INWASCON
ISSN: 2710-5873 (Online)
CODEN: ITMNBH

***i* TECH MAG**

DOI: http://doi.org/10.26480/itechmag.03.2021.13.19

RESEARCH ARTICLE

PHOTOCATALYTIC DEGRADATION OF BISPHENOL E WITH NANO-SCLAED TIO_2 IN AQUEOUS SOLUTION UNDER SOLAR RADIATION

Tomoki Sugiyama[a], Ahmed H. A. Dabwan[b]*, Mai Furukawa[a], ikki Tateishi[c], Hideyuki Katsumata[a] and Satoshi Kaneco[a,c]

[a]Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu, Mie 514-8507, Japan.
[b]University College TATI, Jalan Panchur, Teluk Kalong, 24000, Kemaman, Terengganu, Malaysia.
[c]Global Environment Center for Education & Research, Mie University, Tsu, Mie 514-8507, Japan.
**Corresponding Author E-mail: drahmedtati@gmail.com*

ARTICLE DETAILS

Article History:

Received 01 February 2021
Accepted 17 March 2021
Available online 29 March 2021

ABSTRACT

In this work focus was paid to the photocatalytic degradation of Bisphenol E with nano-scaled TiO_2 solution under sunlight. Instruments used for characterization and study the removal efficiency were; visible ultraviolet spectrophotometer, SEM (acceleration voltage 25kV) and TEM (acceleration voltage 80kV), *X-ray diffraction and BET surface area.* Under the optimum conditions; (pH;6, Radiation time; 90 min, Catalyst wt; 0.2g, reaction temperature; 20 °C), complete degradation was obtained. Byproducts from this study could be similar to our previous ones since Bisphenol A and Bisphenol E have very similar structures, hence their decomposition intermediates most probable not to be far. it was found that the decomposition reaction of bisphenol E follows the pseudo-first-order reaction kinetics.

KEYWORDS

Photocatalysts Degradation, Nano Scaled TiO_2, Bisphenol E, Endocrine Disruptors, Pseudo-first-order.

1. INTRODUCTION

As people's lives become more phosphorous and easier with the development of science and technology, environmental problems are becoming more serious. As one of them, there are concerns about the effects of exogenous endocrine disruptors (environmental hormones) on ecosystems and humans. Many wildlife reproductive abnormalities have been reported as the effects of environmental hormones on the ecosystem. Currently, 70 to 80,000 kinds of chemical substances are being used all over the world, and about 70 kinds of these substances are suspected to be endocrine disrupters. Bisphenol E is one of them and is used in epoxy resin, polycarbonate, dental materials and rubber (Figure 1).

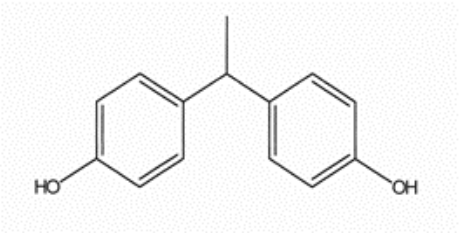

Figure 1: Chemical formula of Bisphenol E

Bisphenol E is thought to work the same as female hormones that called "estrogen". It is a hormone that prepares for the egg, and its secretion increases from the end of menstruation to before ovulation. Secretion begins to decrease sharply from the mid-40s, causing various menopausal symptoms such as depression, insomnia, and malaise. However, hormones maintain a delicate balance, and too much hormones have an adverse effect. In recent years, research on the decomposition of pollutants using a semiconductor photocatalyst has been actively conducted as one of the means for purifying environmental pollutants. Titanium oxide (TiO_2) is a typical semiconductor photocatalyst. It has been reported that this photocatalyst is used for the decomposition of many organic pollutants such as organochlorine compounds and pigments. It has been proven that photocatalytic decomposition causes organic pollutants to be mineralized to carbon dioxide and other inorganic ions. TiO_2 is an n-type semiconductor due to its oxygen deficiency.

It has three types of polymorphs, including tetrahedral anatase, rutile, and orthorhombic brookite. Among them, anatase TiO_2 Nano particles (NPs) have the highest photocatalytic activity due to the retardancy of the recombination of holes and electrons (Bui et al., 2020; Guo et al., 2010; Jang et al., 2008; Liu et al., 2002; Prabhu et al., 2004; Liu et al., 2005; Rodriguez et al., 2003; Weng et al., 2006; Ma et al., 2018; Fujishima et al., 2000). Of these three types, the general ones are the rutile type and the anatase type, and in terms of photoactivity, anatase is recommended due to the difference in the energy band structure. It is well known that the The energy bandgaps of anatase, rutile, and brookite are 3.2, 3.0, and ~3.2 eV, respectively. Besides in general TiO_2 is a very stable substance that is insoluble in most acids, bases and organic solvents and does not undergo photolysis (Tao et al., 2008; Gong et al., 2001; Mor et al., 2003; Eder et al., 2006; Huang et al., 2010). Since little research has been done on Bisphenol E and its decomposition and detoxification, in this study, we focused on the development of comprehensive decomposition method. Titanium oxide photocatalyst was used as a photo catalyst because of it is simplicity, the negligible environmental load also availability and inexpensive.

2. MATERIAL AND METHODS

2.1 Creation of titanium oxide nanotubes

Carbon nanotubes (50 mg) were added to ethanol (1.2 ml). At this time, the outer diameters of the carbon nanotubes were changed to 10-20, 20-40, 40-60, and 60-100 nm. Ultrasonic irradiation was performed for 10 minutes to disperse. Then, the mixture was cooled to 0 °C., benzyl alcohol (0.39 ml) and water (0.14 ml) were added, then mixture was stirred. A solution prepared by dissolving titanium (IV) tetrabutoxide monomer in ethanol was gradually added then the mixture was stirred for 1 hour. After that mixture was filtered under reduced pressure, the filtrate was washed with ethanol, and dried at room temperature for 24 hours. The obtained substance was calcined at 550 ° C. for 2 hours to obtain titanium oxide nano-tubes. Effect of sintering temperature was examined to see the effect

of temperature on the outer diameter of carbon nano-tubes. Examined temperatures were 350, 450, 550, and 650 ° C.

2.2 Preparation of Bisphenol E

Bisphenol E was used as the study component, and it was dissolved in water treated with an ultrapure water device (GSH-2000, Advantech Toyo Co., Ltd.) with stirring for about 1 day to prepare a stock solution with a concentration of 100 ppm. This was diluted to 10 ppm each time before conducting experiments.

2.3 Light irradiation experiment

50 ml of Bisphenol E aqueous solution (10 ppm) and from 0 to 10 mg/l of photocatalyst were added to a Pyrex glass reaction vessel. After stirring in a dark place for 30 minutes to reach the absorption / desorption equilibrium, light was irradiated with a xenon lamp (2.5 mW /cm^2). At this time, the reaction vessel was placed in a constant temperature bath (a water tank with a quartz plate window) and the temperature was adjusted to the study range of temperature (20 - 50 °C). Irradiation process is illustrated in Figure 1. Experimental conditions & parameters investigated are summarized in Table 1.

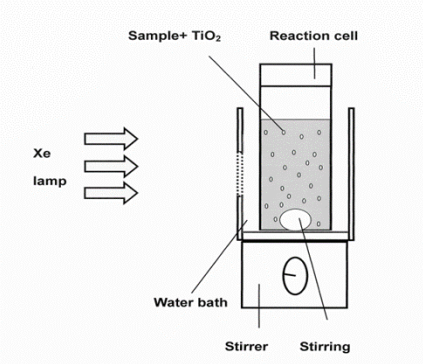

Figure 2: Photoreactor

Table 1: Experimental conditions.

Catalyst	TiO_2
Light Source	Xe Lamp
Light Intensity	2.5 mW/cm^2
Sample Volume	50 ml
Irradiation Time	10-90 min
Catalyst Concentration	0-10 mg/ml
Bisphenol E Concentration	10 ppm
Temperature	20-50 °C
pH	3 - 10

2.4 Analysis

2.4.1 Analysis of Bisphenol E

After light irradiation, the reaction solution was filtered through a 0.20 μm membrane filter to remove the photocatalyst, and then the absorbance was measured with a visible ultraviolet spectrophotometer and calculated by comparing to the concentration of prepared standard solution

2.4.2 Absorption spectrum of catalyst

50 mg of photocatalyst was diluted with 3.5 g of barium sulfate, and the absorbance was measured with a visible ultraviolet spectrophotometer.

2.4.3 Observation with an electron microscope

SEM (acceleration voltage 25kV) and TEM (acceleration voltage 80kV) images of the photocatalyst were taken.

2.4.4 X-ray diffraction

SRD measurement of photocatalyst was performed.

2.4.5 BET surface area

Using liquid nitrogen, the BET surface area of the photocatalyst was measured by adsorption and desorption of nitrogen. The BJH method was used as the calculation method.

3. Results and Discussion

3.1 Effect of photocatalytic amount

Effect of the amount of photocatalyst on the decomposition of Bisphenol E was examined. The experimental conditions at this time are shown in Table1 and the results are shown in Fig. 3. Catalyst study range was 0-10 mg/ml. The decomposition rate was determined by photocatalytic decomposition of Bisphenol E, measuring its concentration by high performance liquid chromatography, and calculating the ratio of the Bisphenol E concentration after decomposition to the initial concentration. From Fig. 3 the decomposition rate increased as the amount of TiO_2 increased up to 0.4 g, and the decomposition rate became constant at 0.5 g. The reason behind is attributed to the amount of light irradiation that hits the Pyrex glass container that makes the decomposition rate is constant. Based on this result, the amount of TiO_2 was set to 0.4 g in the subsequent experiments.

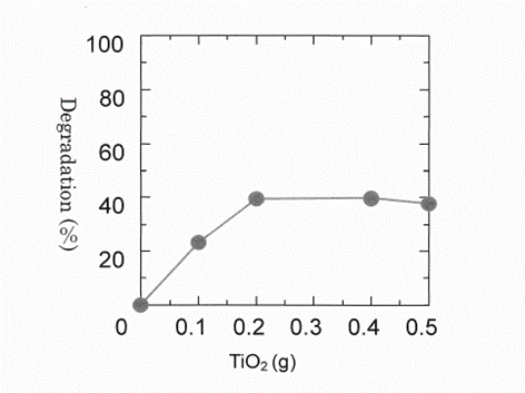

Figure 3: Effect of TiO2 amount on photocatalytic degradation

3.2 Effect of pH

The pH of the solution is also one of the important factors in the photocatalytic decomposition on the surface of semiconductor particles. This is because the pH value of the solution changes the charge property of the photocatalyst surface, which determines the adsorption property of the decomposition target. Therefore, the effect of the initial concentration of Bisphenol E on the decomposition rate was investigated. The experimental conditions are shown in Table 1 (pH study range was 3-10.) and the results are shown in Fig. 4 where the decomposition rate was maximized at pH 6, and it was confirmed that the decomposition rate decreased even if it became more basic or acidic. Therefore, the experiment was carried out with the optimum pH set at 6.

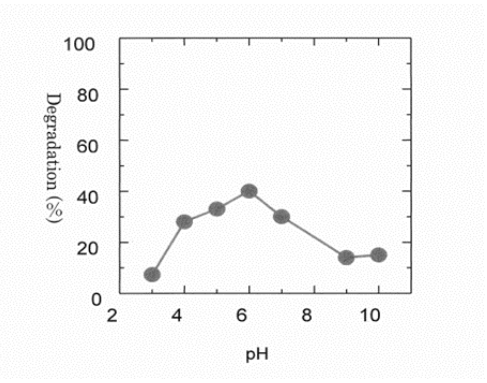

Figure 4: Effect of pH value on photocatalytic degradation

Next, we consider the factors that affect pH in photocatalytic decomposition of Bisphenol E. In photocatalytic decomposition, it is necessary that the decomposition target is adsorbed on the photocatalyst. Here, the charge on the surface of the photocatalyst will be described. At pH 6.25, the charge on the surface of TiO_2 is zero (pH_{zpc} =6.25) whivh means in the region more acidic than this pH, the surface of TiO_2 is positively charged, and conversely, in the basic region, it is negatively charged. It is considered that the pH of the solution affected the decomposition rate as a result of the difference in the amount of Bisphenol E adsorbed on TiO_2 due to this property.

Cite the Article: Tomoki Sugiyama, Ahmed H. A. Dabwan, Mai Furukawa, ikki Tateishi, Hideyuki Katsumata and Satoshi Kaneco (2021). Photocatalytic Degradation of Bisphenol E with Nano-Sclaed Tio_2 in Aqueous Solution Under Solar Radiation. *i TECH MAG, Vol 3: 13-19.*

That is, the adsorption of relatively non-polar Bisphenol E is best in the vicinity of pH H_{zpc}, so that the decomposition rate is also considered to be high. It has also been reported that in photocatalytic decomposition of other organic substances, the decomposition rate increases as the pH value increases. It is considered that the reason is that hydroxyl radicals are abundantly generated due to the abundance of hydroxyl ions in the basic region. It is considered that the reason why the increase in the decomposition rate was not confirmed in the basic region in this study is that the decomposition was performed preferentially by the holes generated in TiO2 over the hydroxyl radicals.

3.3 Effect of reaction temperature

Here, the effect of the decomposition reaction temperature on the Bisphenol E photocatalytic decomposition was investigated. The experimental conditions are shown in Table 1 and the results are shown in Figure 5. Study temperature range was from 20 to 50 °C. It was confirmed that the decomposition rate increased with the increase in temperature. From this, it was found that the temperature should be raised in order to increase the decomposition rate, but the energy cost is required to raise the temperature. From the viewpoint of practical use, it is not desirable that the energy cost is high. Therefore, in this study, the reaction temperature was set to 20 °C, which is close to room temperature.

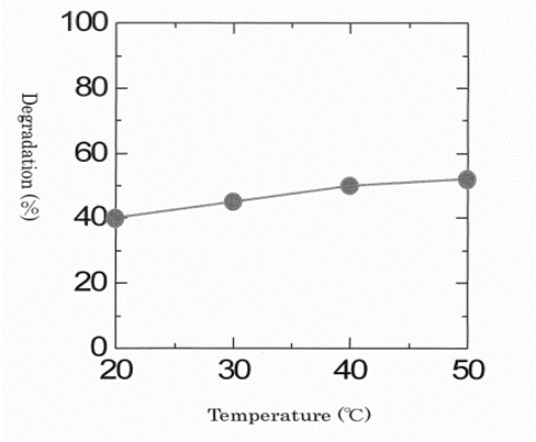

Figure 5: Effect of temperature on photocatalytic degradation

3.4 Effect of light irradiation time

In this experiment, the decomposition rate of Bisphenol E with respect to the light irradiation time was investigated. Experimental conditions are shown in Table 1. Irradiation time range was 10-90min. Results are depicted in Fig. 6. The decomposition rate of Bisphenol E increased with the passage of time, and the decomposition rate reached almost 100% in 90 minutes. From this, it can be said that TiO_2 is suitable for decomposing Bisphenol E.

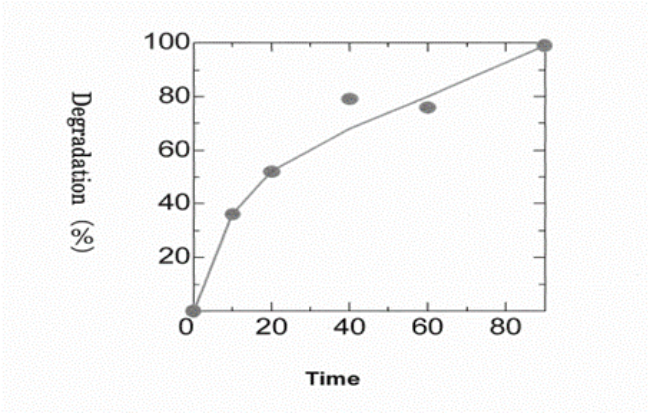

Figure 6: Effect of irradiation time on photocatalytic degradation

3.5 Decomposition kinetics

Previous studies showed that the photocatalytic initial decomposition reactions follow pseudo-primary kinetics. This is expressed by the following equation.

$$dC/dt=k_{obs}C \quad (1)$$

Here, C is the concentration of Bisphenol E at time t, and K_{obs} is the first-order reaction rate constant. The initial concentration of Bisphenol E is C_o (t =0), and equation (1) can be expressed as follows.

$$Ln(C/Co) = k_{obs} \quad (2)$$

Linear graph from the plotted graph of ln (C/C_o) with respect to time as shown in Figure 7 was obtained. it was found that the decomposition reaction of Bisphenol E follows the pseudo-first-order reaction kinetics. In the decomposition of organic pollutants, it is very important to identify the decomposition route and intermediates. This is because it is possible that more dangerous substances will be produced in the process of decomposition. Since the intermediate was not identified in this study, our previous studies, were conducted in details and we predict that the intermediates byproducts from this study will be similar to our previous ones since Bisphenol A and Bisphenol E have very similar structures, and their decomposition intermediates appear to be similar (Fujishima et al., 2000; Kaneco et al., 2004; Hoshiyama et al., 2016). The structure of the expected intermediates are shown in Fig. 8. In the decomposition study of Bisphenol A, it was confirmed that water and carbon dioxide were finally decomposed, and it seems that there are no residual phenols with high toxicity and high stability in this experiment. However, further research is needed to confirm this fact.

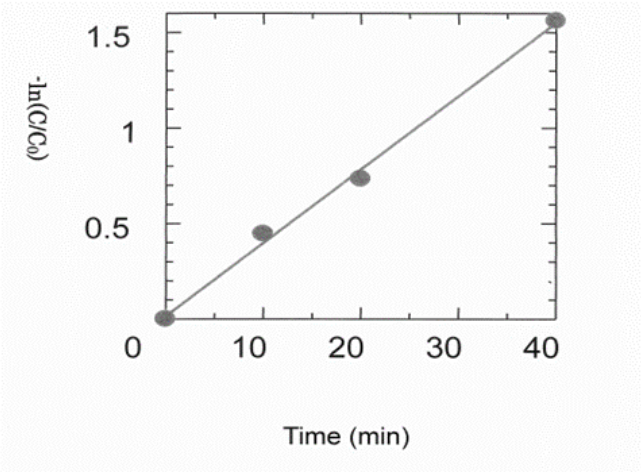

Figure 7: Plot of -Ln(C/Co) versus irradiation time

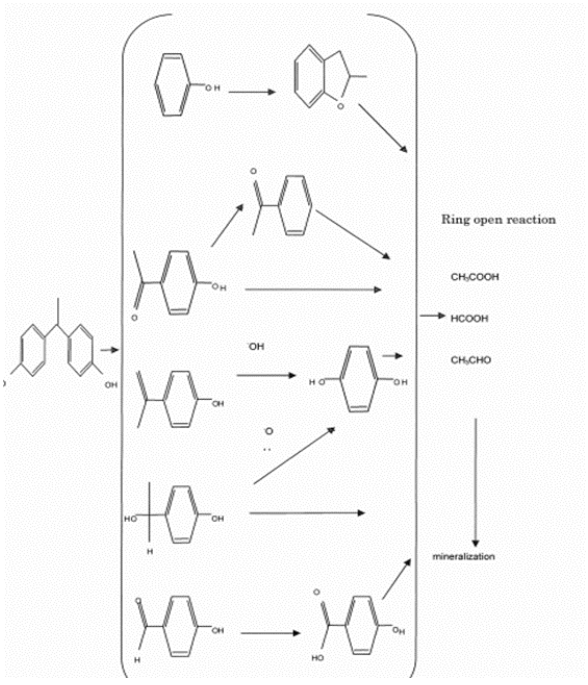

Figure 8: Proposed step of photodegradation of Bisphenol E

3.6 Decomposition Mechanism

The photocatalytic decomposition mechanism of pollutants by TiO_2 is illustrated by Figure 9.

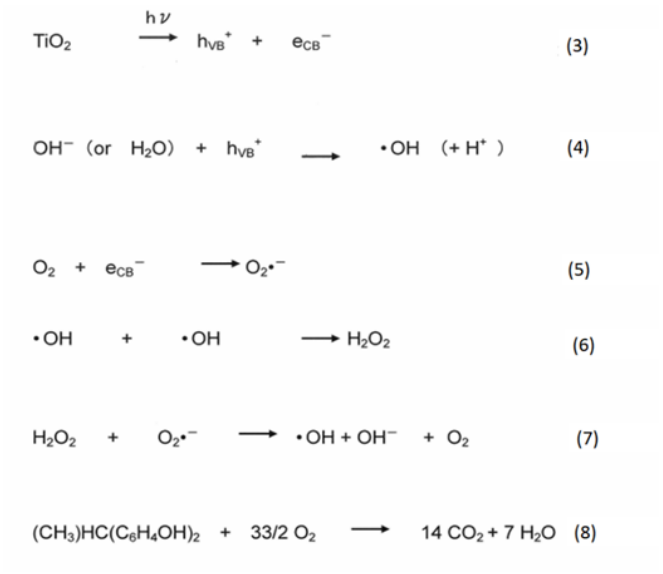

Figure 9: Decomposition mechanism of Bisphenol E

Description can be summarized in the following steps; First, an electron hole is formed in TiO_2 when light of 3.2 eV or more emitted (light having a wavelength of 387 nm or less), which is the energy band gap of TiO_2 (Equation 3). Second step is some of these electrons may recombine, but holes in the valence band generate hydroxyl radicals from hydroxyl ions in water or water (Equation 4). In addition, oxygen existing all over the surface of semiconductor particles becomes superoxide radical anions (Equation 5) due to the electrons of the conductor, and hydroperoxide radicals and hydroxyl radicals are generated (Equation 6 & 7). It is believed that the radicals generated in this way are highly reactive and can be used to decompose various organic compounds. In addition, decomposition of organic compounds by direct oxidation by holes generated in titanium oxide is also conceivable. Therefore, final results will be decomposition into carbon dioxide and water (Equation 8).

4. Conclusion

In this experiment, Bisphenol E could be photo-catalytically decomposed using TiO_2. In the presence of TiO_2, the decomposition rate of Bisphenol E (10ppm) for 90 minutes under light irradiation reached 100%. One more advantage of this photocatalytic decomposition of TiO_2, the optimum pH was 6 which is close to the neutral range, so no need for adjusting pH value as a result cost of treatment will be reduced. Since the mineralization of Bisphenol E could not be investigated, further research is needed to identify the intermediate product. It has been confirmed that this is a useful and reliable treatment method under mild conditions.

Acknowledgement

Part of this research was carried out in University Collage TATI, GRANT NO. 9001-2011. Any opinions, findings, Conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the view of the supporting organizations.

References

Akira Fujishima Tata N. Rao Donald A. Tryk. 2000. Titanium dioxide photocatalysis. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 1 (1), Pp. 1-21.

Bui, V.K.H., Tran, V.V., Moon, J.Y., Park, D., Lee, Y.C., 2020. Titanium Dioxide Microscale and Macroscale Structures: A Mini-Review. Nanomaterials, 10, Pp. 1190.

Eder, D., Kinloch, I.A., Windle, A.H., 2006. Pure rutilenanotubes, Chemical. Communications, 13, Pp. 1448-1450.

Fujishima, A., Hashimoto, K., Watanabe, T., 2000. Mechanism of Photocatalyst. Nihon Jitsugyo Publishing Co., Ltd.

Gong, D., Grimes, C.A., Varghese, O.K., Hu, W., Singh, R.S., Chen, Z., Dickey, E.C., 2001. Titanium oxide nanotube arrays prepared by anodic oxidation. Journal of Materials Research, 16, Pp. 3331–3334.

Guo, R.S., Wanga, C.W., Chen, J.B., Wanga, J., Wanga, L.Q., Liu, W.M., 2010. Field emission from TiO2/Ti nanotube arrays with different morphologies. Physica B: Condensed Matter, Pp. 405, –4686.

Hoshiyama, N., Dabwan, A.H.A., Katsumata, H., Suzuki, T., Furukawa, M., Kaneco, S., 2016. Enhanced Photocatalytic Degradation of Bisphenol A in Aqueous Solution by Ag-Doping ZnO. Open Journal of Inorganic Non-metallic Materials, 06 (03), DOI:10.4236/ojinm.2016.63003

Huang, B.S., Chang, F.Y., Wey, M.Y., 2010. An efficient composite growing N-doped TiO_2 on multi-walled carbon nanotubes through sol–gel process. Journal of Nanoparticle Research, 12, Pp. 2503–2510.

Jang, H.D., Chang, H., Cho, K., Kim, S.J., Park, J.H., Choi, J.W., Okuyama, K., 2008. Fabrication of porous nanostructured TiO_2 particles by an aerosol templating method. Journal Ultramicroscopy, 108 (10), Pp. 1241-1245.

Kaneco, S., Rahman, M.A., Suzuki, T., Katsumata, H., Ohta, K., 2004. Optimization of solar photocatalytic degradation conditions of bisphenol A in water using titanium dioxide. Journal of Photochemistry and Photobiology A: Chemistry, 163 (3), Pp. 419-424.

Liu, S.M., Gan, L.M., Liu, L.H., Zhang, W.D., Zeng, H.C., 2005. Preparation and characterization of nanosized Pt/Au particles on TiO2-nanotubes. Chem. Mater., 152 (1–3), Pp. 333-336.

Liu, S.M., Gan, L.M., Liu, L.H., Zhang, W.D., Zeng, H.C., 2002. Synthesis of Single-Crystalline TiO_2 Nanotubes. Chem. Mater.,14 (3), Pp. 1391–1397.

Ma, L., Jiang, G.W.C., Bao, H., Xu, Q., 2018. Synthesis of core-shell TiO2@g-C3N4 hollow microspheres for efficient photocatalytic degradation of rhodamine B under visible light. Phys. Chem. Solids, Applied Surface Science, 430, Pp. 263-272.

Mor, G.K., Varghese, O.K., Paulose, M., Mukherjee, N., Grimes, C.A., 2003. Fabrication of tapered, conical-shaped titania nanotubes. Journal of Materials Research, Pp. 2588.

Prabhu, S., Nithya, A., Mohan, S.C., Jothivenkatachalam, K., 2004. Synthesis, Surface Acidity and Photocatalytic Activity of O_3/TiO_2 Nanocomposites – An Overview. Materials Science Forum, 781, Pp. 63-78.

R. Rodriguez, K. Kim, J.L. Ong, 2003. In vitro osteoblast response to anodized titanium and anodized titanium followed by hydrothermal treatment. Biomed. Mater. Res. A., 65A, No. 3, Pp. 352-358.

Tao, J., Xixin, J.Z., Kang, W.Y., Li, Y., 2008. Fabrication of titania nanotube arrays on curved surface. Electrochemistry Communications, 10 (8), Pp. 1161-1163.

Weng, L.Q., Songa, S.H., Hodgsonb, S., 2006. Synthesis and characterisation of nanotubular titanates and titania. Journal of the European Ceramic Society, 26, Pp. 1405-1409.