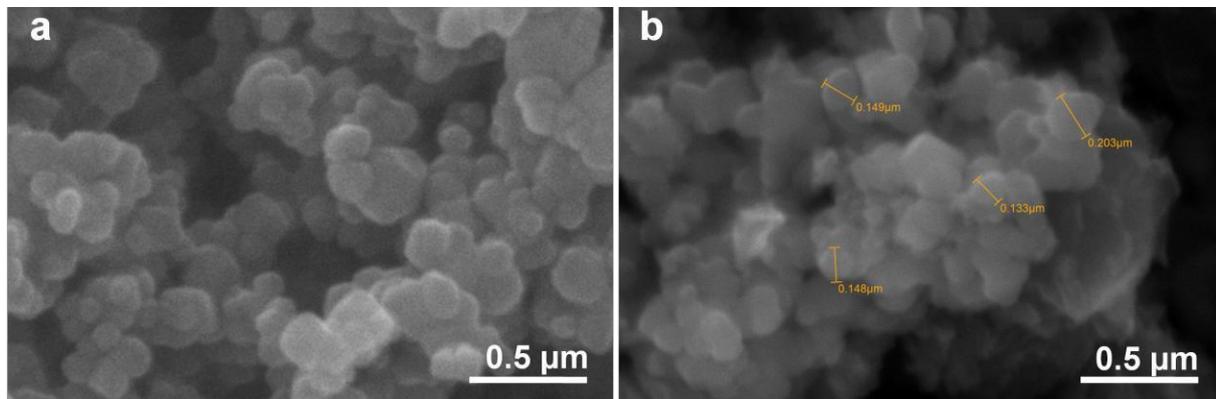
**Figure 2.** FTIR spectrum of carbon graphite,  $\text{TiO}_2$  anatase,  $\text{TiO}_2/\text{C}$  0,  $\text{TiO}_2/\text{C}$  5,  $\text{TiO}_2/\text{C}$  12,  $\text{TiO}_2/\text{C}$  25,  $\text{TiO}_2/\text{C}$  37 and  $\text{TiO}_2/\text{C}$  50.

Figure 2 shows the spectra of the carbon graphite and the  $\text{TiO}_2$  anatase and compares them with those of the  $\text{TiO}_2/\text{C}$  nanoparticles treated by adding acetic acid. This comparison indicated that the organic acid interacted with the surface of the graphite through the carboxylic group, as expected. The region in the range of  $450\text{--}550\text{ cm}^{-1}$  corresponded to the stretching vibration of the Ti-O. A broadband at  $3300\text{--}2500\text{ cm}^{-1}$  corresponded to the stretching of the -OH group of alcohol or phenol on the adsorbent surface. The peaks in the region of  $2850\text{--}3000\text{ cm}^{-1}$  corresponded to the stretching of C-H. A broad peak at about  $1600\text{ cm}^{-1}$  signified the presence of C=C bonds in aromatic rings. There was a C=O bond at about  $1700\text{ cm}^{-1}$ , although it is not prominent. Similarly, the presence of C-O of alcohol, ether, carboxylic acid, and ester was signaled in the range from  $1000\text{--}1320\text{ cm}^{-1}$ . As can be seen in Figure 2, the FTIR spectrum of  $\text{TiO}_2/\text{C}$  12 nanoparticles had a different pattern, and the area of -OH vibration was larger than the others. The vibration areas of the samples  $\text{TiO}_2/\text{C}$  0,  $\text{TiO}_2/\text{C}$  5,  $\text{TiO}_2/\text{C}$  12,  $\text{TiO}_2/\text{C}$  25,  $\text{TiO}_2/\text{C}$  37 and  $\text{TiO}_2/\text{C}$  50 were 745.6, 132.3, 911.2, 452.8, 439.8 and 576.4, respectively. These results indicated that  $\text{TiO}_2/\text{C}$  12 nanoparticles had better dispersion in the liquid medium because there were interactions by which hydrogen bonding formed.

Also, the samples were investigated using a scanning electron microscope (SEM) to identify the morphology and structures of the constituents in the  $\text{TiO}_2$  anatase and  $\text{TiO}_2/\text{C}$  12. Figure 3 shows the results of morphological examination of  $\text{TiO}_2$  anatase and  $\text{TiO}_2/\text{C}$  nanoparticles. The SEM image with  $50,000\times$  magnification showed that the nanoparticles were in spherical structures, with  $\text{TiO}_2/\text{C}$  12 clusters varying in size from  $140\text{--}180\text{ nm}$ .

A dispersion test was applied to confirm that  $\text{TiO}_2/\text{C}$  12 nanoparticles had better dispersion than  $\text{TiO}_2/\text{C}$  0 (without an addition of acetic acid). In this case, distilled water was used as the liquid medium and ethanol was employed as the comparison. Figure 4 shows the dispersion test results of

each nanoparticle sample.



**Figure 3.** SEM images of (a) TiO<sub>2</sub> anatase and (b) TiO<sub>2</sub>/C 12.

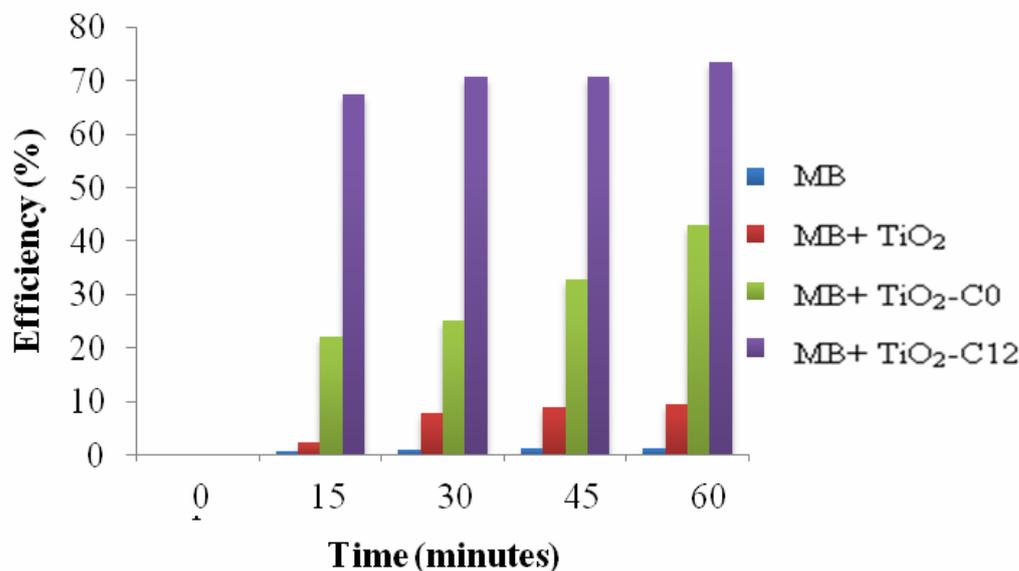


**Figure 4.** Dispersion of TiO<sub>2</sub>/C nanoparticles (left to the right) TiO<sub>2</sub>/C 0, TiO<sub>2</sub>/C 5, and TiO<sub>2</sub>/C 12, in (a) distilled water and (b) ethanol.

As presented in Figure 4, the TiO<sub>2</sub>/C 12 nanoparticles had better dispersion than the other samples in both distilled water and ethanol. It indicated that oxygen-containing functional groups, including –OH, C–O and C=O, successfully attached to the surface of the nanoparticles. An experiment was performed using an MB dye solution as a model substance to evaluate the photocatalytic activity of the samples (TiO<sub>2</sub> anatase, TiO<sub>2</sub>/C 0 and TiO<sub>2</sub>/C 12). The initial MB concentration was 3 ppm. The direct photolysis used a 125-W mercury lamp. The adsorption of MB was measured every 15 minutes by a Uv-vis spectrophotometer. Figure 5 shows the percentages of MB removed.

As shown in figure 5, photodegradation of MB was optimally reached when TiO<sub>2</sub>-C 12 fabricated using submerged arc discharge in ethanol/acetic acid medium were applied as a photocatalyst. This best result was achieved due to the effects of both adsorption and photodegradation. The presence of carbon graphite layers and also C<sub>60</sub> (fullerene), carbon onions and other carbon allotropes with sp<sup>2</sup> hybridization carbon structures played a role in adsorbing the dye molecules from the solution. The adsorbed molecules on the surface of the graphite came in contact with the TiO<sub>2</sub>, causing

photodegradation. Therefore, both effects of adsorption and photodegradation increased the efficiency of the photodegradation.



**Figure 5.** Percentage of MB removal (without photocatalyst), MB removal using photocatalyst of TiO<sub>2</sub> anatase powder (MB+TiO<sub>2</sub>), MB removal using MB+TiO<sub>2</sub>/C 0 photocatalyst, and MB removal using TiO<sub>2</sub>/C 12 photocatalyst.

#### 4. Conclusion

The TiO<sub>2</sub>/C nanoparticles were successfully prepared using an arc-discharge method in an ethanol/acetic acid liquid medium. XRD analysis of the TiO<sub>2</sub>/C nanoparticles showed that the main peaks of the original materials (TiO<sub>2</sub> and carbon) had high crystallinity, indicating that the materials were composites. The FTIR spectra of the TiO<sub>2</sub>/C showed the presence of oxygen-containing functional groups, including –OH, C=O and C-O. Therefore, this material had better dispersion. SEM studies showed that the nanoparticles product had spherical structures with clusters that varied in size from 140–180 nm. The better dispersion exhibited by TiO<sub>2</sub>/C 12 nanoparticles indicated that this material was more capable of increasing the efficiency of photodegradation. MB removal using TiO<sub>2</sub>/C 12 photocatalyst had a higher efficiency of photodegradation (73.60%) than MB removal using TiO<sub>2</sub>/C 0 which was fabricated by submerging arc discharge in ethanol medium without the addition of acetic acid (43.01%).

#### 5. References

- [1] Fu D G, Zhang Y, Wang X, Liu J-z and Lu Z-h 2002 *Chem. Lett.* **30**
- [2] Sano N, Wang H, Alexandrou I, Chhowalla M, Teo K B K, Amaratunga G A J and Iimura K 2002 *J. Appl. Phys.* **92** 2783-8
- [3] Morawski A W, Janus M, Tryba B, Inagaki M and Kalucki K 2006 *C. R. Chim.* **9** 800-5
- [4] Sakthivel S and Kisch H 2003 *Angew. Chem. Int. Ed.* **42** 4908-11
- [5] Zhao L, Chen X, Wang X, Zhang Y, Wei W, Sun Y, Antonietti M and Titirici M-M 2010 *Adv.Mater.* **22** 3317-21
- [6] Kim C H, Kim B-H and Yang K S 2012 *Carbon* **50** 2472-81
- [7] Peining Z, Nair A S, Shengjie P, Shengyuan Y and Ramakrishna S 2012 *ACS Appl. Mater. Interfaces* **4** 581-5
- [8] Wojtoniszak M, Dolat D, Morawski A and Mijowska E 2012 *Nanoscale Res. Lett.* **7** 1-6

- [9] Zhang H, Lv X, Li Y, Wang Y and Li J 2009 *ACS Nano* **4** 380-6
- [10] Morawski A, Janus M, Tryba B, Toyoda M, Tsumura T and Inagaki M 2009 Carbon modified TiO<sub>2</sub> photocatalysts for water purification. In: *Pol. J. Chem. Technol.*, p 46
- [11] Torimoto T, Ito S, Kuwabata S and Yoneyama H 1996 *Environmental Science & Technology* **30** 1275-81
- [12] Saraswati T E, Andika I F, Anwar M, Purnawan C, Wahyuningsih S and Patiha 2015 *Advanced Research Materials* **1123** 285-8
- [13] Boudou J P, Paredes J I, Cuesta A, Martínez-Alonso A and Tascón J M D 2003 *Carbon* **41** 41-56
- [14] Pittman C U, Jiang W, He G R and Gardner S D 1998 *Carbon* **36** 25-37
- [15] Pittman C U, He G R, Wu B and Gardner S D 1997 *Carbon* **35** 317-31
- [16] Xie F, Phillips J, Silva I F, Palma M C and Menéndez J A 2000 *Carbon* **38** 691-700
- [17] Hu C-C and Wang C-C 2004 *J. Power Sources* **125** 299-308
- [18] Shen W, Li Z and Liu Y 2008 *Recent Patents on Chemical Engineering* **1** 27-40
- [19] Swift G A and Koc R 1999 *Journal of Materials Science* **34** 3083-93

### Acknowledgments

This work was supported in part by research grants provided by the Minister of Research, Technology and Higher Education, Republic of Indonesia, under project No. 458/UN27.21/LT/2016 and 632/UN27.21/LT/2016.